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Scientific Report 413

THE REACTIONS OF HO_2 WITH CO AND NO AND THE REACTION OF $O(^1D)$ WITH H_2O

by

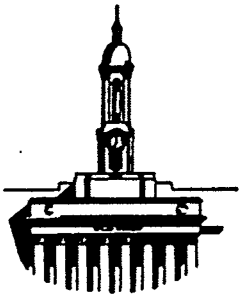
R. Simonaitis and Julian Heicklen

February 8, 1973

The research reported in this document has been supported by the National Science Foundation under Grant GA-12385 and the National Aeronautics Space Administration under Grant ~~NGL-009-003.~~

NGL-39-009-003

IONOSPHERE RESEARCH LABORATORY



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ACKNOWLEDGMENT

The authors wish to thank Professors Marcel Nicolet and Eduardo Lissi for useful discussions. This work was supported by the Atmosphere Sciences Section of the National Science Foundation through Grant No. GA-12385 and the National Aeronautics Space Administration through Grant No. NGL-009-003 for which we are grateful.

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ABSTRACT

HO_2 radicals were generated by the photolysis of N_2O at 2139A in the presence of excess H_2O or H_2 and smaller amounts of CO and O_2. The $O(^1D)$ atoms produced from the photolysis of N_2O react with H_2O to give HO radicals or H_2 to give HO + H. With H_2O, two HO radicals are produced for each $O(^1D)$ removed at low pressures (i.e. $\sim$ 20 torr H_2O), but the HO yield drops as the pressure is raised. This drop is attributed to the insertion reaction

$$O(^1D) + H_2O + M \rightarrow H_2O_2 + M$$

This reaction removes 20±10% of the $O(^1D)$ atoms at $\sim$ 650 torr H_2O (at 200°C).

The HO radicals generated can react with either CO or H_2 to produce H atoms which then add to O_2 to produce HO_2. In the absence of NO, the HO_2 radicals could react by two routes

$$HO_2 + CO \rightarrow HO + CO_2 \qquad 1$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad 11$$

Reaction 1 is so slow, even at 200°C, that only an upper limiting value of 1.9×10^{-12} $(cm^3/sec)^{\frac{1}{2}}$ could be found for $k_1/k_{11}^{\frac{1}{2}}$. When combined with the value of $k_{11} = 6 \times 10^{-12}$ cm^3/sec, this ratio gives $k_1 < 5 \times 10^{-18}$ cm^3/sec at both 100 and 200°C.

With NO present, NO_2 is produced in a long chain process via

$$HO_2 + NO \rightarrow HO + NO_2 \qquad 2$$

In this case reaction 2 is so rapid at 25°C that only a lower limiting value of 0.6×10^{-7} $(cm^3/sec)^{\frac{1}{2}}$ could be found for $k_2/k_{11}^{\frac{1}{2}}$. Thus $k_2 > 1.5 \times 10^{-13}$ cm^3/sec at 25°C.

INTRODUCTION

The hydroperoxyl radical is an important intermediate in atmospheric and combustion chemistry. However, up to the present time the reactions of this radical have not been extensively studied. This is due, no doubt, to the fact that a good method for generating this radical in systems free from complications has not been available.

Two reactions of the hydroperoxyl radical which are of particular interest are with CO and NO

$$HO_2 + CO \rightarrow CO_2 + OH \qquad 1$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad 2$$

The reaction with CO has already been studied by several investigators, but k_2 has not yet, as far as we know, been reported in the literature. Baldwin et al.[1] studied the chain decomposition of H_2O_2 in the presence of CO at temperatures > 440°C. They obtained an approximate Arrhenius expression for the rate constant of reaction 1, $k_1 = 10^{-10} \exp(-23000/RT)$ cm^3/sec. At room temperature k_1 extrapolates to $\sim 10^{-26}$ cm^3/sec. On the other hand Westenberg and De Haas[2] studied reaction 1 in the $H-O_2-CO$ system and found reaction 1 to be very fast at room temperature with $k_1 \sim 10^{-12}$ cm^3/sec. Consequently, a serious descrepancy exists between these two studies. If the latter value of k_1 is correct, reaction 1 plays an important role in the chemistry of the terrestrial atmosphere, whereas if the former value is correct then reaction 1 is completely unimportant as far as the earth's atmosphere is concerned.

In this paper we report a study of reactions 1 and 2 in a static system. Also we reexamine the reaction of $O(^1D)$ with H_2O. The HO_2

radicals were generated by the photolysis of N_2O at 2139A in the presence of excess H_2O or H_2 and smaller amounts of CO and O_2. The $O(^1D)$ atoms produced from the photolysis of N_2O react with H_2O or with H_2 to give OH radicals in the case of H_2O or OH radicals and H atoms in the case of H_2.

$O(^1D) + H_2O \rightarrow 2HO$ 3a

$O(^1D) + H_2 \rightarrow HO + H$ 4

In a previous report from this laboratory,[3] reaction 3a was shown to be the dominant, if not exclusive, fate of the reaction between $O(^1D)$ and H_2O. This reaction is further examined in the present paper. Reaction 4 has been shown to be the exclusive fate of the $O(^1D)$-H_2 interaction.[4]

The $O(^1D)$ atom might be removed by reaction with the other gases added in substantial amounts, i.e. N_2O, CO, or O_2.

$O(^1D) + N_2O \rightarrow N_2 + O_2$ 5a

$\rightarrow 2NO$ 5b

$O(^1D) + CO \rightarrow O(^3P) + CO$ 6

$O(^1D) + O_2 \rightarrow O(^3P) + O_2$ 7

These are reactions which we wish to minimize. The relative rate coefficients for the pertinent reactions are listed in Table I. The experiments were so designed that reactions 5-7 were unimportant compared to reactions 3a or 4. Reactions 6 and 7 have been neglected, but the somewhat larger, but still small, correction due to reaction 5 has been included in our analysis.

The only fate of HO radicals in the absence of H_2 is to react with CO to give H atoms via

$HO + CO \rightarrow CO_2 + H$ 8

In the presence of H_2, the HO radicals also react with H_2

$$HO + H_2 \rightarrow H_2O + H \qquad 9$$

Thus in the presence of either excess H_2O or H_2 and a smaller amount of CO, the net result is the production of H atoms. The resulting H atoms react exclusively with O_2 to give HO_2 radicals

$$H + O_2 + M \rightarrow HO_2 + M \qquad 10$$

The resulting HO_2 radicals may be removed by reactions 1 or 2, or they may disproportionate

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad 11$$

The measurement of the quantum yield of CO_2, $\Phi\{CO_2\}$, in the absence of NO permits the determination of $k_1/k_{11}^{\frac{1}{2}}$, and the measurement of the quantum yield of NO_2, $\Phi\{NO_2\}$, in the presence of NO permits the determination of $k_2/k_{11}^{\frac{1}{2}}$. Since reactions 1 and 2 are chain regenerating reactions, even low values of their rate coefficients should be accessible to measurement.

EXPERIMENTAL

NO absent

A conventional high-vacuum line utilizing Teflon stopcocks with Viton "O" rings was used. The reaction vessel was a cylindrical quartz cell 10 cm long and 5 cm in diameter. The cell was enclosed in a wire-wound aluminum block furnace, the temperature of which was controlled to ±1°C by a Cole-Parmer Proportio Null Regulator Series 1300.

The N_2O and CO used were Matheson C.P. grade. The N_2O was purified by passage over ascarite and degassed at -196°C. Gas chromatographic analysis indicated no detectable impurities. In particular CO_2 and N_2 were absent. The CO was purified by passage over glass beads and several traps at -196°C, degassing at -196°C and distillation from liquid Argon. The CO thus purified was free of CO_2 but contained 540 ppm of N_2. The N_2 yield in any photolysis experiment was appropriately corrected for this background N_2. Small amounts of tap water were degassed at -96°C prior to use in order to remove dissolved air and CO_2. Air Products research grade O_2 was purified by passage over traps at -196°C. The only remaining detectable impurity was 7 ppm of N_2. This amount of N_2 was entirely negligible.

All gas pressures including H_2O below its room temperature vapor pressure were measured with either a McCleoud gauge or a Hg manometer. The high H_2O pressures were not measured directly, but calculated assuming the perfect gas law. Our procedure was to introduce H_2O below its room temperature vapor pressure into the line, measure its pressure on the Hg manometer, and condense it into the reaction vessel. The stopcock to the insulated reaction vessel was closed and the temperature raised to 100°C or 200°C. From the known volume ratios the H_2O pressure was calculated.

Irradiation was from a Phillips Zn resonance lamp Typ 93106E. The effective radiation was at 2139A. After irradiation the gases noncondensable at -196°C were collected with a Toepler pump and analyzed for N_2 by gas chromatography using a 10-ft. long by 1/4 in. diameter column packed with 5A molecular sieves. A second fraction volatile at -96°C was removed and analyzed for CO_2 using a 24-ft. long by 1/4-in. column packed with Porapak Q operating at 25°C.

At 100°C a very small amount of CO_2 ($\sim$ 0.03 mtorr/min.) was produced in the dark. At 200°C the dark reaction was somewhat larger ($\sim$ 0.15 mtorr/min.). The correction for the dark reaction was small, usually less than a few percent.

NO present

For this system a conventional greaseless high-vacuum line was also employed, but Hg was rigorously excluded. The reaction vessel was also a cylindrical quartz cell 10 cm long and 5 cm in diameter.

The N_2O, CO, and O_2 were purified as described for the HO_2-CO system. The H_2, Matheson (C. P. grade), was purified by passage over traps at -196°C. The pressure of all gases in this system was measured with an alphatron gauge.

Irradiation was from a Zn lamp similar to that described for the HO_2-CO system. The NO concentration was maintained at $\leq$120 mtorr, so that the 2139A radiation was absorbed only by the N_2O.

The NO_2 was analyzed photometrically using a simple dual beam photometer. Light from a tungsten lamp was split in two beams. One of these passed through the reaction vessel and was focused on an RCA 935 photodiode, the other beam was focused on a second RCA 935 photodiode without passing through the vessel. The diodes were part of a simple electrical circuit which allowed the difference of the two signals to be measured. The minimum NO_2 pressure that could be measured in this way was $\sim$ 15 mtorr.

Actinometry was performed by the photolysis of N_2O at 2139A at the same pressure as used in an actual run. For this system $\Phi\{N_2\}$ is accurately known to be 1.41.[5] Thus a determination of the nitrogen produced allows the absorbed light intensity, I_a, to be determined. After irradiation an aliquot of the N_2 was analyzed by gas chromatography as described for the HO_2-CO system.

$O(^1D) + H_2O$

Results

First experiments were performed in the absence of O_2 and NO in order to measure the importance of reaction 5a compared to other possible reactions of $O(^1D)$ with H_2O. Mixtures of N_2O and CO were irradiated at 2139A in the presence of excess H_2O. The HO radicals produced in the $O(^1D) + H_2O$ interaction are scavenged by CO to give CO_2. The resulting CO_2 is a measure of the HO production efficiency. These experiments are similar to those already reported in our earlier study of the $O(^1D)$-H_2O system,[3] but have been extended to higher pressures and temperatures. The results are presented in Table II.

Measurements were made at 25°C, 100°C, and two runs were done at 200°C. At room temperature all the runs were at about the same conditions ($[N_2O] \sim 3$ torr, $[H_2O] \sim 18$ torr, and $[CO] \sim 5$ torr) due to constraints placed by the H_2O vapor pressure and the requirements that $[N_2O] << [H_2O]$ and $[CO] << [H_2O]$. The average ratio of $R\{CO_2\}/R\{N_2\}$ is 1.63 in close agreement with the earlier measurements.[3] At 100°C the pressure of each component as well as the total pressure was varied by a factor of almost 20. Except for minor variations, most of which may be accounted for by some quenching of $O(^1D)$ by N_2O and CO (see Discussion), $R\{CO_2\}/R\{N_2\}$ is independent of the $[N_2O]/[CO]$, $[H_2O]/[CO]$, and $[N_2O]/[H_2O]$ ratios and is almost independent of the total pressure. The results are also independent of the absorbed light intensity and of the percent conversion. However, $R\{CO_2\}/R\{N_2\}$ is always lower at 100°C than at 25°C. We have found earlier that if the CO is not carefully purified, irradiation of CO-N_2O mixtures result in high quantum yields of CO_2 and N_2 formation.[7]

To be sure that this impurity-initiated reaction does not play a role we have made careful comparison of the rate of N_2 production in the absence and presence of CO. To be certain that the light intensity did not change from run to run the experiments were done in two identical vessels simultaneously, one containing mixtures of N_2O-H_2O-CO and the other containig mixtures of N_2O-H_2O and small amounts of C_3H_6 to scavenge the OH radicals. The values of I_a for the two cells was obtained by irradiating N_2O at the same pressure in both cells. The rate of N_2 production, $R\{N_2\}$, was identical with either CO or C_3H_6 present.

Two runs were done at 200°C and a total pressure of H_2O of about 650 torr. The results at 200°C are similar to those at 100°C.

Discussion

The reaction scheme is

$$N_2O + h\nu \rightarrow N_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2HO \qquad 3a$$

$$\rightarrow O(^3P) + H_2O \qquad 3b$$

$$\rightarrow H_2O_2 \qquad 3c$$

$$\rightarrow H_2 + O_2 \qquad 3d$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad 5a$$

$$\rightarrow 2NO \qquad 5b$$

$$HO + CO \rightarrow CO_2 + H \qquad 8$$

where reaction 6 has been neglected because it is unimportant. Even when it does occur some CO_2 is formed by the interaction of $O(^3P)$ and CO, so that its inhibiting effect on CO_2 production is further minimized. The H atoms recombine either homogeneously or heterogeneously.

An upper limit on reactions 3b and 3d of 4 and 0.4%, respectively, has been found at 100°C by determination of $O(^3P)$ and H_2 production.[3] Reaction 3c has not been determined directly, but its importance relative to reaction 3a was estimated to be <5% at 25°C.[3]

From the above scheme, the following kinetic expression may be obtained

$$\Phi'\{CO_2\} \equiv \alpha R\{CO_2\}/R\{N_2\} = 2k_{3a}/k_3 \qquad \text{I}$$

where

$$\alpha \equiv 1 + (k_5 + k_{5a})\ [N_2O]/k_3[H_2O]$$

If $\Phi'\{CO_2\}$ is equal to 2 then k_{3a}/k_3 is unity, and reaction 3a is the exclusive reaction of $O(^1D)$ with H_2O. A value of 2.0 ± 0.1 was obtained earlier at 25°C and low H_2O pressures.[3] In the same study the competition of CO and C_3H_6 for OH was also studied at high H_2O pressures and higher temperatures. The value of $\Phi'\{CO_2\}$ deduced from this data was also $\sim$ 2, but with considerably greater uncertainty.

The values of $\Phi'\{CO_2\}$ for different experimental conditions are presented in Table II. Examination of the data shows that at 100° and 200°C, $\Phi'\{CO_2\}$ is significantly less than at 25°C, but is otherwise independent of all other variables, except total pressure. $\Phi'\{CO_2\}$ for the runs at 100°C and a total pressure of about 300 torr is somewhat less than for the runs at 100°C and a total pressure of about 20-30 torr. The average value of $\Phi'\{CO_2\}$ at 100°C is 1.5 ± 0.07 and at 25°C it is 1.82 ± 0.07. The value of 1.82 at 25°C is consistent with our earlier findings, but the values at 100°C and 200°C are significantly lower and are outside the experimental error. The value of $\Phi'\{CO_2\}$ obtained in the C_3H_6 experiments, mentioned above, was $\sim$ 2.0, but the uncertainty was sufficiently large so that the present results are not inconsistent with the earlier measurements. The fact that $\Phi'\{CO_2\}$ at low total pressure is slightly less than 2 may be accounted for by contribution of reaction 3b, and/or by some quenching of $O(^1D)$ by CO which was not taken into account. For the low-pressure runs at 25°C and 100°C it can be estimated that about 10% of the $O(^1D)$ are quenched by CO, consequently the above considerations raise $\Phi'\{CO_2\}$, within experimental error, to a value of 2.0 ± 0.05.

At 100 and 200°C, experiments could be done at higher pressures. It is at these higher pressures that $\Phi'\{CO_2\}$ is significantly below 2.0 to be meaningful. Presumably this is due to reaction 3c, which should increase with importance as the pressure is raised. With about 650 torr of H_2O vapor (at 200°C), reaction 3c apparently accounts for 20 ± 10% of the removal of $O(^1D)$ by H_2O. However, we have not analyzed for H_2O_2, so that this conclusion is not established unambiguously.

$HO_2 + CO$

Results

The previous experiments were repeated with O_2 present at 100°C and 200°C. At each temperature the CO pressure as well as the $[N_2O]/[CO]$ and $[H_2O]/[CO]$ ratio was varied over a substantial range. The light intensity was varied at 100°C by about a factor of 10. The results are presented in Table III. It can be seen that $R\{CO_2\}/R\{N_2\}$ is higher in the presence of O_2 than in its absence (Table II). There is no clear trend in the data with either the CO pressure, total pressure, temperature, or absorbed intensity.

Discussion

In the presence of O_2, three additional reactions are introduced into the reaction scheme

$$H + O_2 + M \rightarrow HO_2 + M \qquad 10$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad 11$$

$$HO_2 + CO \rightarrow HO + CO_2 \qquad 1$$

If H adds to CO, it will be oxidized to produce HO_2 + CO, so that this reaction need not be considered separately.

The rate coefficient for reaction 11 has been determined to be 6×10^{-12} cm^3/sec.[8,9] Thus even at our lowest intensities the HO_2 radical lifetime does not exceed 2 seconds. Usually, it is much less. Therefore wall removal of HO_2 cannot be as important as reaction 11, even if HO_2 is removed at every collision with the wall. A detailed calculation using the method of Jackson and Armstrong[10] shows that wall removal cannot account for more than 20% of the HO_2 loss under any conditions.

The mechanism leads to the prediction that

$$\Phi'\{CO_2\} - \Phi'_0\{CO_2\} = k_1[CO](2\alpha\Phi'_0\{CO_2\}/k_{11}R\{N_2\})^{\frac{1}{2}} \qquad \text{II}$$

where $\Phi'_0\{CO_2\}$ is $\Phi'\{CO_2\}$ in the absence of O_2, but for otherwise comparable conditions, i.e. the same $[N_2O]/[H_2O]$ ratio. From the data in Table III, it can be seen that the functional form of eqn II is not followed. Thus there must be an additional source of CO_2. However from the data in Tables II and III an upper limit to $k_1/k_{11}^{\frac{1}{2}}$ can be computed to be $1.9 \times 10^{-12}(cm^3/sec)^{\frac{1}{2}}$. When combined with the value of $k_{11} = 6 \times 10^{-12}$ cm^3/sec, this ratio gives $k_1 < 5 \times 10^{-18}$ cm^3/sec at both 100 and 200°C. This value is consistent with the results of Baldwin et al,[1] which when extrapolated to 200°C gives $k_1 \sim 10^{-20}$ cm^3/sec, but is much lower than the measurement of Westenberg and de Haas[2] who obtained $\sim 10^{-12}$ cm^3/sec at room temperature.

In addition to the reaction steps discussed above, some role may be played by the photolysis of H_2O_2 as it accumulates

$$H_2O_2 + h\nu \rightarrow 2HO$$

At the end of a run, the H_2O_2 pressure is about 0.1 - 1% of that of N_2O. However, the extinction coefficients at 2139A are 0.09[11] and 7.35[12] atm^{-1}cm^{-1}, respectively, for N_2O and H_2O_2. The photolysis of H_2O_2 regenerates HO radicals and thus enhances CO_2 production. This could account for all or part of the increase in $\Phi'\{CO_2\}$ observed in the presence of O_2. The upper limiting value for k_1 would then be even lower than 5×10^{-18} cm^3/sec.

HO_2 + NO

Results

The results for the photolysis of N_2O at 2139A and 25°C in the presence of H_2, O_2, CO and NO are presented in Table IV and in graphical form in Figures 1 and 2. Table IV and the figures give the NO_2 pressure as a function of the irradiation time for different experimental conditions.

The NO pressures used were 30, 60, and 120 mtorr. The CO pressure was either 0, 50, or 100 torr. Most runs were done with an O_2 pressure of 50 torr. However, a few were done at lower O_2 pressure. The N_2O pressure was always 47 torr and the H_2 pressure was always maintained at 760 torr. The total pressure was 970 torr in most runs except in a few runs it was somewhat lower. The $[H_2]/([O_2] + [CO] + [N_2O])$ ratio was maintained as high as possible to minimize the reaction of $O(^1D)$ with O_2, CO, and N_2O. The $[N_2O]/[NO]$ ratio was maintained at $\gtrsim 390$ to insure that radiation is absorbed only by the N_2O. An O_2 pressure of 50 torr was employed to prevent the reaction of H atoms with NO, CO, or the NO_2 product. Experiments were done at absorbed light intensities of 1.4×10^{12} and 1.9×10^{11} quanta/cc-sec.

At the pressures of NO and O_2 employed some NO_2 was produced in the well-known dark reaction

$$2NO + O_2 \rightarrow 2NO$$

with a rate which was in good agreement with the rate predicted from the known rate constant. At 30 and 60 mtorr the dark reaction amounted to less than 10% and 20% respectively. But at 120 mtorr the NO produced in the dark reaction was about the same as in the light reaction for the points at lower conversions. Most of the dark reaction occurred during the gas mixing period prior to irradiation. Since this period was accurately known, accurate corrections could be applied. The amount of dark reaction during the irradiation was generally negligible.

In Table IV both the corrected and observed NO_2 pressures are presented. The NO_2 pressures plotted in Figures 1 and 2 are corrected for the dark reaction and only the data for the maximum CO and O_2 pressures are plotted.

It can be seen that the NO_2 pressure at first increases with irradiation time up to a maximum value and then declines on further irradiation. Examination of Table IV shows that the maximum observed NO_2 pressure (uncorrected for the dark reaction) is very close to the initial NO pressure employed. Consequently, the stoichiometric relation

$$[NO_2] = [NO]_0 - [NO]$$

applies to a good approximation for conversions below the maximum, where $[NO]_0$ is the initial NO concentration.

From the graphs it is obvious that initial rates, and therefore the initial quantum yields may be obtained from the data at 60 and 120 mtorr, but not at 30 mtorr due to insufficient data. The initial rates and quantum yields are given in Table V. From Table V it is clear that the initial quantum yields of NO_2 production, $\Phi_i\{NO_2\}$ are very large. $\Phi_i\{NO_2\}$ decreases by almost a factor of 2 when the NO pressure changes from 60-120 mtorr. From Table IV it is evident that the initial rate at 60 mtorr and 120 mtorr increases by about a factor of 3 upon the addition of 55 torr of CO; a further increase occurs upon addition of more CO. Approximately the same effect is observed at 30 mtorr of NO as well. An increase of O_2 from 14 torr to 50 torr at 60 mtorr NO and 60 seconds exposure increases the rate of oxidation slightly, but not significantly. A change in the light intensity by a factor of 7.3 did not significantly alter the initial quantum yields.

Discussion

The results may be discussed in terms of the following chain mechanism for the conversion of NO into NO_2

$$N_2O + h\nu \rightarrow N_2 + O(^1D)$$

$$O(^1D) + H_2 \rightarrow HO + H \tag{4}$$

$$HO + CO \rightarrow CO_2 + H \tag{8}$$

$$HO + H_2 \rightarrow H_2O + H \tag{9}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{10}$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{11}$$

$$HO_2 + NO \rightarrow HO + NO_2 \tag{2}$$

$$HO + NO\ (+M) \rightarrow HONO\ (+M) \tag{12}$$

$$HO + NO_2\ (+M) \rightarrow HONO_2\ (+M) \tag{13}$$

The reactions of $O(^1D)$ with gases other than H_2 have been ignored since they cannot be important. Under all of our conditions at least 90% of the $O(^1D)$ atoms must react with H_2, as deduced from the relative rate coefficients in Table I.

The H atoms produced in reactions 8 and 9 will react predominantly with O_2 to give HO_2. The possible competing reactions of H with NO or the NO_2 produced in the reaction cannot be important based on computations with the known rate coefficients for these reactions. Furthermore this was demonstrated experimentally, since a reduction in the O_2 pressure from 50 to 14 torr had no substantial effect.

In addition to the chain terminating step, reaction 11, it is also necessary to consider reactions 12 and 13 as termination reaction. Both are rapid, and in fact are the dominant chain terminating reactions, as we will demonstrate.

Because $\Phi_i\{NO_2\} >> 2$, NO_2 is produced primarily in chain propagating reactions. Reaction 2 is the only conceivable reaction to do this, and it must account for the NO_2 production. The outlined mechanism explains the general features of the curves in Figures 1 and 2. Initially NO is rapidly oxidized to NO_2 via reaction 2 until conversion is complete. On further photolysis the NO_2 pressure declines, because now NO_2 is slowly consumed by reaction with HO and possibly HO_2 radicals.

The complete mechanism leads to a complex rate law for NO_2 formation. However simplifications can be made if reaction 11 is either the dominant or unimportant terminating reaction. If reaction 11 is dominant, i.e. reactions 12 and 13 are unimportant, then

$$\Phi_i\{NO_2\} = k_2[NO]/(I_a k_{11})^{\frac{1}{2}} \qquad \text{III}$$

On the other hand if reaction 11 is unimportant compared to reactions 12 and 13, then

$$\Phi_i\{NO_2\} = 2(k_8[CO] + k_9[H_2])/(k_{12}[NO] + k_{13}[NO_2]) \qquad \text{IV}$$

Our results indicate that $\Phi_i\{NO_2\}$ varies inversely with [NO], linearly with CO, and is independent of I_a. Thus Eqn. IV applies for all of our conditions. It is interesting to note that two other possible reactions might be involved in termination

$$HO_2 + NO\ (+M) \rightarrow HONO_2\ (+M)$$

$$HO_2 + NO_2 \rightarrow O_2 + HONO$$

There is no prior evidence for either reaction. They cannot be the dominant chain termination reactions in our system because then the rate expression would be independent of [CO], The dependence of our data on [CO] excludes the possibility that these reactions occur to any significant extent.

With the known values of k_8 and k_9, and the initial rates at 60 and 120 mtorr of NO, the value of k_{12} may be computed with equation IV. The result is 5.6×10^{-12} and 6.5×10^{-12} cm^3/sec at 120 and 60 mtorr, respectively. The average value is 6.0×10^{-12} cm^3/sec. The values of $k_9 = 7 \times 10^{-15}$ and $k_8 = 1.35 \times 10^{-13}$ cm^3/sec used in the calculation are those obtained by Niki et al.[13] These values for k_8 and k_9 are in very good agreement with other determinations[14] and are probably good to 20%. Recently two measurements of k_{12} have been reported. One of these is by Stuhl and Niki[13] who found reaction 12 to be in the fall off region at ∿ 80 torr of He. They calculated a limiting high pressure rate constant $k_{12}^{\infty} = 2 \times 10^{-12}$ cm^3/sec. The other report was by Morley and Smith[15] who, contrary to Stuhl and Niki, found the reaction to be entirely in the third order region at similar pressures with $k_{12}^{\circ} = 9.4 \times 10^{-31}$ cm^6/sec for H_2 as the third body. Using RRKM theory, Morley and Smith computed the high pressure limiting rate constant, k_{12}^{∞} to be 1.7×10^{-10} cm^3/sec. With this value for k_{12}^{∞} and the value for k_{12}°, it may be computed that at 1 atm of H_2, reaction 12 should still be almost entirely in the third order regime, with a pseudo second-order rate constant of 2×10^{-11} cm^3/sec. Thus the value of $k_{12} = 6.0 \times 10^{-12}$ cm^3/sec obtained in this work at 1 atm of H_2 is midway between the values of Morley and Smith and of Stuhl and Niki.

Since reaction 11 is not important in this system, a value of $k_2/k_{11}^{\frac{1}{2}}$ cannot be determined. However a lower limit can be found since $[HO_2] < (I_a/k_{11})^{\frac{1}{2}}$. Then

$$\Phi_1\{NO_2\} = k_2[NO][HO_2]/I_a < k_2[NO]/(k_{11}I_a)^{\frac{1}{2}}$$

Our data led to the result that $k_2/k_{11}^{\frac{1}{2}} \geq 0.6 \times 10^{-7}$ $(cm^3/sec)^{\frac{1}{2}}$. With the average value of $k_{11} = 6 \times 10^{-12}$ cm^3/sec found by Paukert and Johnston[8] and Hochanadel et al,[9] $k_2 > 1.5 \times 10^{-13}$ cm^3/sec.

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Table I: Relative Rate of $O(^1D)$ Reactions

Ratio	Value	Reference
k_3/k_5	2.1	Simonaitis and Heicklen[3]
k_4/k_5	2.0	Paraskevopoulos and Cvetanović[4]
k_{5a}/k_5	0.41	Simonaitis, Greenberg, and Heicklen[5]
k_6/k_5	0.36	Scott and Cvetanović[6]
k_7/k_5	0.59	Paraskevopoulos and Cvetanović[4]

Table II: Photolysis of N_2O at 2139A in the Presence of H_2O and CO

$[N_2O]$, torr	$[H_2O]$, torr	[CO], torr	Irradiation time, min.	$R\{N_2\}^a$, μ/min.	$R\{CO_2\}^a$, μ/min.	$\frac{R\{CO_2\}}{R\{N_2\}}$	$\Phi'\{CO_2\}$
			25°C				
3.00	17.5	5.0	393	0.51	0.77	1.53	1.71
3.05	16.5	7.0	945	0.27	0.46	1.71	1.92
2.90	17.1	4.5	762	0.33	0.52	1.59	1.78
2.70	19.3	6.0	455	0.37	0.63	1.71	1.87
			100°C				
40.0	273	47.0	45	5.20	7.45	1.42	1.54
35.0	280	19.5	56	5.00	7.25	1.43	1.54
39.0	266	41.0	35	5.00	6.93	1.40	1.53
18.0	266	10.0	795	0.40	0.59	1.48	1.54
10.3	280	54.0	185	2.14	3.08	1.44	1.47
10.2	280	9.00	113	2.45	3.40	1.38	1.41
10.0	280	9.00	60	1.84	2.62	1.48	1.45
9.00	280	40.0	90	1.60	2.37	1.48	1.51
7.40	273	16.5	950	0.26	3.95	1.51	1.53
2.95	21.0	1.10	780	0.43	0.63	1.51	1.66
2.65	19.9	5.50	1140	0.30	0.455	1.51	1.85
2.65	19.9	5.00	1140	0.36	0.61	1.69	1.84

Table II (concluded)

$[N_2O]$, torr	$[H_2O]$, torr	$[CO]$, torr	Irradiation time, min.	$R\{N_2\}^a$, μ/min.	$R\{CO_2\}^a$, μ/min.	$\frac{R\{CO_2\}}{R\{O_2\}}$	$\Phi^1\{CO_2\}$
			200°C				
48.0	610	44	30	13.2	1.86	1.41	1.49
10.0	640	8.0	20	3.79	4.91	1.32	1.34

a. Pressures for products are given at 25°C.

Table III: Photolysis of N_2O at 2139A in the Presence of H_2O, CO, and O_2

[CO], torr	$[H_2O]$, torr	$[N_2O]$, torr	$[O_2]$, torr	Irradiation time, min.	$R\{N_2\}^a$, μ/min.	$R\{CO_2\}^a$, μ/min.	$\frac{R\{CO_2\}}{R\{N_2\}}$	$\Phi'\{CO_2\}$
				100°C				
66	290	48	46	46	6.10	12.5	1.93	2.14
60	126	19	21	60	3.43	5.85	1.70	1.87
56	126	20	21.5	60	3.40	6.58	1.94	2.13
58	320	8.0	42	144	1.18	3.75	3.10	3.14
57	240	52.0	45	45	7.32	18.1	2.47	2.83
59	280	52.0	43	175	0.692	1.74	2.52	2.84
54	280	55.0	46	23	7.40	19.1	2.61	2.95
52	270	50.0	40	210	0.114	0.285	2.50	2.81
50	270	51.0	43	300	0.533	1.66	3.13	3.52
12.0	300	51.5	40	30	0.735	1.41	1.93	2.15
9.0	270	49.0	43	32	8.60	22.0	2.53	2.84
49.5	126	19.0	18.5	55	2.16	4.95	2.20	2.42

Table III (concluded)

[CO], torr	$[H_2O]$, torr	$[N_2O]$, torr	$[O_2]$, torr	Irradiation time, min.	R$\{N_2\}$a, μ/min.	R$\{CO_2\}$a μ/min.	$\frac{R\{CO_2\}}{R\{N_2\}}$	$\Phi^1\{CO_2\}$
				200°C				
108	630	48	46	46	7.80	20.0	2.58	2.70
99	600	46.5	42	31	7.55	23.0	3.03	3.19
59	635	60.0	50	45	5.80	16.9	2.92	3.10
50	635	55	50	46	6.30	19.6	3.10	3.19
47	142	15	15	133	2.40	9.25	3.84	4.08
10	570	48	40	12	8.70	22.4	2.58	2.71
8.5	620	47	48	32	6.65	12.8	1.93	2.03
60	635	50	42.5	45	8.00	22.4	2.80	2.94

a. *Pressure for products are given at 25°C.*

Table IV: Photolysis of N_2O at 2139A and 25°C in the Presence of H_2, O_2, NO, and CO[a]

[CO], torr	Irradiation time, sec.	[NO_2], mtorr[c]	[NO_2], mtorr[d]
$I_a = 1.4 \times 10^{12}$ quanta/cc-sec, [NO] = 30 mtorr			
0	5	7.5	6.0
55	5	20.6	18.6
110	5	21	19.0
110	5	17	15.0
$I_a = 1.4 \times 10^{12}$ quanta/cc-sec, [NO] = 60 mtorr			
0	10	12	7
0	10	12	8
55	10	27	22
110	5	25	21
110	10	37	32
110	10	33	30
110	10	37	33
110	10	35	31
110	10	36	32
110	10	33	29
110	10	33	29
110	20	49	42
110	30	37	32
110	40	56	52
110	70	55	50
$I_a = 1.4 \times 10^{12}$ quanta/cc-sec, [NO] = 120 mtorr			
110	5	26	13
110	10	36	23
110	10	33	20
110	20	47	37
110	35	68	55
110	70	110	97
110	120	109	96
110	375	95	95
110	1200	39	39

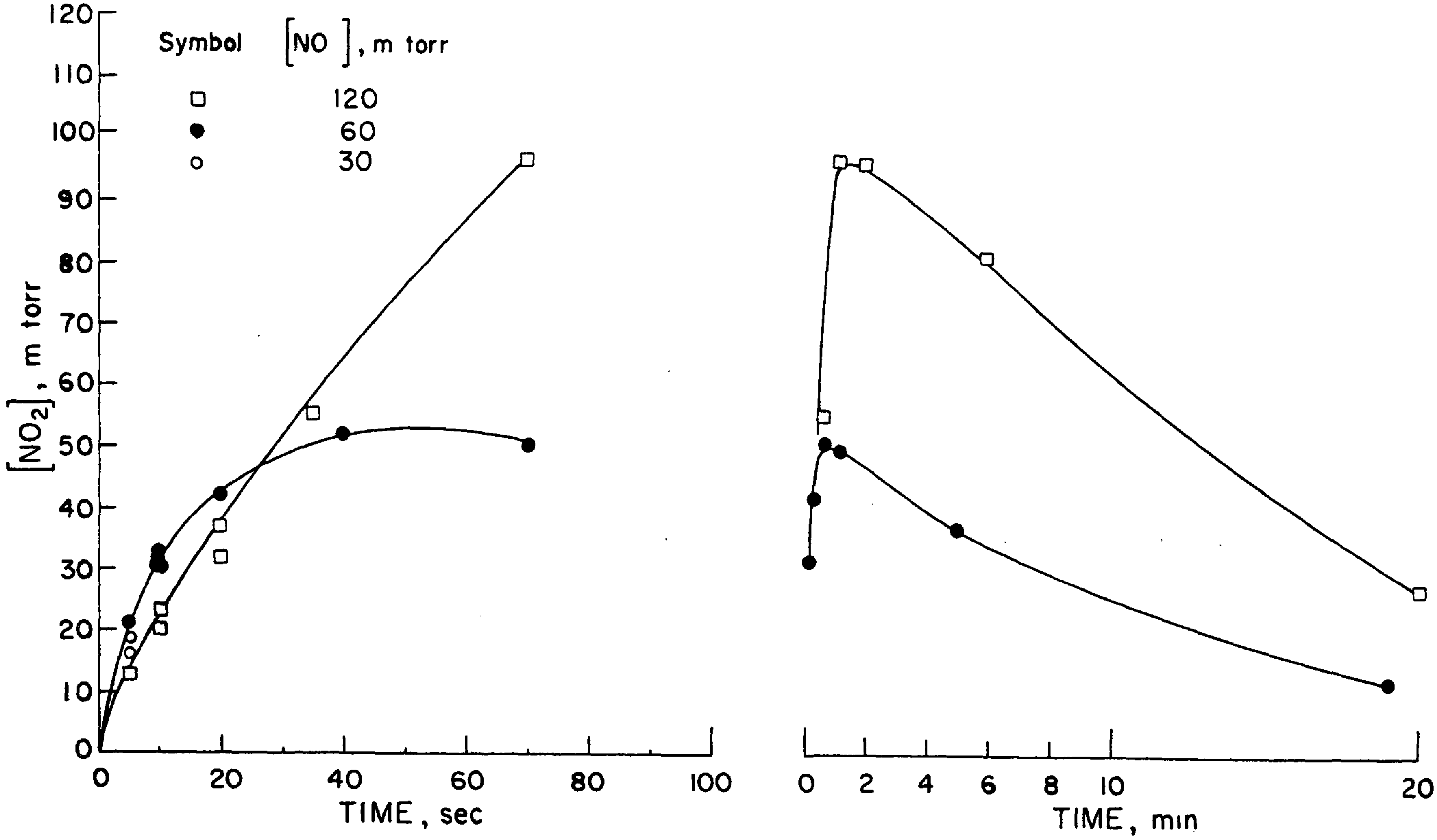
Table IV (continued)

[CO], torr	Irradiation time, sec.	$[NO_2]$, mtorr[c]	$[NO_2]$, mtorr[d]
	$I_a = 1.9 \times 10^{11}$ quanta/cc-sec, [NO] = 30 mtorr		
0	30	9.2	8.2
0	150	25.5	24
0	150	26.0	25
55	30	17	17
110	30	18	17
110	30	19	18
	$I_a = 1.9 \times 10^{11}$ quanta/cc-sec, [NO] = 60 mtorr		
0	150	22.7	18
0	300	40	35
0	600	56	51
0	1800	50	45
55	60	29	24
110	60	42	36
110	30	25	21
110	15	15	10
110	120	45	40
110	300	57	53
110	600	55	51
110	60	36	31
110[b]	60	28	27
110[b]	60	24	23
	$I_a = 1.9 \times 10^{11}$ quanta/cc-sec, [NO] = 120 mtorr		
0	300	45	25
0	330	45	25
0	600	59	39
0	1800	95	75
110	60	44	24
110	180	71	51
110	360	107	87
110	600	108	88
110	1800	84	64

a. $[N_2]$ = 760 torr, $[O_2]$ = 50 torr, $[N_2O]$ = 47 torr. b. $[O_2]$ = 14 torr
c. observed d. corrected for dark reaction

Table V: Initial Quantum Yields of NO_2

[NO], mtorr	I_a, quanta/cc-sec	$\Phi_i\{NO_2\}$
60	1.4×10^{12}	100
120	1.4×10^{12}	59
60	1.9×10^{11}	119
120	1.9×10^{11}	73


Symbol
[NO], m torr
□ 120
● 60
○ 30
[NO$_2$], m torr
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10
20
30
40
50
60
70
80
90
100
110
120
TIME, sec
0
20
40
60
80
100
TIME, min
0
2
4
6
8
10
20

Fig. 1

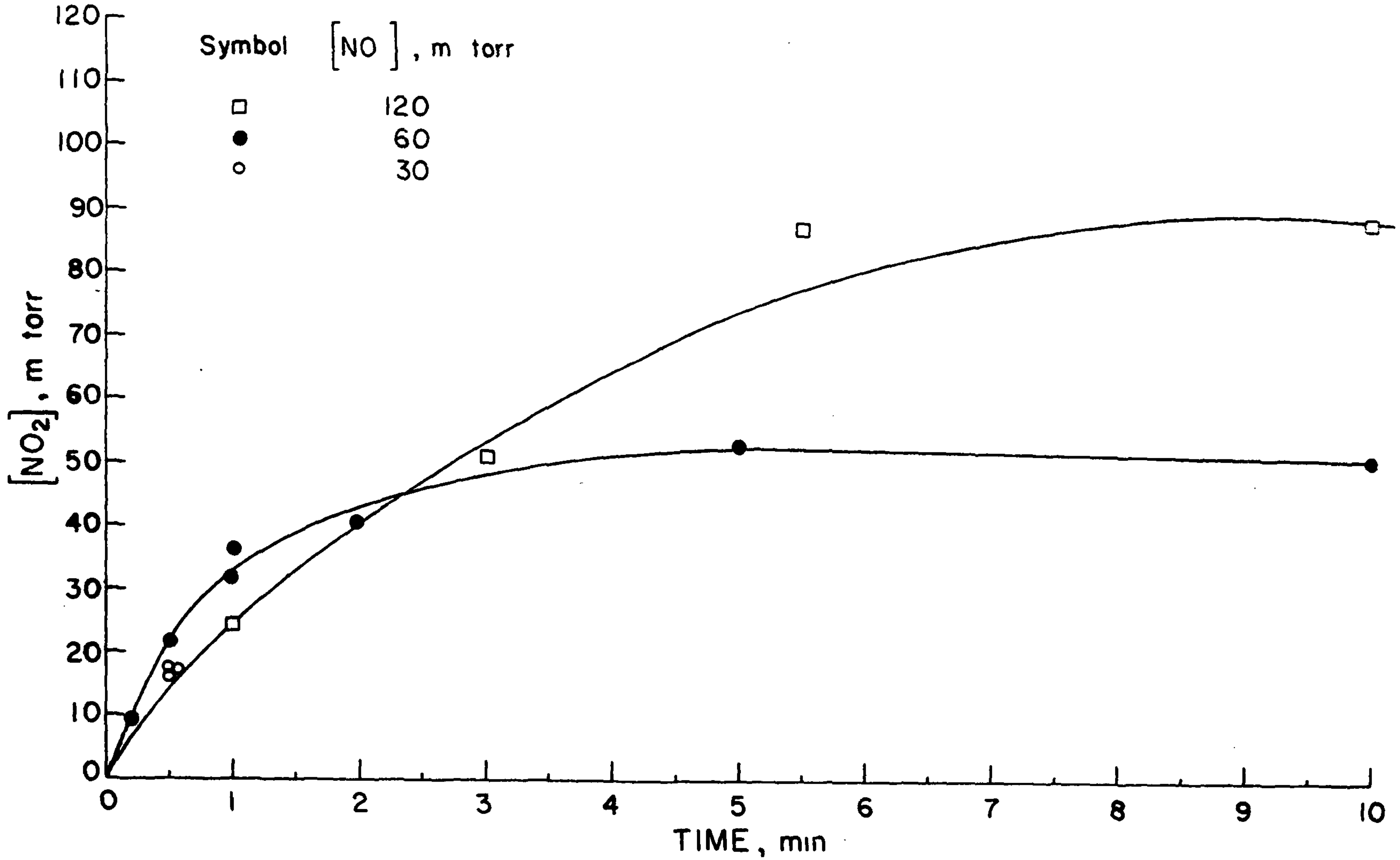
Symbol
[NO], m torr
□ 120
● 60
○ 30
[NO$_2$], m torr
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME, min
0
1
2
3
4
5
6
7
8
9
10

Fig. 2

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* The Ionosphere Research Laboratory	2a. REPORT SECURITY CLASSIFICATION 2b. GROUP

3. REPORT TITLE

The Reactions of HO_2 with CO and NO and the Reaction of $O(^1D)$ with H_2O

4. DESCRIPTIVE NOTES *(Type of report and, inclusive dates)*
Scientific Report

5. AUTHOR(S) *(First name, middle initial, last name)*

R. Simonaitis and Julian Heicklen

6. REPORT DATE February 8, 1973	7a. TOTAL NO. OF PAGES 35	7b. NO. OF REFS

8a. CONTRACT OR GRANT NO. NSF GA-12385 NASA NGL-009-003 b. PROJECT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) PSU-IRL-SCI-413
c. d.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

Supporting Agencies

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY National Science Foundation National Aeronautics and Space Administration

13. ABSTRACT

HO_2 radicals were generated by the photolysis of N_2O at 2139 A in the presence of excess H_2O or H_2 and smaller amounts of CO and O_2. The $O(^1D)$ atoms produced from the photolysis of N_2O react with H_2O to give HO radicals or H_2 to give HO + H. With H_2O two HO radicals are produced for each $O(^1D)$ removed at low pressures (i.e., ~20 torr H_2O), but the HO yield drops as the pressure is raised. This drop is attributed to the insertion reaction

$$O(^1D) + H_2O + M \rightarrow H_2O_2 + M$$

This reaction removes 20 ± 10% of the $O(^1D)$ atoms at ~650 torr H_2O (at 200°C).

The HO radicals generated can react with either CO or H_2 to produce H atoms which then add to O_2 to produce HO_2. In the absence of NO the HO_2 radicals could react by two routes

$$HO_2 + CO \rightarrow HO + CO_2 \qquad 1$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad 11$$

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6811

NONE
Security Classification

A-31408

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

2a. REPORT SECURITY CLASSIFICATION

2b. GROUP

3. REPORT TITLE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

6. REPORT DATE

7a. TOTAL NO. OF PAGES

7b. NO. OF REFS

8a. CONTRACT OR GRANT NO.

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

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Reaction 1 is so slow, even at 200°C, that only an upper limiting value of 1.9×10^{-12} $(cm^3/sec)^{1/2}$ could be found for $k_1/k_{11}^{1/2}$. When combined with the value of $k_{11} = 6 \times 10^{-12}$ cm^3/sec, this ratio gives $k_1 < 5 \times 10^{-18}$ cm^3/sec at both 100 and 200°C.

With NO present, NO_2 is produced in a long chain process via

$$HO_2 + NO \rightarrow HO + NO_2 \qquad 2$$

In this case reaction 2 is so rapid at 25°C that only a lower limiting value of 0.6×10^{-7} $(cm^3/sec)^{1/2}$ could be found for $k_2/k_{11}^{1/2}$. Thus, $k_2 > 1.5 \times 10^{-13}$ cm^3/sec at 25°C.