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MassSpectrometric Investigation of the Reactions of O Atoms with H2 and NH3

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is thus based on the data of BL. The other values are unchanged. We have also extended the energy range of our quantum-efficiency measurements up to 4.5 eV. At 4.29 eV, the efficiency is 1.2; at 4.45 eV, the efficiency is 1.4. The presence of the peak at 3.7 eV instead of the plateau may have an influence on our value for E_c. We feel, however, that the altered value of E_c is sufficiently close to 3.7 eV to make it unnecessary to change any of our conclusions based on E_c.

ACKNOWLEDGMENTS

We wish to express our appreciation to Dr. H. Kallmann for helpful discussions and suggestions. Our discussions with Dr. N. Geacintov, Dr. M. Sano, and Mr. R. Laupheimer have also been stimulating.

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Mass-Spectrometric Investigation of the Reactions of O Atoms with H_2 and NH_3

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The reaction of H_2 with O in the absence of O_2 was studied in the temperature range 400° to 600°K by using a stirred reactor with a mass spectrometer for analysis. The rate constant for the $H_2+O\rightarrow OH+H$ reaction was found to be $4.3\times10^{13}\exp(-10\,200/RT)$ cc/mole·sec. The rate of O consumption was about three to five times smaller in the absence of O_2 than in its presence. This difference was quantitatively explained as a result of the reaction sequence

$$H+O_2+M\rightarrow HO_2+M;$$

$$HO_2+O\rightarrow OH+O_2.$$

The reaction of NH_3 with O in the absence of O_2 was also studied for the temperature range 350° to 600°K. The stoichiometry of the reaction could be approximately represented by

$$NH_3+4.4O\rightarrow NO+0.5H_2+1.2O_2+1.0H_2O.$$

In contrast to the H_2+O reaction, the rates for consumption of O were not affected by the presence or absence of excess O_2 within experimental error. A reaction mechanism was proposed, and using this mechanism the rate constant for the $NH_3+O\rightarrow NH_2+OH$ reaction was estimated to be $1\times10^{12}\exp(-4800/RT)$ cc/mole·sec.

INTRODUCTION

Recently the mass-spectrometric technique[1] was used to make kinetic measurement of the H_2+O and NH_3+O reactions in the presence of excess O_2. Since it seems likely that the presence of excess molecular oxygen might affect the course of the reaction, the measurements were repeated in the absence of molecular oxygen.

The reaction of H_2+O has been studied previously by other investigators using various experimental methods.[2–6] The purpose for repeating this measurement was to test the authors' experimental technique[1] and provide additional information on this important reaction.

The reaction of NH_3+O has also been investigated previously[1,2,7–9] but never thoroughly and never in the absence of O_2.

EXPERIMENTAL

Apparatus

The 300-cc stirred reactor and its connection to the Bendix time-of-flight mass spectrometer (Model 14-101) has been described in Ref. 1. One change from the previous arrangement was the use of a stainless-steel leak-hole diameter of 0.005 in. instead of the former Pyrex leak-hole diameter of $\sim$0.01 in. It was found that the smaller metallic leak hole could be used pro-

[1] E. L. Wong and A. E. Potter, J. Chem. Phys. **39**, 2211 (1963).
[2] P. Harteck and U. Kopsch, Z. Physik. Chem. **B12**, 327 (1931).
[3] C. P. Fenimore and G. W. Jones, J. Phys. Chem. **65**, 993 (1961).
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[6] V. V. Azatyan, V. V. Voevodsky, and A. B. Nalbandyan, Kinetika i Kataliz **2**, 340 (1961).
[7] G. E. Moore, K. E. Shuler, S. Silverman, and R. Herman, J. Phys. Chem. **60**, 813 (1956).
[8] C. P. Fenimore and G. W. Jones, J. Phys. Chem. **65**, 298 (1961).
[9] L. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznetsova, Izv. Akad. Nauk SSSR Otd. Khim. Nauk **6**, 983 (1962).

TABLE I. Gases used in present investigation.

Gas	Purity (%)
H_2	99.9
N_2	99.9
O_2	99.5
NH_3	99.9
ND_3	99.5
Ar	99.9
NO	99.5

vided that the mass-spectrometer sensitivity is at a high enough level to monitor small changes in O concentration easily.

Materials

The various gases used in this work are described in Table I. The purity of these gases was checked mass spectrometrically. NO was purified by the usual trapping procedures and then analyzed mass spectrometrically to be at least 99.5% pure before it was used.

Nitrogen dioxide gas was prepared by adding pure O_2 gas to purified NO gas and subjecting the resulting mixture to a trapping procedure to remove the excess O_2.

Oxygen atoms were produced by adding NO to a stream of active N_2 gas,[10] or by subjecting a dilute O_2 in argon gas mixture to a microwave discharge. The microwave generator was a Raytheon Model KV 104 (NB), 100-W.[1]

Mass-Spectrometric Monitoring of O-Atom Concentrations

Atomic oxygen can be monitored with the mass spectrometer either at $m/e=16$ or at $m/e=8$. The former can be used only in the absence of interference from O_2, NH_3, or other molecules which yield prominent $m/e=16$ peaks. The latter can be used whenever such interference is present. It is definitely preferable to work at $m/e=16$ when possible, since the instrument is operated at 30 ionizing eV and at a relative low-sensitivity level. In this manner of operation, the noise level is so low that an excellent signal-to-noise ratio can be achieved. When it is necessary to work at $m/e=8$, 85 ionizing eV and a very high sensitivity setting is required to detect the atomic-oxygen peak. Such operating conditions result in a poor signal-to-noise ratio. The use of $m/e=8$ to detect oxygen atoms has been discussed in detail in a preceding reference.[1]

In this report, it was possible to use the peak at $m/e=16$ for the reaction of H_2+O, where the O was generated by the N+NO reaction so that no O_2 was present. For the reaction of NH_3 with O, however, it was necessary to use the peak at $m/e=8$, since NH_3 produces a strong $m/e=16$ peak because of NH_2.

Calibration of the mass spectrometer for O was accomplished by the usual NO_2+O or NO+N titrations.[4,10] The former calibration method was described in a previous report.[1] The latter NO+N titration technique is shown in Fig. 1 where a typical set of titration curves is shown. The equivalence point, where the flow of NO just equals the flow of N before reaction and the flow of O after reaction, can be seen in this figure.

Calculation of Rate Constants

In the present investigation the O-atom and O_2 concentrations were so low that O-atom recombination, due to the reactions

$$O+O+M\rightarrow O_2+M,$$

$$O+O_2+M\rightarrow O_3+M,$$

and

$$O_3+O\rightarrow 2O_2,$$

was so small that it can be neglected.

As a result for the bimolecular reaction of O with a gas B in the stirred reactor, the decrease of O-atom concentration, $-\Delta[O]$, upon addition of B, is related to the rate constant k by the following expression:

$$-\Delta[O]/\Delta t=k[O][B], \quad (1)$$

where Δt is residence time of the gas in the stirred reactor and [O] is the O-atom concentration in moles/cm³ in the reactor after addition of B. The quantity [B] is the concentration in moles/cm³ of B inside the stirred reactor.

The quantity [B] can be evaluated by taking the flow rate of B into the reactor and subtracting from it the amount of B consumed by chemical reaction. Dividing this difference by the total flow rate yields the mole fraction of B, from which [B] can be found, since the pressure and temperature of the gas are known. In this investigation, however, only a small fraction

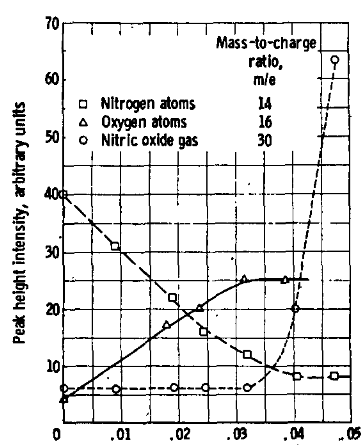

FIG. 1. Titration curves for $NO+N\rightarrow O+N_2$ reaction. Bendix operating at 30 ionizing electron volts; nitrogen carrier gas, flow rate, 1.5 cc/sec (normal temperature and pressure, NTP); pressure, 0.62 mm Hg.

[10] G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. 27, 1141 (1957).

of B was consumed by chemical reaction so that direct mass-spectrometric measurements were very difficult. A better procedure was to calculate this fraction on the basis of the amount of O atom consumed and the reaction stoichiometry. The reaction stoichiometry was calculated from known rate constants for the H_2+O reaction and measured from NO production for the NH_3+O reaction, as is described later.

Precision and Accuracy

As mentioned in a previous report[1] our rate-constant data had a precision of ±20% and an accuracy of ±50% leading to an accuracy of ~±20% (~±1.5 kcal) for the activation energies.

The precision of mass-spectrometric analyses for reactant products was low. Part of this low precision could be attributed to the instability of the mass spectrometer. In order to minimize errors due to instrument instability, all reaction products were measured simultaneously with the O-atom concentration and expressed as a ratio of O-atom concentration to reaction-product concentration. Mass-spectrometer calibration curves for each of the reaction products were obtained immediately after a run by metering known amounts of the reaction product into the main gas flow. The precision for measurement of this ratio was about ±25% for most of this investigation.

REACTION OF H_2+O

O-Atom Consumption in the Stirred Reactor

For study of the H_2+O reaction, O was produced by the N+NO technique. A constant flow of O into the stirred reactor was maintained by a constant flow of NO into the dissociated nitrogen stream upstream of the reactor. The flow rate of NO was adjusted so that all the N atoms were replaced by O atoms, with no excess of NO. Then, H_2 was added to the stirred reactor in increasing steps, and the O-atom concentration was measured at each step. The results from measurements of this kind at four different temperatures are presented in Table II and plotted in Fig. 2. Shown in this figure are plots of $\Delta[O]/[O]$ against the ratio F_{H_2}/F_t, the ratio of the hydrogen flow rate F_{H_2} to the total flow rate F_t. Since the amount of hydrogen used up by chemical reaction is small, F_{H_2}/F_t is approximately equal to the mole fraction of H_2 in the stirred reactor.

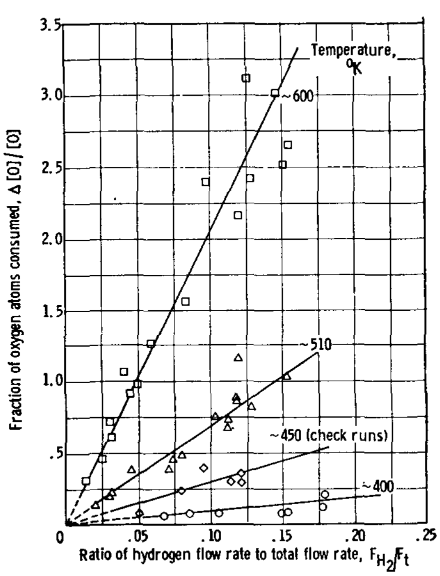

FIG. 2. Oxygen atoms consumed by added molecular hydrogen. Temperature range, 400° to 600°K; nitrogen carrier gas flow rate, 1.5 cc/sec; pressure, 0.7 to 0.8 mm Hg.

Products of the Reaction

The only products of the reaction that could be detected were O_2, H_2O, and H. In a previous report,[1] only H_2O and H could be identified as major products. The presence of a large excess of O_2 in that case prevented the detection of O_2 as a reaction product.

Mechanism of the Reaction

Enough is known about the reactions of hydrogen with oxygen to allow a mechanism to be written, based on the observed products of the reaction and the experimental conditions. This mechanism is

$$H_2+O\rightarrow OH+H, \tag{2}$$

$$OH+O\rightarrow O_2+H, \tag{3}$$

$$OH+H_2\rightarrow H_2O+H. \tag{4}$$

Reaction (4) is selected over the alternate water-forming reaction $2\,OH\rightarrow H_2O+O$ since it may be shown (using rate constants from Ref. 11) that the rate of this reaction must be negligible in comparison to Reaction (4).

Calculation of Rate Constant for $H_2+O\rightarrow OH+H$ Reaction

An expression for k_2, the rate constant for the initial elementary Reaction (2) in terms of experimentally measured quantities, and the two other rate constants k_3 and k_4 can be derived from the above reaction scheme by assuming the steady state for OH. This expression is, as follows (differentials have been replaced by finite differences, appropriate to the stirred reactor):

$$-\Delta[O]/\Delta t=k_2[O][H_2] \times\{(2k_3[O]+k_4[H_2])/(k_3[O]+k_4[H_2])\}. \tag{5}$$

Equation (5) showed that, for our experimental condition, k_2 is related to the total O-atom consumption by the bracketed term, which will be called f. The

[11] F. Kaufman, Symp. Combust., 9th, Cornell Univ., Ithaca, N.Y. 1962, 659 (1963).

TABLE II. Stirred reactor measurements of atomic oxygen with molecular hydrogen.

Run	Added molecular hydrogen flow (NTP),[a] cc/sec	Temperature, °K	Nitrogen carrier gas flow into discharge (NTP),[a] cc/sec	Nitric oxide gas added or oxygen atoms produced (NTP),[a] cc/sec	Fraction of oxygen atoms consumed in reactor uncorrected for pressure, $\Delta[O]/[O]^*$ (b)	Fraction of oxygen atoms consumed in reactor by reaction with added molecular hydrogen, $\Delta[O]/[O]$	Pressure, mm Hg	Residence time, Δt, sec	Fraction of hydrogen gas consumed (calculated), $\Delta[H_2]/[H_2]_0$	Factor relating k_2 to $-\Delta[O]$ (calculated),[c] f	Rate constant, k_2, cc/(mole)(sec)
1a	0.163	396	1.46	0.034	0.15	0.07	0.66	0.13	0.01	2.0	1.1×10^8
2a	.314	397	1.46	.033	.24	.12	.69	.13	.01	2.0	1.0
3a	.318	397	1.46	.034	.33	.20	.70	.13	.01	2.0	1.6
										Average value Average deviation	1.2×10^8 ±19 percent
6a	0.200	506	1.46	0.034	1.25	1.17	0.67	0.10	0.04	1.9	2.4×10^9
6b	.195	506		.034	.93	.85	.67		.04	1.9	1.9
7b	.185	510		.033	.78	.70	.67		.04	1.9	1.6
8a	.070	510		.034	.40	.37	.64		.07	2.0	2.1
8b	.169	510		.034	.82	.75	.66		.05	1.9	2.0
										Average value Average deviation	2.0×10^9 ±10 percent
9a	0.060	596	1.46	0.034	1.10	1.07	0.64	0.09	0.12	1.9	$10.7+10^9$
9b	.216	596		.034	3.21	3.12	.68		.08	1.7	10.0
10a	.046	600		.032	.74	.72	.64		.12	2.0	9.3
10b	.093	600			1.31	1.27	.65		.11	1.9	8.3
10c	.200	600			2.24	2.16	.67		.08	1.7	7.4
11a	.038	601			.48	.46	.64		.12	2.0	6.9
11b	.077				1.01	.98	.64		.11	1.9	7.9
11c	.158				2.47	2.40	.66		.09	1.8	9.9
11d	.250				3.12	3.02	.68		.07	1.6	9.9
										Average value Average deviation	8.9×10^9 ±13 percent
12a	0.263	399	1.46	0.037	0.19	0.08	0.68	0.13	0.01	2.0	0.76×10^8
12b	.254	399		.037	.18	.07	.68		.01		.67
13a	.107	400		.033	.10	.05	.65		.02		1.2
14a	.138	400		.031	.13	.07	.66		.01		1.2
										Average value Average deviation	0.96×10^8 ±24 percent
15b	0.213	595	1.44	0.032	2.51	2.42	0.67	0.09	0.08	1.7	7.7×10^9
16a	.046	597		.033	.63	.6	.64		.12	2.0	7.5
16b	.132	597		.033	1.62	1.56	.65		.09	1.8	7.6
17a	.020	595		.034	.32	.31	.63		.13	2.0	8.7
17b	.068				.95	.92	.64		.11	1.9	8.3
17c	.269				2.77	2.66	.69		.07	1.5	7.6
17d	.260				2.77	2.66	.68		.07	1.6	7.4
										Average value Average deviation	7.8×10^9 ±5 percent
18a	0.047	507	1.44	0.032	0.23	0.21	0.64	0.10	0.07	2.0	1.8×10^9
18b	.124				.54	.48	.65		.05	2.0	1.6
18c	.213				.91	.82	.67		.04	1.9	1.6
18d	.196				.96	.87	.67		.04	1.9	1.9
19a	.045	509		.031	.22	.20	.64		.07	2.0	1.8
19b	.117				.51	.46	.65		.05	2.0	1.6
19c	.185				.80	.72	.67		.04	1.9	1.6
20a	.030				.15	.13	.63		.08	2.0	1.6
20b	.111				.43	.38	.65		.06	2.0	1.4
20c	.265				1.14	1.03	.69		.03	1.9	1.7
										Average value Average deviation	1.7×10^9 ±6 percent
21	0.081	451	1.50	0.032	0.08	0.08	0.66	0.11	0.04	2.0	2.9×10^8
22	.132	451			.28	.22	.67	.12	.03	2.0	5.2
23	.196	449			.37	.30	.68		.03	2.0	4.8
24	.209				.37	.28	.68		.02	1.9	4.5
25	.210				.45	.36	.69		.02	1.9	5.6
26	.159				.45	.38	.67		.03	2.0	7.4
										Average value Average deviation	5.1×10^8 ±20 percent
27	0.091	430	1.69	0.035	0.09	0.05	0.70	0.12	0.03	2.0	1.6×10^8
28	.078	430		.034	.09	.06	.70		.03		2.3
29	.095	430		.030	.09	.05	.70		.03		1.6
30	.171	425		.027	.30	.22	.67		.02		3.6
31	.184	425		.039	.26	.18	.68		.02		2.7
32	.251	425		.027	.31	.21	.69		.02		2.4
										Average value Average deviation	2.4×10^8 ±21 percent

[a] Normal temperature and pressure. [b] $\Delta[O]=[O]_0$ (initial oxygen atom concentration) $-[O]$ (final oxygen atom concentration). [c] See p. 3373 of text.

rate-constant factor f can be calculated since $[O]$ was measured directly. The rate constants k_3 and k_4 can be obtained from Ref. 11, and $[H_2]$ can be obtained with sufficient accuracy from the flow of added H_2 into the reactor since only about 5% of the added H_2 was consumed in the reaction as discussed in the next paragraph. Figure 3 shows a plot of calculated f values against temperature for three different values of H_2 mole fraction F_{H_2}/F_t, which covered the experimental condition encountered here. The largest deviation of f from its limiting values of 2 was about 20% at the highest temperature and largest H_2 concentration. For most of the experimental conditions, the deviation from the value 2 is $<10\%$.

In order to calculate k_2 precisely, $[H_2]$ in the reactor must also be obtained. In principle, the mass spectrometer can be used to make this measurement. However, since only a small percentage of the added H_2 was consumed by chemical reaction, the precision of the mass-spectrometric measurements was very poor. Consequently, it was decided to calculate $[H_2]$ from the measured O loss. This calculation is described below.

By assuming steady state for OH, Reactions (2) to (4) give, for the stirred reactor,

$$\Delta[H_2]/\Delta t=-k_2[H_2][O]\times\{(k_3[O]+2k_4[H_2])/(k_3[O]+k_4[H_2])\}. \quad (6)$$

Then, dividing Eq. (5) by Eq. (6) gives an expression for the relative stoichiometry, $\Delta O/\Delta H_2$,

$$\Delta[O]/\Delta[H_2]=(2k_3[O]+k_4[H_2])/(k_3[O]+2k_4[H_2]). \quad (7)$$

This equation indicates the relative number of moles of O consumed per mole of H_2 consumed, and it may be calculated with sufficient accuracy in the same manner as f. The results of this calculation are presented in Fig. 4(a) which shows $\Delta[O]/\Delta[H_2]$ as a function of temperature and F_{H_2}/F_t for our experimental condition. The values of $\Delta[O]/\Delta[H_2]$ vary from about 1.1 to 2.0.

These $\Delta[O]/\Delta[H_2]$ values can now be used with experimental values of $\Delta[O]$ and $[H_2]_0$, concentration of H_2 in the reactor in the absence of reaction, to find $\Delta[H_2]/[H_2]_0$, the fraction of H_2 consumed in the reaction. Figure 4(b) shows these fractions for our experimental condition and indicates that $\Delta[H_2]/[H_2]_0$ ranges from 1% to 10%. The curves of Fig. 4(b) can be used to obtain values of $[H_2]$ from the experimental values of $[H_2]_0$.

The results of the calculation of k_2 outlined above are given in Table II and are shown in Fig. 5, where a semilogarithmic plot of the rate constant k_2 against $1/T$ is shown. The equation of the line through the data is

$$k_2=4.3\times10^{13}\exp(-10\,200/RT) \text{ cc/mole}\cdot\text{sec}. \quad (8)$$

This result is compared with data from Clyne and Thrush, Fenimore and Jones, Baldwin, and Azatyan in Fig. 6. The most recent data covering a range of temperature similar to the range in this report are those of Clyne and Thrush. Our rate constants average about 20% higher than theirs, and our activation energy is 0.8 kcal/mole higher than theirs. The agreement is satisfactory, considering the completely different methods used.

EFFECT OF MOLECULAR OXYGEN ON THE OXIDATION RATE OF H_2 BY O

In a previous paper[1] we studied the reaction of hydrogen with mixtures of molecular and atomic oxygen. The over-all rate constant, as defined in Eq. (1), for disappearance of atomic oxygen in the stirred reactor was found for this case to be

$$k^{O,O_2}=3\times10^{13}\exp(-8300/RT) \text{ cc/mole}\cdot\text{sec}. \quad (9)$$

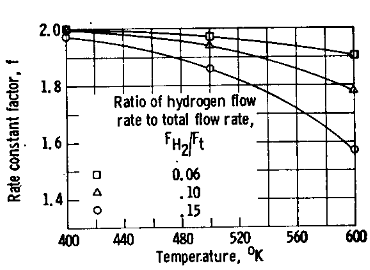

FIG. 3. Calculations of rate-constant factor f for $H_2+O\rightarrow OH+H$ reaction.

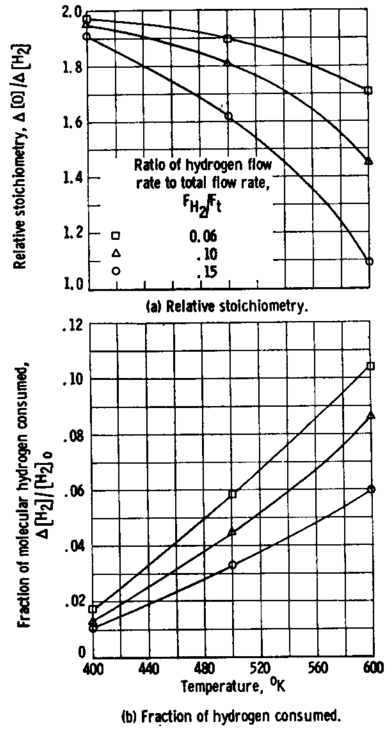

FIG. 4. Calculations of relative stoichiometry and fraction of molecular hydrogen consumed.

It is interesting to compare these rate constants with those for the disappearance of O in the absence of O_2. In the preceding section, data for the consumption of O were used to calculate rate constants for the reaction $H_2+O\rightarrow OH+O$. These same data (Table II) can be used to calculate over-all rate constants k^O for O disappearance in the absence of O_2. Equation (1) defines the over-all rate constant k^O that is calculated in this way. Comparison of Eqs. (1) and (5) show that $k^O\approx2k_2$, since the term in brackets in Eq. (5) is ≈2. The results are shown in Fig. 7, along with rate constants for the case of excess molecular oxygen. It can be seen that the presence of molecular oxygen greatly increases the rate of disappearance of atomic oxygen. The increase ranges from a factor of 5 at low temperatures to about 3 at high temperatures. In the following paragraphs, this increase in rate is explained.

In the presence of O_2, it is necessary to add[5] two reactions to the three-reaction scheme proposed above for the reaction of H_2 with O. With these reactions, the reaction scheme for the reaction of H_2 with $(O+O_2)$ is

$$H_2+O\rightarrow OH+H, \quad (2)$$

$$OH+O\rightarrow O_2+H, \quad (3)$$

$$OH+H_2\rightarrow H_2O+H, \quad (4)$$

$$O_2+H+M\rightarrow HO_2+M, \quad (10)$$

$$HO_2+O\rightarrow OH+O_2. \quad (11)$$

The purpose herein is to show how the preceding

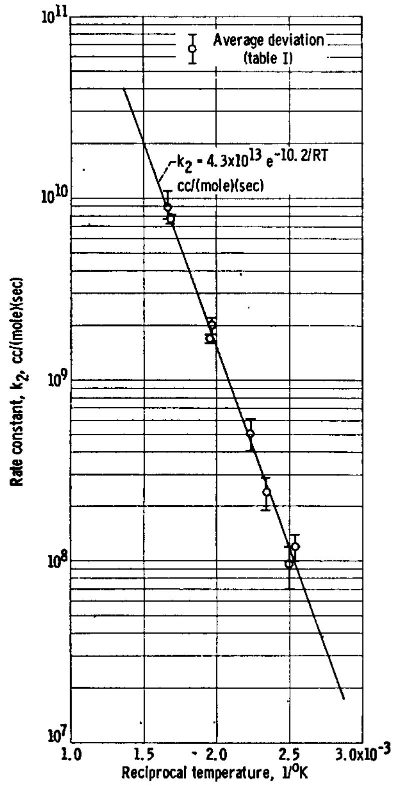

FIG. 5. Rate constants for $H_2+O\rightarrow OH+H$ reaction.

reaction mechanism can explain the effect of excess O_2 on the rate of O disappearance. In order to do this, the reaction mechanism is used with the data for the $H_2+(O+O_2)$ reaction to deduce rate constants for the $H_2+O\rightarrow OH+H$ reaction. These rate constants

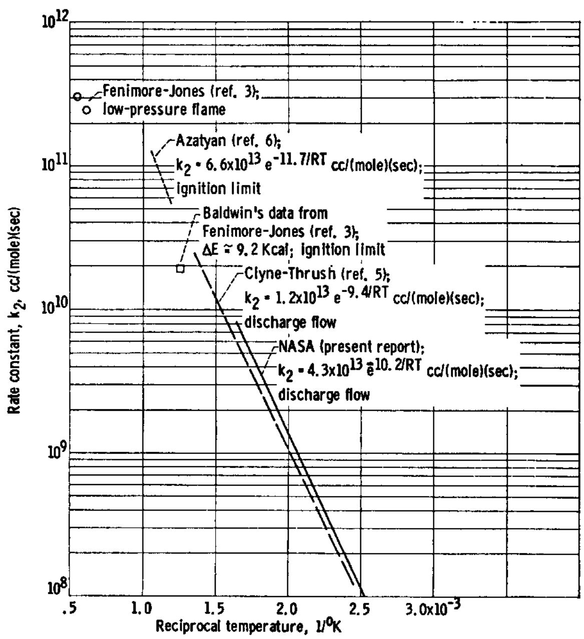

FIG. 6. Comparisons of rate constants for $H_2+O\rightarrow OH$ reaction.

can then be compared with the rate constants for this reaction obtained in the previous section from the reaction in the absence of molecular oxygen.

On the basis of the preceding reaction mechanism the O-atom decay rate $-d[O]/dt$ may be expressed as follows:

$$-d[O]/dt=k_2[O][H_2]+k_3[OH][O]+k_{11}[HO_2][O]. \tag{12}$$

Then, by assuming steady state for OH and HO_2, Eq.

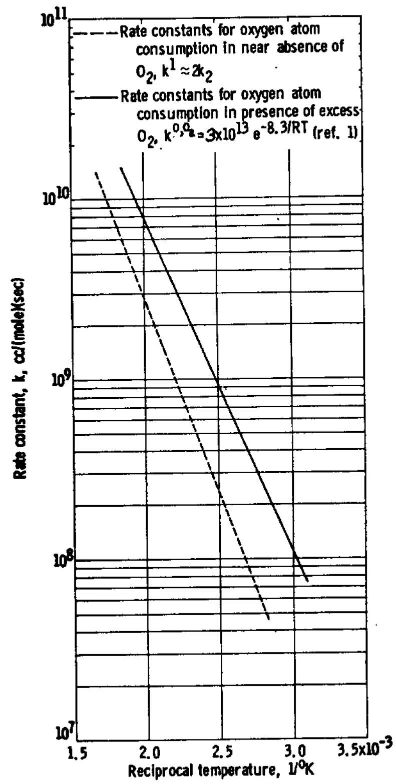

FIG. 7. Comparison of rate constants for oxygen-atom consumption for the H_2+O reaction.

(12) may be rewritten as

$$-d[O]/dt=k_2[O][H_2]+k_3[OH][O]+k_{10}[H][O_2][M]. \tag{13}$$

Expressions for [H] and [OH] were obtained as follows: For [H] one makes use of the equation

$$d[H]/dt=2k_2[H_2][O]. \tag{14}$$

This equation can be put into the finite difference form appropriate to the stirred reactor. Since the initial atomic-hydrogen concentration is zero, Eq. (14) gives

$$[H]=2k_2[H_2][O]\Delta t, \tag{15}$$

where Δt is the residence time in the stirred reactor.

For [OH] one finds that

$$[OH]=\frac{k_2[H_2][O](1+2k_{10}[O_2][M]\Delta t)}{k_3[O]+k_4[H_2]}. \quad (16)$$

Now, after proper substitution and conversion to the finite-difference form, Eq. (13) may be written as

$$\Delta[O]/\Delta t=-k_2[H_2][O]$$
$$\times\left\{\left(\frac{2k_3[O]+k_4[H_2]}{k_3[O]+k_4[H_2]}\right)(1+2k_{10}[O_2][M]\Delta t)\right\}. \quad (17)$$

Values of k_2 were calculated from this equation by using the experimental data for the H_2 and $(O+O_2)$ reaction,[1] and a value of k_{10} based upon Refs. 12 and 13. Reference 12 reported a value of $k_{10}=0.8\times10^{16}$ $cc^2/mole^2\cdot sec$ at 293°K for M as argon and an activation energy $\Delta E=-1600$ cal. Reference 13 provided information to calculate k_{10} for the experimental condition[1] where $M=O_2$. Values of k_3 and k_4 were again from Ref. 11. The results of this calculation are shown in Fig. 8, where the calculated rate constants are compared with k_2 values from the preceding section. This figure shows that the calculated rate constants agree fairly well with the values measured more directly. This agreement gives evidence favoring the reaction mechanism proposed for

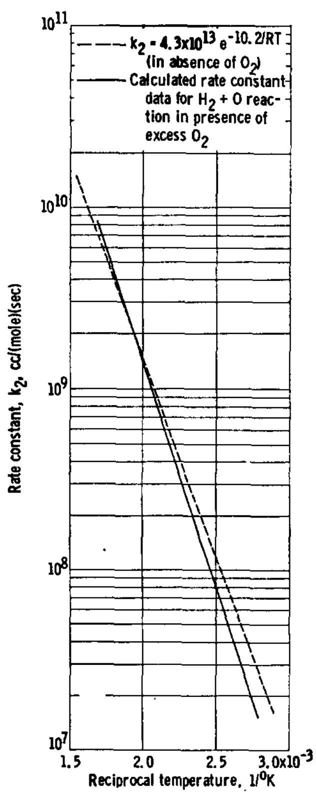

FIG. 8. Calculated rate constants for $H_2+O\rightarrow OH+H$ reaction in presence of excess molecular oxygen.

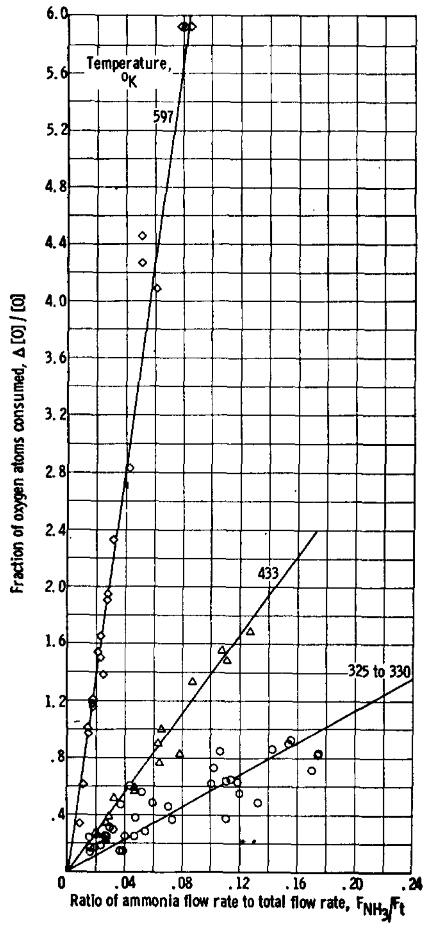

FIG. 9. Oxygen atoms consumed by added ammonia.

the reaction of H_2 with $O+O_2$ mixtures. Thus, the increased rate of O-atom disappearance in the presence of O_2 is due to the $H+O_2+M\rightarrow HO_2+M$ reaction. The HO_2 formed in this reaction reacts with O to form OH and O_2. The OH formed removes an O atom by reaction to form O_2 and H, thus regenerating H. The net effect is that each molecule of HO_2 formed removes two oxygen atoms.

REACTION OF NH_3 WITH O

Atomic Oxygen Consumption in Stirred Reactor

For study of the NH_3+O reaction, O was produced both by the N+NO titration technique and by subjecting a 1.8% O_2–Ar mixture to a microwave discharge. Since ammonia produces a strong peak in the mass spectrometer at $m/e=16$, it was necessary to monitor O consumption at $m/e=8$ with an ionizing voltage of 85 V.

This technique was used to measure the amount of O consumed in the stirred reactor at increasing levels of NH_3 concentration for three different temperatures. These data are shown in Table III and plotted in Fig. 9.

[12] M. A. A. Clyne, Symp. Combust., 9th, Cornell Univ., Ithaca, N.Y. 1962, 659 (1963).
[13] B. Lewis and G. von Elbe, *Combustion, Flames, and Explosions of Gases* (Academic Press Inc., New York, 1951), p. 33.

TABLE III. Stirred reactor measurements of atomic oxygen with ammonia.

(a) Atomic nitrogen and nitric oxide technique used as atomic oxygen source.

Run	Added ammonia flow (NTP),[a] cc/sec	Temperature, °K	Nitrogen carrier gas flow into discharge (NTP),[a] cc/sec	Nitric oxide gas added or oxygen atoms produced (NTP),[a] cc/sec	Fraction of oxygen atoms consumed in reactor uncorrected for pressure, $\Delta[O]/[O]^*$ (b)	Fraction of oxygen atoms consumed in reactor by reaction with added ammonia, $\Delta[O]/[O]$	Pressure, mm Hg	Residence time, Δt, sec	Relative stoichiometry, $\Delta[O]/\Delta[NH_3]$ or $\Delta[O]/\Delta[NO]$	Rate constant for oxygen atom consumption, k_{22}^0, cc/(mole)(sec)
1a	0.077	320	1.55	0.020	0.42	0.38	0.67	0.15	4.4	1.6×10^9
2a	.051	323		.034	.32	.30	.66			2.0
2b	.193	323		.034	.71	.64	.69			1.1
3a	.043	325		.037	.27	.25	.66			2.0
3b	.200	325		.037	.73	.65	.69			1.1
4a	.042	330		.020	.27	.25	.66			2.1
									Average value Average deviation	1.7×10^9 ±22 percent
5a	0.057	328	1.51	0.030	0.18	0.15	0.66	0.16	4.4	0.85×10^9
6a	.059	328		.036	.18	.15	.66			.81
6b	.236	331			.59	.49	.69			.72
7a	.035	330			.21	.19	.66			1.8
7b	.323				.96	.83	.71			.89
7c	.253				.96	.86	.69			1.2
8b	.170				.69	.62	.68			1.2
9a	.096			.033	.52	.48	.66			1.7
9b	.283			.033	1.04	.93	.70			1.1
10a	.087			.029	.32	.28	.66			1.1
10b	.203			.029	.71	.63	.68			1.1
									Average value Average deviation	1.1×10^9 ±22 percent
11a	0.221	443	1.51	0.035	1.77	1.68	0.69	0.12	4.4	4.6×10^9
12a	.042	440		.035	.36	.34	.67			4.7
12b	.104	440		.035	.82	.77	.66			4.4
13a	.074	433		.034	.62	.58	.66			4.5
14a	.046	432		.027	.41	.39	.66			4.8
14b	.129	433			.88	.82	.67			3.6
15a	.033				.28	.26	.67			4.4
15b	.106				1.05	1.00	.66			5.4
15c	.181				1.63	1.55	.68			4.9
16a	.034			.024	.28	.26	.67			4.2
16b	.052				.54	.51	.66			5.6
16c	.102				.95	.90	.66			5.1
16d	.190				1.56	1.48	.68			4.5
17a	.040	432		.027	.24	.22	.65			3.0
17b	.072	432		.027	.61	.58	.66			4.5
17c	.146	432		.027	1.39	1.33	.67			5.2
									Average value Average deviation	4.6×10^9 ±10 percent
18a	0.028	593	1.51	0.036	1.21	1.20	0.65	0.087	4.4	5.3×10^{10}
18b	.069	594			2.86	2.83	.66			4.7
18c	.140	593			5.94	5.88	.67			4.7
18d	.135	593			5.94	5.88	.67			4.9
19a	.044	596		.032	1.97	1.95	.66			5.2
19b	.083	596		.032	4.27	4.23	.66			5.9
19c	.130	596			5.99	5.93	.67			5.1
20a	.036	597			1.52	1.50	.66			5.1
20b	.083				4.50	4.46	.66			6.2
20c	.143				8.57	8.51	.67			6.7
21a	.023			.029	.99	.98	.65			5.1
21b	.044				1.94	1.92	.65			5.0
22a	.050				2.36	2.34	.65			5.5
22b	.097				4.13	4.09	.66			4.7
									Average value Average deviation	5.3×10^{10} ±8 percent
23b	0.182	324	1.51	0.030	0.93	0.85	0.68	0.16	4.4	1.5×10^9
23c	.175	324		.030	.80	.73	.68			1.3
24b	.083	326		.033	.60	.56	.66			2.2
25a	.025	326		.029	.16	.15	.65			1.9
26a	.024	326		.033	.17	.16	.65			2.3
26b	.116	331		.033	.51	.46	.67			1.3
26d	.279			.033	1.01	.90	.70			1.1
27a	.029			.036	.18	.17	.65			1.9
27b	.120			.036	.42	.37	.67			1.0
28a	.063			.028	.28	.25	.65			1.3
28b	.207			.028	.64	.55	.69			.9
29a	.073			.029	.27	.24	.65			1.1
									Average value Average deviation	1.5×10^8 ±27 percent
30a	0.015	588	1.51	0.030	0.35	0.34	0.65	0.088	4.4	2.7×10^{10}
31	.021	593		.029	1.01	1.00		.087		5.9
32	.026	594		.024	1.21	1.19		.087		5.3
33	.038	591		.020	1.40	1.38		.087		3.9
34	.029	589		.026	1.20	1.19		.088		4.6
35	.017	589		.022	.61	.60	.64	.088		4.1
36	.034	595		.022	1.65	1.63	.65	.087		5.5
37	.033	595		.022	1.55	1.53	.65	.087		5.3
									Average value Average deviation	4.7×10^{10} ±18 percent

[a] Normal temperature and pressure. [b] $\Delta[O]=[O]_0$ (initial oxygen atom concentration) $-$ [O] (final oxygen atom concentration).

TABLE III (*Continued*). (b) Molecular-oxygen–argon mixture (1.8%) used as atomic oxygen source.

Run	Added ammonia flow (NTP),[a] cc/sec	Temperature, °K	Oxygen carrier gas flow into discharge (NTP),[a] cc/sec	Fraction of oxygen atoms consumed in reactor uncorrected for pressure, Δ[O]/[O]*	Fraction of oxygen atoms consumed in reactor by reaction with added ammonia, Δ[O]/[O]	Initial oxygen atom or nitrogen dioxide concentration, $[O]_0$ cc/sec (b)	Pressure, mm Hg	Residence time, Δt, sec	Relative stoichiometry, $\Delta[O]/\Delta[NH_3]$ or Δ[O]/Δ[NO]	Rate constant for oxygen atom consumption, k_{22}^0, cc/(mole)(sec)
1a	0.103	306	1.50	0.31	0.26	(0.04)	0.65	0.17	4.4	7.1×10^8
1b	.097			.46	.42					13.0
1c	.097			.35	.31					9.2
3a	.042			.24	.22		.64			14.7
3b	.039			.26	.24		.64			17.9
									Average value Average deviation	1.2×10^9 ±29 percent
4a	0.0087	541	1.50	0.34	0.34	(0.04)	0.64	0.10	4.4	4.4×10^{10}
4b	.0072	553		.35	.35			.09		6.3
4c	.0077	559		.38	.38					6.5
4d	.0064	561		.37	.37					8.5
5a	.032	566		1.95	1.93					6.9
5b	.035	567		1.76	1.74					5.7
5c	.058	567		3.06	3.08		.65			5.6
									Average value Average deviation	6.3×10^{10} ±14 percent
1'a	0.0092	565	1.50	0.42	0.42	(0.04)	0.64	0.09	4.4	5.9×10^{10}
1'b	.0092			.58	.58					9.1
1'c	.0083			.44	.44					7.3
1'd	.0083			.60	.60					11.3
2'b	.033			1.96	1.94					6.6
3a	.081			5.64	5.60		.65			7.7
3b	.081			5.92	5.88		.65			8.1
									Average value Average deviation	8.0×10^{10} ±16 percent
5'a	0.036	428	1.50	0.58	0.56	(0.04)	0.67	0.12	4.4	9.0×10^9
5'b	.041			.52	.50					6.9
5'c	.036			.52	.50					7.9
6'a	.133			1.66	1.60		.66			10.9
6'b	.131			1.59	1.53		.66			6.7
7'a	.252			2.85	2.74		.69			6.3
7'b	.232			2.69	2.59		.68			6.5
8'a	.104			1.17	1.12		.66			6.0
8'b	.102			1.28	1.23		.66			6.7
9'a	.194			2.29	2.20		.65			6.4
9'b	.196			2.34	2.25		.66			6.4
									Average value Average deviation	7.2×10^9 ±15 percent
10'a	0.057	305	1.50	0.34	0.31	(0.04)	0.65	0.17	4.4	1.5×10^9
10'b	.057	307		.35	.32		.65			1.6
11'a	.149	306		.68	.61		.67			1.2
11'b	.148	306		.68	.61		.67			1.2
12'b	.278	306		1.12	1.01		.70			1.1
14'a	.062	305		.31	.28		.65			1.3
14'b	.062			.25	.22					1.0
14'c	.065			.32	.29					1.3
14'd	.062			.30	.27					1.3
15'a	.128			.51	.45			.16		1.0
15'b	.125			.58	.52		.66	.17		1.0
16'a	.273			.97	.86		.70			.9
16'b	.252			.97	.86		.69			1.0
									Average value Average deviation	1.2×10^9 ±17 percent

[a] Normal temperature and pressure. [b] Estimated initial oxygen atom concentration $[O]_0$ based on approximately 75% molecular oxygen dissociation.

Products of the Reaction

In a previous investigation[1] on the $NH_3+(O_2+O)$ reaction the principal products were NO and H_2O, the secondary product was H_2, with possibly a trace of H.

In the work reported herein, the products from ammonia reacting with atomic oxygen produced from the N+NO reaction were measured first. As before, the principal products included NO and H_2O; however, a mass-spectrometer peak at $m/e=32$ was also observed. This could not have been detected in our previous work because of the excess of molecular oxygen present. The peak at $m/e=32$ could arise either from O_2 or from hydrazine, N_2H_4. In order to differentiate between the two, fully deuterated ammonia ND_3 was reacted with O free of O_2. The peak at $m/e=32$ did not shift, so that it must have originated from O_2 and not from N_2H_4.

When using O from the N+NO reaction, a large excess of N_2 is present, so that any N_2 formed as a reaction product could escape undetected. To test this possibility, NH_3 was reacted with O produced by microwave discharge through a dilute (1.8%) O_2 mixture with argon. No N_2 could be detected.

In all the experiments described in Table III, H_2 was detectable as a minor product, although H was not.

There was no N_2-containing product other than NO; O_2, H_2, and H_2O were the remaining reaction products.

Stoichiometry of Reaction

Since there is no N_2-containing product other than NO, each mole of NH_3 used in the reaction must yield one mole of NO. If arbitrary values of x and y are assigned to the moles of H_2 and O_2 produced in the

TABLE IV. Summary of reaction stoichiometry measurements for $O+NH_3$ reaction.

Temperature (°K)	$\Delta[O]/\Delta[O_2]$	$\Delta[O]/\Delta[H_2]$	$\Delta[O]/\Delta[H_2O]$	$\Delta[O]/\Delta[NO]$
325	3	9 to 10	6 to 7	...
437	3	9	4 to 5	...
569	5	9	5 to 9	...
Average	3.7	9	~6	4.4 (Fig. 11)

reaction, the reaction can be written as

$$NH_3+(\tfrac{5}{2}-x+2y)O\rightarrow NO+xH_2+yO_2+(\tfrac{3}{2}-x)H_2O. \quad (18)$$

Study of this equation shows that x is limited in value to $0\leq x\leq\frac{3}{2}$, but y can vary from 0 to $+\infty$. Also, since there are only two unknowns, x and y, the complete stoichiometry of the reaction can be found from measurement of only two components, such as O and O_2, relative to NO or NH_3.

To determine one of the necessary coefficients, measurements of the O stoichiometry were obtained by measuring $\Delta[O]/\Delta[NO]$ since it was observed that each mole of NH_3 consumed yields one mole of NO. The value of $\Delta[NO]$ can be measured with much greater accuracy than $\Delta[NH_3]$ since the initial NO concentration is zero. Values of $\Delta[O]/\Delta[NO]$ for two different temperature and various F_{NH_3}/F_t are shown in Fig. 10. Although there is much scatter in the data, the average value of $\Delta[O]/\Delta[NO]$, neglecting any temperature trend, is ~4.4.

Additional support for the above relative stoichiometry value was obtained by $\Delta[O]/\Delta[NH_3]$ measurements at temperatures of 350° and 550°K. At the lower temperature the measurement was impractical since values of $\Delta[NH_3]$ were too small to be measured reliably. For the higher temperature the values of $\Delta[O]/\Delta[NH_3]$ were 4 to 5, agreeing with the previously stated $\Delta[O]/\Delta[NO]$ value.

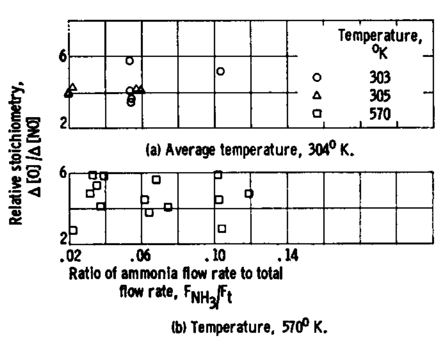

FIG. 10. Measured relative stoichiometry for ammonia–atomic-oxygen reaction; source of oxygen atoms, dilute molecular-oxygen–argon mixture.

In order to determine the other stoichiometric ratios, $\Delta[O]/\Delta[O_2]$ and $\Delta[O]/\Delta[H_2]$, the values of $\Delta[O]_f$, $\Delta[O_2]_f$, and $\Delta[H_2]_f$, the changes in flow rates of these species, were measured as a function of NH_3 flow rate. These results are shown in Fig. 11. Values for the stoichiometric ratios were obtained by drawing mean lines through the data, and dividing the slopes of the $\Delta[O]_f$ line by the slopes of the $\Delta[O_2]_f$ or $\Delta[H_2]_f$ lines, as shown in Table IV. No significant trends with temperature are noted. The average value for $\Delta[O]/\Delta[O_2]$ was 4 and for $\Delta[O]/\Delta[H_2]$ was 9.

Additional stoichiometric information was obtained by measuring $\Delta[H_2O]$. Here it was necessary to express $[H_2O]$ in terms of ion currents only, because of the difficulty of calibrating for small amount of H_2O. These results are compared with ΔO_2 and ΔH_2, also in terms of ion current, and shown in Fig. 12. This figure shows that $\Delta[H_2O]$ lies about midway between $\Delta[O]$ and and $\Delta[H_2]$. Since $\Delta[O]/\Delta[O_2]\approx3.7$ and $\Delta[O]/\Delta[H_2]\approx 9$, $\Delta[O]/\Delta[H_2]$ must be about 6.

The two more reliable stoichiometric ratios, $\Delta[O]/\Delta[NO]$ and $\Delta[O]/\Delta[O_2]$, can be used to calculate the reaction stoichiometry.

Equation (18) shows that

$$\Delta[O]/\Delta[NO]=\tfrac{5}{2}-x+2y\approx4.4 \quad (19)$$

and

$$\Delta[O]/\Delta[O_2]=(5/2y)-(x/y)+2\approx3.7. \quad (20)$$

From the experimental values of these ratios it was found that $x\approx0.5$ and $y\approx1.2$. The reaction can then be written as

$$NH_3+4.4O\rightarrow NO+0.5H_2+1.2O_2+1.0H_2O. \quad (21)$$

The ratio $\Delta[O]/\Delta[H_2]$ derived from this equation is 9, which is in good agreement with the value of 9 obtained experimentally. Similarly, the ratio $\Delta[O]/\Delta[H_2O]$ from the equation is 4, which agrees qualitatively with the experimental value of 6.

Rate Constants for Consumption of Atomic Oxygen

The data on O consumption were used with Eq. (1) to calculate bimolecular rate constants. The required $[NH_3]$ term was calculated from the NH_3 flow into the reactor by subtracting from it the NH_3 consumed. The amount of NH_3 consumed was found from the

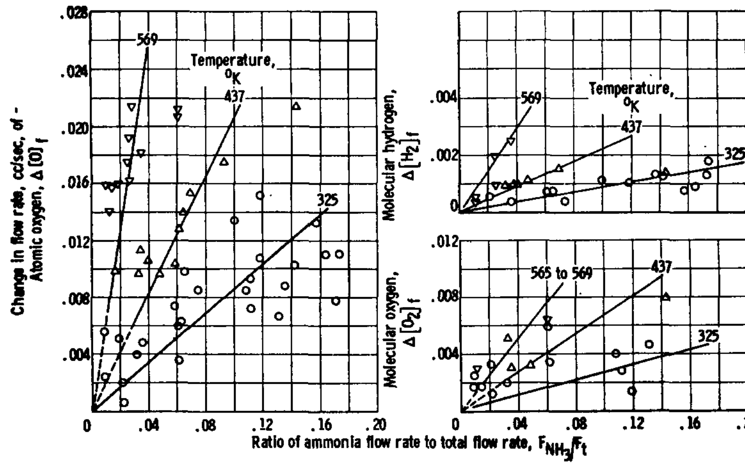

FIG. 11. Changes in flow rates of atomic oxygen, molecular oxygen, and molecular hydrogen for ammonia–atomic-oxygen reaction at conditions of normal temperature and pressure.

amount of O consumed and the reaction stoichiometry. The results are plotted in Fig. 13. Data for atomic oxygen produced both from N+NO and from O_2+Ar are shown and are compared with data from Ref. 1 for O+O_2 mixtures, shown as a dashed line, and Avramenko's work.[9]

It is interesting to note in Fig. 13 that the rate constant is unaffected by presence or absence of O_2, within experimental error. This is quite different from the oxidation of hydrogen where the rate constant was increased about a factor of 3 to 5 by excess O_2. It follows from this that O_2 does not play a significant role in the oxidation of NH_3. The rate constant for O consumption k_{22}^{O} can be taken to be $3\times10^{12}\exp(-4900/RT)$ cc/mole·sec as found in Ref. 1.

Possible Reaction Mechanism

A series of reaction steps can be written to account for the reaction products. The most plausible set of reactions are as follows:

$$NH_3+O\rightarrow NH_2+OH, \tag{22}$$

$$NH_2+O\rightarrow NH+OH, \tag{23}$$

$$NH+O\rightarrow NO+H, \tag{24}$$

$$OH+O\rightarrow O_2+H, \tag{25}$$

$$OH+NH_3\rightarrow NH_2+H_2O, \tag{26}$$

$$H+NO+M\rightarrow HNO+M, \tag{27}$$

$$HNO+H\rightarrow H_2+NO. \tag{28}$$

Other reactions certainly occur, but are thought to be of minor importance.

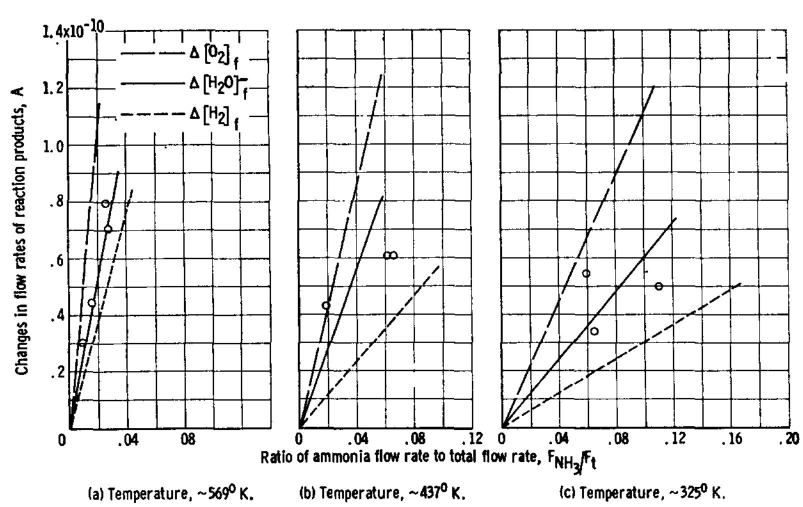

FIG. 12. Changes in flow rates of molecular oxygen, molecular hydrogen, and water for ammonia–atomic-oxygen reaction in terms of ion current.

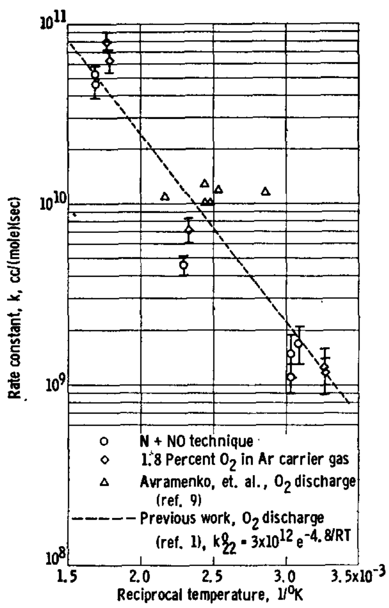

FIG. 13. Rate constants for oxygen-atom consumption due to added ammonia.

The initial reaction step must be the attack of NH_3 by O. By analogy with H_2, the products are thought to be NH_2 and OH. The amino radical (NH_2) is expected to be very reactive, and a reaction with O probably predominates. By analogy with the initial step, the products are probably NH and OH. The imino radical (NH) can react with O to give NO and H. This reaction is energetically possible and is the most plausible process that yields NO. The appearance of O_2 among the products can be accounted for by the reaction of OH and O, which is known to be extremely fast. The reaction of OH and NH_3 to yield NH_2 and H_2O is the most plausible reaction for the production of H_2O. The presence of H_2 and the absence of H can be accounted for by the NO-catalyzed H recombination reactions shown in Eqs. (27) and (28). These two reactions were selected over other alternate reactions since they are known to be fast.[14]

The preceding reaction scheme can also explain why the over-all rate constant is unaffected by the presence or absence of excess O_2, since the termolecular reaction $H+O_2+M\rightarrow HO_2+M$ is relatively unimportant because Reaction (27) is so fast.

The reaction mechanism outlined in Eqs. (22) to (28) can be used to relate the atomic-oxygen consumption rate constant $k_{22}{}^{O}$ to the rate constant k_{22} for the initial oxidation step $NH_3+O\rightarrow NH_2+OH$. With the steady state assumed for NH_2, NH, and OH, it can be shown that

$$k_{22}=(\Delta[O]-\Delta[O_2]-2\Delta[NO])/\Delta t[O][NH_3], \quad (29)$$

where differentials have been replaced by finite differences appropriate to the stirred reactor.

Defining A as

$$A=(\Delta[O]-\Delta[O_2]-2\Delta[NO])/\Delta[O] \quad (30)$$

and recalling from Eq. (1) that

$$k_{22}{}^{O}=\Delta[O]/\Delta t[O][NH_3] \quad (31)$$

then

$$k_{22}=Ak_{22}{}^{O}. \quad (32)$$

From the experimental stoichiometry, it is found that

$$A=(4.4-1.2-2)/4.4=0.27, \quad (33)$$

so that

$$k_{22}=0.27k_{22}{}^{O}. \quad (34)$$

From the above result the rate expression for the primary reaction Eq. (22) is, as follows:

$$k_{22}=1\times10^{12}\exp(-4900/RT)\ \text{cc/mole}\cdot\text{sec}. \quad (35)$$

[14] T. M. Sugden, E. M. Bulewicz, and A. Demerdache, *Chemical Reactions in the Lower and Upper Atmosphere* (Interscience Publishers, Inc., New York, 1961), p. 89.