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Scientific Report 372

REACTIONS OF O(^{1}D) WITH NITROUS OXIDE AND METHANE

by

Raymond I. Greenberg

July 23, 1971

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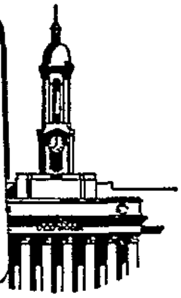

University Park, Pennsylvania

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CHAPTER 1

INTRODUCTION

The O(^{1}D) Atom in the Upper Atmosphere

One of the most important constituents of the upper atmosphere is the electronically excited oxygen atom in the $^1D_2$ state. The O(^{1}D) atom is of particular interest for several reasons. One is that it is responsible for the airglow and aurora red lines at $\lambda = 6300$ A and $\lambda = 6364$ A due to radiative transitions to the O($^3P_2$) and O($^3P_1$) states respectively.

Due to the difference in multiplicity between the ground and first excited state of the oxygen atom, certain reactions of the O(^{3}P) atom violate the spin conservation law, while the same reactions for the O(^{1}D) atom do not:

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

$$O(^1D) + CO \rightarrow CO_2 + h\nu \qquad (2)$$

The fact that the O(^{1}D) to O(^{3}P) transition is spin forbidden, radiative removal will be of minor importance compared to chemical reaction and physical deactivation under conditions of reasonably high pressures. The radiative lifetime of the O(^{1}D) atom is of the order of 100 seconds.

Furthermore, the excitation energy of the O(^{1}D) atom, 45 kcal/mole, is high enough to make its chemical reactivity important but not as high as to make its occurrence unlikely. This excitation energy can reduce or eliminate any activation energy requirement of certain reactions. For example, the $O(^3P) + CH_4$ reaction requires an activation energy between 8-10 kcal/mole.

In summary, even though the concentration of the $O(^1D)$ atom is several orders of magnitude smaller than the concentration of $O(^3P)$ atom, in the upper atmosphere certain reactions of the $O(^1D)$ atom may occur at comparable velocities with those of $O(^3P)$ atoms.

In the upper atmosphere there are two important processes which lead to the production of $O(^1D)$ atoms:

1. At high altitudes, above 90 km.

$$O_2(^3\Sigma_g^-) + h\nu \rightarrow O(^3P) + O(^1D) \qquad (\lambda < 1750\,A)$$

2. At low altitudes, between 8-50 km., the following reactions are possible

$$O_3(^1A) + h\nu \rightarrow O_2(^3\Sigma_g^-) + O(^1D) \qquad (\lambda < 4110\,A) \qquad (4)$$

$$O_3(^1A) + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D) \qquad (\lambda < 3080\,A) \qquad (5)$$

$$O_3(^1A) + h\nu \rightarrow O_2(^1\Sigma_g^+) + O(^1D) \qquad (\lambda < 2660\,A) \qquad (6)$$

DeMore and Raper[1] have shown that in the condensed phase at wavelengths less than 3000 A for every O_3 photolyzed an $O(^1D)$ atom is formed.

At the higher wavelengths where reaction (4) might occur ozone does not absorb; therefore, this reaction can not be an important process leading to the formation of $O(^1D)$ atoms. A definite decision between reactions (5) and (6) as to which is the major process leading to the formation of $O(^1D)$ has not been made however, above 2660 A reaction (5) is the only possibility.

Other species which are minor constituents of the upper atmosphere which might be photolytically decomposed to produce O(^{1}D) are: N_2O, NO_2, and CO_2. The contribution from these species to the O(^{1}D) concentration in the atmosphere is of minor importance.

In order to determine the concentration of O(^{1}D) atoms in a sunlight atmosphere it is necessary to introduce the effect of the principal loss process, the physical deactivation by N_2 and O_2. Nicolet[2] adopted the following value for the whole homosphere for the quenching rate constant:

$$k_Q = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$$

The photostationary concentration of O(^{1}D) for an overhead sun as a function of altitude is shown in Table 1.

From Table 1 it can be seen that the O(^{1}D) atom concentration increases from 20 to 50 km. This is due to the photolytic decomposition of O_3, reactions (4) - (6). A further increase in the concentration of the O(^{1}D) occurs above 90 km. due to the photolysis of molecular oxygen, reaction (3). Finally at altitudes greater than 120 km. the concentration of atomic oxygen becomes greater than that of molecular oxygen.[3]

N_2O and CH_4 as Minor Constituents of the Upper Atmosphere

There are two possible sources of N_2O in the upper atmosphere:

1. N_2O is produced by soil bacteria upon decomposition of nitrogen compounds.

TABLE 1

CONCENTRATION OF O(^{1}D) FOR AN OVERHEAD SUN UNDER EQUILIBRIUM CONDITIONS[2]

Altitude (km)	Atoms/cc	Altitude(km)	Atoms/cc
20	2.5	65	2.0×10^2
25	1.1×10^1	70	1.2×10^2
30	4.4×10^1	95	4.0×10^2
35	1.5×10^2	100	1.0×10^3
40	4.4×10^2	105	2.0×10^3
45	7.8×10^2	110	4.0×10^3
50	7.9×10^2	115	5.0×10^3
55	5.6×10^2	120	4.0×10^3
60	3.3×10^2		

2. N_2O can be photochemically produced in the stratosphere.

Adel[4-5] was the first to consider the soil bacterial process and the work of Goody and Walshaw[6] indicates that this is the most important source. Harteck and Dondes[7-8] consider the formation of N_2O by the reaction in the ozone layer:

$$N_2 + O_3^* \rightarrow N_2O + O_2 \tag{7}$$

at higher altitudes

$$O(^1D) + N_2 + M \rightarrow N_2O + M \tag{8}$$

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

may contribute significantly to the N_2O content of the upper atmosphere.

The earth's surface is the major source for methane in the atmosphere. Methane is the major hydrocarbon product in all anaerobic bacterial decomposition of organic matter in swamps, lakes, marshes and sewage.[9] In addition, natural gas which contains a large percentage of methane does escape to the atmosphere. Table 2 compares the relative content of methane and nitrous oxide to other minor constituents of the atmosphere at ground level. The same relative contents as listed in Table 2 are expected to altitudes of 100 km. except for O_3 and N_2O.

Both methane and nitrous oxide can be photolytically destroyed by solar radiation in the upper atmosphere. However, at altitudes below 50-70 km. the N_2O and CH_4 is protected by the oxygen-ozone layer. At these altitudes, the reactions of oxygen atoms with

TABLE 2

MOLECULAR CONTENT OF MINOR CONSTITUENTS OF THE ATMOSPHERE[3]

Molecule	Ratio by Volume[a]
H_2O	10^{-5} to 10^{-2}
CO_2	3×10^{-3}
O_3	10^{-8} to 10^{-7}
CH_4	1.5×10^{-6}
N_2O	2.5×10^{-7}
CO	5×10^{-8} to 2×10^{-7}
H_2	5×10^{-7}

(a) compared to the major gases N_2 and O_2

methane and nitrous oxide become important:

$$O(^1D) + CH_4 \rightarrow \text{products} \qquad (9)$$

$$O(^1D) + N_2O \rightarrow 2NO \qquad (15)$$

The oxidation of nitrous oxide to form nitric oxide is an important source of NO in the stratosphere.

Methods of Production of $O(^1D)$ in the Laboratory

Since the photolysis of ozone below 3100 A results in the production of $O(^1D)$ atom in the upper atmosphere, this is a convenient method of production in the laboratory:

$$O_3(^1A) + h\nu \rightarrow O_2^* + O(^1D) \qquad (10)$$

where O_2^* is either the $^1\Delta$ and $^1\Sigma$-state.

Sato and Cvetanovic[10] photolyzed NO_2 at wavelengths below 2288 A to produce $O(^1D)$:

$$NO_2 + h\nu \rightarrow NO(^2\Pi) + O(^1D) \qquad (11)$$

In addition, the photolysis of N_2O with 2139 A or 1849 A leads to the production of $O(^1D)$:

$$N_2O + h\nu \rightleftharpoons N_2 + O(^1D) \qquad (12)$$

A more detailed description of the production and reaction of $O(^1D)$ atoms can be found in an excellent review article by McGrath and McGarvey.[11]

Previous Investigations of the Photolysis of Nitrous Oxide

The photolysis of nitrous oxide has been studied by Noyes and co-workers.[12-14] They found two primary processes:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (12)$$

$$N_2O + h\nu \rightarrow NO + N \qquad (13)$$

Doering and Mahan[15] have also given evidence that at 1830 A about 20% of the primary decomposition might occur by reaction (13).

It has been shown that the photolysis of N_2O with either 1849 A or 2139 A radiation leads almost exclusively to the production of $O(^1D)$[16-20] as indicated in reaction (12). The excited oxygen atom can then react further to produce O_2, NO, and additional N_2:

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (14)$$

$$O(^1D) + N_2O \rightarrow 2NO \qquad (15)$$

Previous Investigations of the Reactions of $O(^1D)$ Atoms with Methane

Basco and Norrish[21] flash photolyzed ozone in the presence of methane. They observed (spectroscopically) the presence of vibrationally hot hydroxyl radicals indicating the occurrence of the reaction:

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \qquad (16)$$

DeMore and Raper[22] studied the reaction of $O(^1D)$ with CH_4 by the photolysis of O_3-CH_4 mixtures dissolved in liquid argon at 87°K. The products they found were CH_3OH, CH_2O, and H_2 and they indicated that the reaction proceeds by reaction (16) and two additional paths:

$$O(^1D) + CH_4 + M \rightarrow CH_3OH + M \tag{17}$$

$$O(^1D) + CH_4 \rightarrow CH_2O + H_2 \tag{18}$$

However, Groth[23] represents the primary process for the reaction between (^1D) oxygen atoms and methane as:

$$O(^1D) + CH_4 \rightarrow CH_2 + H_2O \tag{19}$$

The Present Investigation

The purpose of the present investigation was several fold. In the photolysis of N_2O by itself at 2139 A it was hoped to determine accurately the ratio of rate constants k_{14}/k_{15}, to determine the extent of occurrence of reaction (13) and the extent of the reactions leading to the production of ground state $O(^3P)$ atoms.

In the photolysis of N_2O-CH_4 mixtures it was hoped to determine the detailed mechanism and the relative rate constants for reaction and collisional deactivation of the $O(^1D)$ atom.

Finally, another goal of this research was to observe the effect of removal of the excess translational energy of the $O(^1D)$ atom by added helium in both the photolysis of N_2O by itself and in the photolysis of N_2O-CH_4 mixtures.

A new technique "the method of chemical difference" is introduced and its advantages in determining the ratio of rate constants are shown.

CHAPTER 2

EXPERIMENTAL

The High Vacuum Line

The high vacuum system was constructed of Pyrex tubing employing both Teflon stopcocks (West Glass Corporation) and high vacuum grease stopcocks. Both types of stopcocks could be used since none of the reactants attacked the grease. Figure 1 illustrates the location of the various components. The pumping system consisted of a single-stage mercury diffusion pump and a two-stage Welch Duo-Seal air pump (Model 1402). Pressures less than 10 torr were measured on a McLeod Gauge (Consolidated Vacuum Corporation). Pressures greater than 10 torr were measured on a mercury manometer; to increase the accuracy of the pressure measurements for the N_2O-CH_4 experiments a cathetometer (Gaertner Scientific Corporation, Model M-911) was employed. Finally, a thermocouple gauge (Veeco Instrument, Inc., Model TG-7 with a vacuum gauge tube Model DV-1M) was used to measure low pressures (< 1 torr) of methanol which is condensable in the McLeod Gauge. In addition, the thermocouple gauge was used to monitor the admission of gases into the vacuum line. Ace Glass adapters (5027-20) were employed for introducing the various gases into the line.

The Optical System

The photolyses were done in two cylindrical quartz cells, each 10 cm. long and 5 cm. in diameter. The effective radiation was at 2139A from a Philips 93106 A Zn resonance lamp.

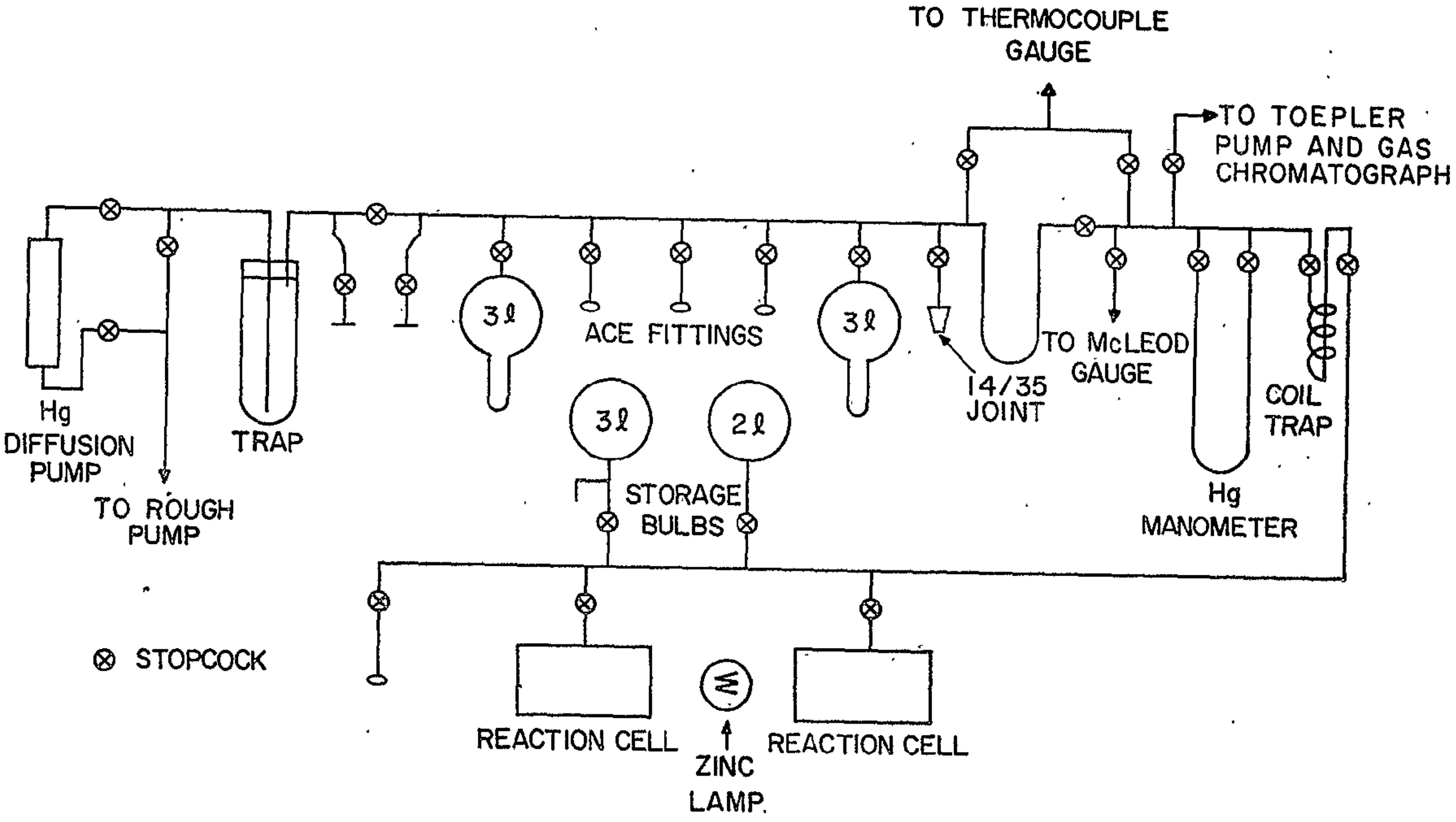

FIGURE 1

VACUUM LINE

The initial purpose of the two cell system was to allow an experiment to be performed in one cell while the intensity of the lamp could be monitored by an actinometry experiment in the other cell. This technique was employed since the intensity of the initially obtained zinc lamps varied. However, good zinc lamps were obtained and therefore the two cells could be used to perform two different simultaneously run experiments.

Reagents and Methods of Purification

Nitrous Oxide (Matheson Co.) was purified by passing through ascarite and degassing at -196°C. Propylene (Matheson Co.) was degassed at -196°C. Ultra High Purity Methane (Matheson Co.) was partially degassed at -196°C then twice distilled at -186°C (liquid argon) to a trap at -196°C to remove any ethane. Gas chromatographic analysis showed approximately 15 ppm O_2, 35 ppm N_2, and 5 ppm C_2H_6 in the CH_4 after purification.

Helium was purified in the same manner as the helium used in the gas chromatographic system.

Gas Chromatography

Gas chromatography was used for the quantitative analysis of all products. The gas chromatographic system was connected directly to the high-vacuum line by the use of a four way stopcock (Kontes Gas Co., K-83350, specially ground for both high pressure and high vacuum use). Figure 2 illustrates schematically the gas chromatographic system.

The gas chromatograph consisted of the following parts:

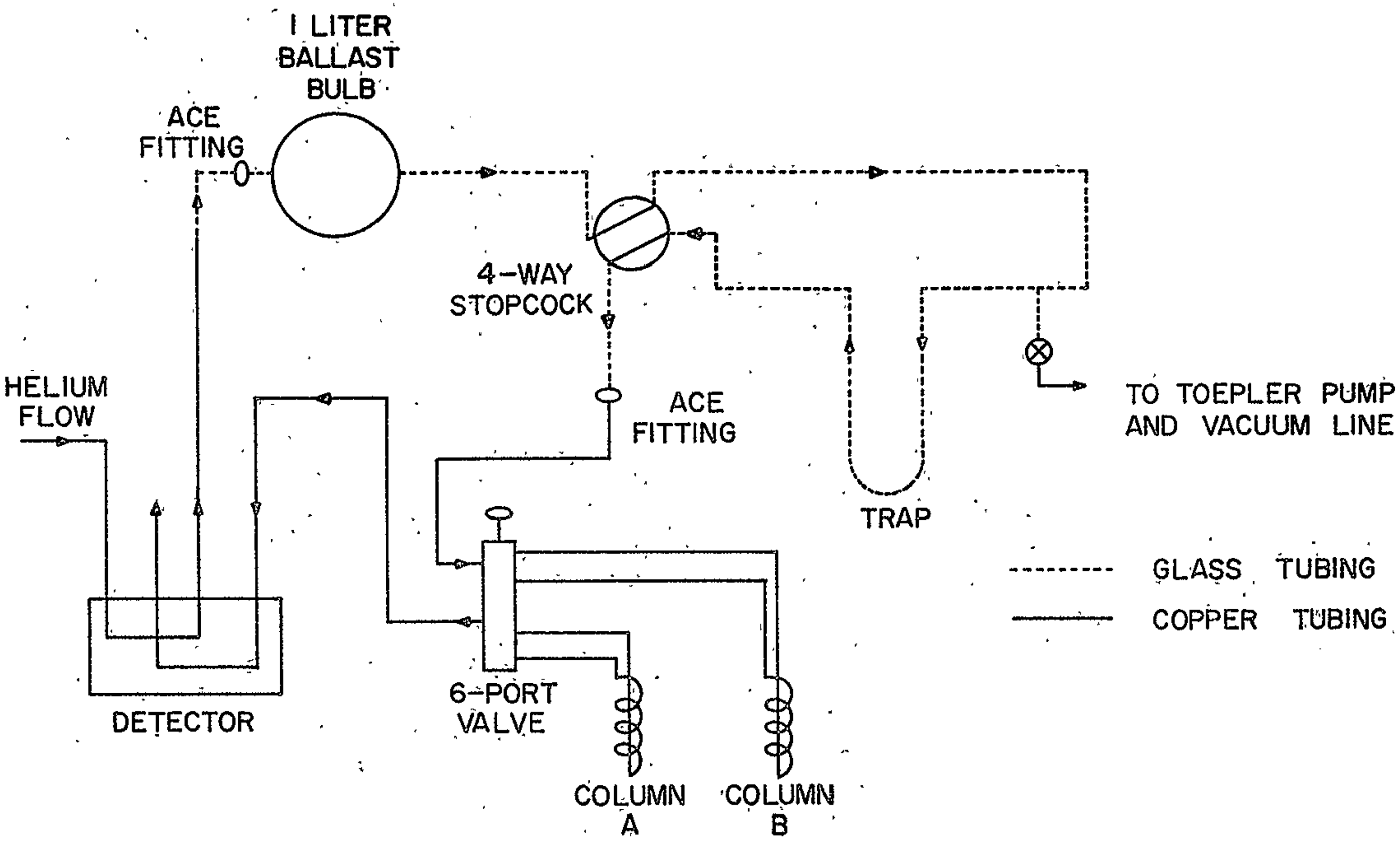

FIGURE 2

GAS CHROMATOGRAPH

1. Thermistor Detector (Gow-Mac Model 10-777)
2. Power Supply (Gow-Mac Model 40-05D)
3. Recorder (Texas Instrument Servo Riter II)
4. 6-port switching value (Loenco Model L-206-6)
5. Columns:
    a. 12 foot long 1/2 inch I. D. copper tube containing 5A molecular sieve resin.
    b. 6 foot long 1/4 inch I. D. copper tube containing porapak Q resin.
    c. 20 foot long 1/4 inch I. D. copper tube containing porapak Q resin.

The detector was kept at 0°C and a constant current of 15 milliamperes was provided by the power supply. Helium was purified before it was allowed to enter the gas chromatograph by passing it through a tube containing indicating drierite and ascarite. The carrier gas pressure was set at 25 psi which gave a flow rate of approximately 100 cc/min.

The noncondensable products, O_2, N_2 and NO were collected by means of the Toepler pump and analyzed on column A. The retention times are: O_2 - 2 1/2 minutes, N_2 - 5 1/2 minutes, and NO - 11 minutes. The condensable products CH_3OH and C_2H_6 were transferred to the gas chromatographic trap at -196°C and analyzed separately in columns B and C, respectively. Ethane was analyzed at room temperature and its retention time was 29 minutes. For the methanol analysis, the non-condensables and N_2O and C_2H_6 were pumped away at -130°C and the methanol was analyzed on column C maintained at 125°C. Calibrations for methanol were performed under identical conditions as an actual experiment including the addition of water to the gas chromatographic sample tube. Water is a product of the $O(^1D)$ - CH_4 reaction and its presence is necessary to reduce the tailing of the CH_3OH peak. The retention of the CH_3OH peak is 5 minutes.

It was found that the calibration of the gas chromatograph for O_2 and N_2 was unaffected for the runs with added helium. The shape and retention times of the curves did change but the peak areas remained essentially unaffected.

General Operational Procedures

The vacuum line was pumped down to 0.01 microns. Nitrous oxide, propylene, methane, and helium in the amounts shown in the table of experimental conditions and results were admitted into the reaction cell and irradiated. The lamp was allowed to warm for at least twenty minutes prior to irradiation. At the end of the irradiation period the contents of the cell were allowed to expand into the right hand manifold of the vacuum line through the coil trap at -196°C. The noncondensable products were collected by the Toepler pump and analyzed first. Then the condensable products were transferred to the sample tube trap at -196°C, allowed to warm to room temperature, and finally analyzed.

CHAPTER 3

REACTION OF $O(^1D)$ WITH NITROUS OXIDE

Actinometry

The output of the lamps was monitored by the photolysis of N_2O in the presence of an excess of C_3H_6 which has negligible absorption at 2139 A. The propylene will scavenge all the $O(^1D)$ atoms before they can react with N_2O and $\Phi\{N_2\}$ will drop to 1.00. In order to ensure that sufficient C_3H_6 was used it was first necessary to obtain the rate constant ratio for the competition between reactions (14) and (15) with (20):

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (14)$$

$$O(^1D) + N_2O \rightarrow 2NO \qquad (15)$$

$$O(^1D) + C_3H_6 \rightarrow \text{Products} \qquad (20)$$

Experiments were performed with various mixtures of C_3H_6 and N_2O. The results are shown in Table 3. As $[C_3H_6]/[N_2O]$ is raised both $\Phi\{N_2\}$ and $\Phi_m\{O_2\}$ drop: the former to 1.00, the latter to 0.00. The rate of reaction (20) is equal to $R\{14\} + R\{15\}$ when the drop is one-half its full value:

$$R\{20\} = R\{14\} + R\{15\}$$

$$k_{20}[O(^1D)][C_3H_6] = (k_{14} + k_{15})[O(^1D)][N_2O]$$

and from the data in Table 3:

TABLE 3

PHOTOLYSIS OF 300 TORR N_2O AT 2139 A IN THE PRESENCE OF C_3H_6 [(a)]

$[C_3H_6]$ (torr)	I_a (μ/hr.)	Exposure Time (hrs.)	$\Phi_m\{O_2\}$ [(b)]	$\Phi\{N_2\}$
0.0	--	0.50	0.054[(c)]	1.46[(c)]
37.5	246	1.00	0.040	1.27
39	327	1.00	0.017	1.16
40	246	1.00	0.014	1.13
41	327	1.00	0.008	1.22
600	327	0.50	0.0	1.03

(a) room temperature

(b) $\Phi_m\{O_2\} = \Phi\{O_2\} - (1/4)\ \Phi\{NO\}$

(c) average value taken from Table 4, C

$$\frac{k_{20}}{(k_{14}+k_{15})} = \frac{[N_2O]}{[C_3H_6]} = \frac{300}{38} \cong 8.0$$

Thus, with

$$\frac{[C_3H_6]}{[N_2O]} \geq 2$$

at least 94% of the excited oxygen atoms are scavenged by C_3H_6, and absolute quantum yields can be calculated.

Stoichiometry of the NO + O_2 Reaction

After irradiation, the products (N_2, O_2, and NO) were collected in the Toepler pump and introduced into the gas chromatograph. At the entrance of the column, the NO and O_2 react quantitatively and the apparent stoichiometric reaction is:

$$4NO + O_2 \rightarrow 2N_2O_3 \qquad (21)$$

Blank experiments were performed seperately but under identical conditions of an actual run to determine the stoichiometry of reaction (21). The experimental procedure is as follows:

a. Fill the cell with 50-500μ NO

b. Fill the right-hand manifold with an excess of air that is needed to react with all the NO.

c. Open the cell stopcock so that only a fraction of the air in the system gets into the cell. If only a fraction of the air gets in, the diffusion of the NO out should be negligible.

d. Measure the nitrogen that was let into the cell on the gas chromatograph.

e. Add 100 torr N_2O to the cell.

f. The oxygen let into the cell can be calculated on the basis of the measured nitrogen. The oxygen that was consumed by the NO is the difference between the oxygen calculated minus the oxygen measured on the gas chromatograph.

The results of the stoichiometric experiments are listed in Table 4.

Results

The results of the photolysis of N_2O alone with 2139 A radiation are shown in Table 5. The pressure of N_2O was varied ten-fold; the absorbed intensity, I_a, by a factor of 14.5; and the extent of decomposition by a factor of six. The results were completely invariant to any of these variations:

$$\Phi\{N_2\} = 1.51 \pm 0.11$$

and

$$\Phi_m\{O_2\} = 0.059 \pm 0.007$$

In these experiments NO was completely consumed and never detected, even though a thorough search was made. In this way the measured quantum yield of O_2 production, $\Phi_m\{O_2\}$ is really $\Phi\{O_2\} - \frac{1}{4}\,\Phi\,\{NO\}$; this is the most useful quantity in determining k_{14}/k_{15}. This method of chemical difference reduced the experimental uncertainty by a factor of 10 or more.

TABLE 4

NO + O_2 STOICHIOMETRY

[NO] (μ)	[NO]/[O_2] Consumed
190	3.68
235	4.24
335	3.97
438	4.10
438	4.10
543	3.76
370	4.19
395	3.64

average = 3.96 ± 0.20

TABLE 5

PHOTOLYSIS OF NITROUS OXIDE AT 2129 A[(a)]

Exposure time, hrs.	I_a (μ/hr.)	$\Phi\{N_2\}$	$\Phi_m\{O_2\}^{(b)}$
(A) 30 torr N_2O			
1.50	30.6	1.43	0.054
1.50	43.0	1.53	-
1.50	30.6	1.35	-
10.00	28.6	1.45	0.060
2.00	46.8	1.59	0.065
2.07	46.8	1.78	0.071
2.00	46.8	1.68	0.054
2.00	48.3	1.66	0.081(c)
6.00	35.0	1.61	0.052
6.00	35.0	1.64	0.061
6.00	35.0	1.27	0.064(c)
(B) 100 torr N_2O			
0.50	166	1.42	0.064
1.00	166	1.36	0.063
1.00	152	1.59	0.069
1.00	120	1.72	0.049(c)
1.00	120	1.50	0.053(c)
3.00	120	1.60	0.060
1.00	97	1.43	0.058

TABLE 5 (cont.)

Exposure time, hrs.	I_a (µ/hr.)	$\Phi\{N_2\}$	$\Phi_m\{O_2\}$(b)
(C) 300 torr N_2O			
4.00	45.0	1.37	0.052
4.00	41.3	1.63	-
4.00	41.3	1.44	0.054
4.00	33.3	1.36	0.042
0.33	414	1.62	0.050
0.50	414	1.56	0.068
0.50	414	1.46	0.062
0.50	414	1.46	0.052
0.50	414	1.39	0.050(c)
0.50	414	1.35	0.055(c)

(a) room temperature

(b) $\Phi_m\{O_2\} = \Phi\{O_2\} - (1/4)\ \Phi\{NO\}$

(c) 1.0 ± 0.2 torr C_3H_6 present

If we assume that the only important reactions are:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (12)$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (14)$$

$$O(^1D) + N_2O \rightarrow 2NO \qquad (15)$$

$$4NO + O_2 \rightarrow 2N_2O_3 \qquad (21)$$

The ratio k_{14}/k_{15} can be computed from either the $\Phi\{N_2\}$ or $\Phi_m\{O_2\}$.

An expression for the quantum yield of nitrogen, $\Phi\{N_2\}$, can be written:

$$\Phi\{N_2\} = 1 + \frac{k_{14}[N_2O][O(^1D)]}{(k_{14} + k_{15})[N_2O][O(^1D)]}$$

$$\Phi\{N_2\} - 1 = \frac{k_{14}}{k_{14} + k_{15}} \qquad (A)$$

rearranging and solving (A) for k_{14}/k_{15}:

$$\frac{k_{14}}{k_{15}} = \frac{\Phi\{N_2\} - 1}{2 - \Phi\{N_2\}} \qquad (B)$$

substituting into (B) the value of $\Phi\{N_2\} = 1.51 \pm 0.11$, $k_{14}/k_{15} = 1.04 \pm 0.48$.

An expression for k_{14}/k_{15} can be derived in terms of the measured quantum yield of oxygen, $\Phi_m\{O_2\}$.

$$\Phi\{O_2\} - (1/4)\,\Phi\{NO\} = \Phi_m\{O_2\} \qquad \text{(C)}$$

From the total possible fate of the $O(^1D)$ atoms, the following relationship can be written:

$$\Phi\{O_2\} + (1/2)\,\Phi\{NO\} = 1.00 \qquad \text{(D)}$$

The $\Phi\{O_2\}$ and $\Phi\{NO\}$ can both be written in terms of the rate contants, I_a, and the $O(^1D)$ and N_2O concentrations:

$$\Phi\{O_2\} = \frac{k_{14}\,[O(^1D)]\,[N_2O]}{I_a}$$

and

$$\Phi\{NO\} = \frac{2k_{15}\,[O(^1D)]\,[N_2O]}{I_a}$$

substituting the above relationships into expressions (C) and (D) and solving simultaneously:

$$\frac{k_{14}}{k_{15}} = \frac{0.5 + \Phi_m\{O_2\}}{1.0 - \Phi_m\{O_2\}} \qquad \text{(E)}$$

substituting into (E) the result for $\Phi_m\{O_2\} = 0.059 \pm 0.007$, $k_{14}/k_{15} = 0.59 \pm 0.01$.

Discussion

From the product quantum yields obtained in previous investigations with 1849 A radiation, the ratio k_{14}/k_{15} can be estimated based on a mechanism consisting solely of:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \tag{12}$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \tag{14}$$

$$O(^1D) + N_2O \rightarrow 2NO \tag{15}$$

These estimates along with the results of this work are listed in Table 6. The estimates from the previous work vary from 0.5 to 1.56, and each estimate has considerable uncertainty. In the value of k_{14}/k_{15} based on the $\Phi\{N_2\}$ from this work also has considerable uncertainty. However, it is clear that the uncertainty in the value of k_{14}/k_{15} based on the $\Phi_m\{O_2\}$ is at least 20 times smaller than that based on the $\Phi\{N_2\}$. This illustrates the advantage of obtaining differences between two quantities of similar value by chemical rather than analytical methods, the method of chemical difference.

In addition to the reaction of $O(^1D)$ it was necessary to consider the possibility of the presence of $O(^3P)$ which might have been produced in one of three ways:

$$N_2O + h\nu\,(2139\,A) \rightarrow N_2 + O(^3P) \tag{22}$$

$$N_2O + O(^1D) \rightarrow N_2O + O(^3P) \tag{23}$$

or a combination of the following two reactions:

$$N_2O + h\nu \rightarrow NO + N \tag{13}$$

$$N + NO \rightarrow N_2 + O(^3P) \tag{24}$$

If the present $O(^3P)$ would react with NO to ultimately produce O_2 by the reactions:

TABLE 6

VALUES OF k_{14}/k_{15}

Value	Basis	Reference
1.0	$\Phi\{O_2\} = 0.5$	MacDonald[24]
0.7	$\Phi\{N_2\} = 1.4$	Noyes[12]
0.5	$\Phi\{O_2\} = 0.35$	Noyes[12]
1.56 (1.1 - 2.2)	$\Phi\{N_2\} = 1.61 \pm 0.08$	Zelikoff and Aschenbrand[25]
1.38 (1.22 - 1.56)	$\Phi\{O_2\} = 0.58 \pm 0.03$	Zelikoff and Aschenbrand[25]
0.78 (0.64 - 0.96)	$\Phi\{N_2\} = 1.44 \pm 0.05$	Castellion and Noyes[26]
1.44	$\Phi\{NO\} = 0.82$	Castellion and Noyes[26]
1.04 (0.67 - 1.63)	$\Phi\{N_2\} = 1.51 \pm 0.11$	This work
0.59 ± 0.01	$\Phi_m\{O_2\} = 0.059 \pm 0.007$	This work

$$O(^3P) + NO + N_2O \rightarrow NO_2 + N_2O \qquad (25)$$

$$O(^3P) + NO_2 \rightarrow NO + O_2 \qquad (26)$$

No NO would be consumed but some O_2 would have been produced in addition to that formed by reaction (14). To check this possibility some experiments were done in the presence of 1 torr of C_3H_6 to scavenge any $O(^3P)$. Under the conditions of the experiments the C_3H_6 removes less than 18% of the $O(^1D)$ atoms and usually much less. If any $O(^3P)$ had been present, $\Phi_m\{O_2\}$ would have been dimished. In fact, for six runs with 1 torr C_3H_6, $\Phi\{N_2\} = 1.48 \pm 0.15$ and $\Phi_m\{O_2\} = 0.059 \pm 0.009$ which are identical to the values found in the absence of C_3H_6. Therefore, it can be concluded that the quantum yield of $O(^3P)$ production is less than 0.02 and probably zero. The absence of $O(^3P)$ means that reactions (13), (22), and (23) are unimportant.

CHAPTER 4

COMPETITIVE REACTIONS OF $O(^1D)$ ATOMS WITH NITROUS OXIDE AND METHANE

Actinometry

The output of the lamps was monitored by the photolysis of N_2O in the presence of an excess of C_3H_6 but in the absence of any CH_4. This procedure is identical to that previously described in the actinometry section of Chapter 3.

Results

Mixtures of methane and nitrous oxide at room temperature were photolyzed with 2139 A radiation. The experimental results are listed in Tables 7-10.

The variation of the quantum yield of ethane, $\Phi\{C_2H_6\}$ as a function of the CH_4 pressure at three different N_2O pressures is listed in Table 8 and a plot of this data is shown in Figures 3-5. For the data at 30 and 100 torr N_2O a maximum value in $\Phi\{C_2H_6\}$ is not obtained. However, the plot of the data for 10 torr N_2O (Figure 3) reaches a limiting value of $\Phi\{C_2H_6\} = 0.87 \pm 0.02$. $\Phi\{C_2H_6\}$ was found to be independent of the N_2O pressure for a given value of $[CH_4]/[N_2O]$, as shown in Figure 6. The intensity was varied by a factor of 30 and the extent of decomposition was varied by a factor of 16 for runs with the same CH_4 and N_2O pressures with no noticeable effect.

From the photolysis at high values of $[CH_4]/[N_2O]$, the quantum yield of methanol, $\Phi\{CH_3OH\}$, can be measured. The average value of $\Phi\{CH_3OH\}$ from Table 7 is 0.06.

TABLE 7

CH_3OH PRODUCTION IN THE PHOTOLYSIS OF N_2O-CH_4 MIXTURES AT HIGH VALUES OF $[CH_4]/[N_2O]$

$[CH_4]$ (torr)	Time (min)	I_a (μ/min)	$[CH_3OH]$ (μ)	$\Phi\{CH_3OH\}$
(A) 10 torr N_2O				
800	1200	0.36	19.5	0.055
792	1200	0.76	42.0	0.054
(B) 300 torr N_2O				
852	626	1.18	27.5	0.047
837	1240	1.18	77.5	0.067
836	300	2.53	27.5	0.053
822	30	11.47	19.0	0.070
819	600	0.64	15.0	0.049
814	600	0.64	19.5	0.064
806	120	6.37	62.5	0.103
793	1240	2.53	85.5	0.034
764	60	11.47	41.0	0.075

TABLE 8

C_2H_6 PRODUCTION IN THE PHOTOLYSIS OF N_2O-CH_4 MIXTURES AT HIGH VALUES OF $[CH_4]/[N_2O]$

$[CH_4]$ (torr)	Time (min)	I_a (μ/min)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$
(A) 10 torr N_2O				
891	120	1.85	185	0.834
881	120	3.17	341	0.898
870	120	1.97	211	0.894
840	60	3.17	151	0.840
818	120	2.80	290	0.864
406	120	1.85	188	0.847
193	120	2.80	289	0.861
97	120	1.78	159	0.743
48	120	2.62	208	0.662
36	120	1.53	105	0.570
26	120	1.53	74	0.403
19	120	2.43	82	0.281
10	120	2.43	9	0.031
(B) 300 torr N_2O				
851	30	10.03	245	0.815
835	60	6.60	331	0.835
823	60	10.03	471	0.783
599	60	6.60	277	0.682
536	30	4.17	86	0.688

TABLE 8 (cont.)

$[CH_4]$ (torr)	Time (min)	I_a (μ/min)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$
415	60	6.60	225	0.568
401	30	6.23	116	0.621
199	30	4.17	67	0.536
195	60	10.03	226	0.543
104	240	5.97	630	0.440
101	240	3.97	397	0.417
100	15	3.97	29	0.488
99	240	0.33	35	0.443
98	15	5.97	50	0.559
94	60	10.03	221	0.366
87	287	0.33	34	0.360
57	30	3.97	32	0.269
37	30	5.97	19	0.109
(C) 100 torr N_2O				
885	15	18.92	190	0.669
874	15	12.25	121	0.658
811	15	18.92	174	0.613
640	15	12.25	111	0.603
422	15	18.92	130	0.458
276	31	12.25	134	0.353
213	30	12.25	70	0.190

TABLE 8 (cont.)

$[CH_4]$ (torr)	Time (min)	I_a (μ/min)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$
210	240	0.92	61	0.277
164	30	18.92	78	0.137
142	31	18.92	61	0.104

TABLE 9

PHOTOLYSIS OF N_2O-CH_4 MIXTURES IN THE REGION WHERE THE TIME EFFECT IS IMPORTANT

$[CH_4]$ (torr)	$R = \frac{[CH_4]}{[N_2O]}$	I_a (μ/min.)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$
(A) 30 torr N_2O, 60 minutes irradiation				
43.45	1.533	6.12	30.2	0.0823
41.65	1.331	6.53	22.2	0.0566
37.80	1.350	5.83	13.4	0.0383
37.70	1.205	6.77	13.2	0.0325
36.70	1.199	6.77	12.5	0.0308
34.25	1.119	6.53	10.0	0.0255
(B) 100 torr N_2O, 30 minutes irradiation				
137.75	1.373	23.21	56.9	0.0817
120.15	1.203	23.21	31.8	0.0457
108.90	1.078	22.27	20.4	0.0305
104.20	1.061	25.07	19.9	0.0265
99.70	1.000	22.97	10.9	0.0158
89.05	0.8865	23.21	6.7	0.0096
80.10	0.7868	22.97	7.2	0.0104
(C) 100 torr N_2O, 60 minutes irradiation				
140.45	1.397	19.97	64.3	0.0537
129.65	1.296	19.65	46.9	0.0397
119.85	1.209	20.00	37.3	0.0311

TABLE 9 (cont.)

$[CH_4]$ (torr)	$R = \frac{[CH_4]}{[N_2O]}$	I_a (μ/min.)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$
115.70	1.175	19.85	22.0	0.0185
112.90	1.110	19.65	24.9	0.0211
103.30	1.020	19.65	18.1	0.0152
101.90	1.026	21.03	18.7	0.0148
98.05	0.978	23.32	14.4	0.0102
95.30	0.963	21.03	13.5	0.0107
91.40	0.929	19.33	9.3	0.0080
87.65	0.882	19.70	8.8	0.0074
85.50	0.867	19.70	10.1	0.0085
84.95	0.848	19.33	8.0	0.0069
79.05	0.786	21.57	7.3	0.0056
76.55	0.773	19.85	4.1	0.0034
70.20	0.700	19.65	4.2	0.0036

TABLE 10

PHOTOLYSIS OF N_2O-CH_4 MIXTURES IN THE REGION WHERE THE TIME EFFECT IS NEGLIGIBLE

$[CH_4]$ (torr)	$R = \frac{[CH_4]}{[N_2O]}$	I_a (μ/min)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$	$\frac{\Phi\{C_2H_6\} + 2.205}{R}$	$\frac{k_{16}}{k_{14} + k_{15}}$
(A) 100 torr N_2O, 10 minutes irradiation						
70.45	0.6743	27.90	3.1	0.0110	3.29	3.10
75.50	0.7446	37.70	2.4	0.0064	2.97	2.70
78.60	0.7680	23.65	3.4	0.0144	2.89	2.77
88.95	0.8905	23.77	5.5	0.0231	2.50	2.48
92.45	0.9328	25.50	11.9	0.0467	2.41	2.55
94.30	0.9461	23.65	10.3	0.0436	2.38	2.49
96.10	0.9756	23.65	13.2	0.0558	2.32	2.49
100.10	0.9950	23.65	15.9	0.0673	2.28	2.51
103.10	1.028	23.77	13.4	0.0564	2.20	2.36
103.85	1.017	23.77	12.0	0.0505	2.22	2.37
110.85	1.119	25.80	31.4	0.122	2.08	2.50

TABLE 10 (cont.)

$[CH_4]$ (torr)	$R = \frac{[CH_4]}{[N_2O]}$	I_a (μ/min)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$	$\frac{\Phi\{C_2H_6\} + 2.205}{R}$	$\frac{k_{16}}{k_{14} + k_{15}}$
112.80	1.114	3.14	7.5	0.0815	2.05	2.31$^{(a)}$
118.85	1.183	3.14	10.4	0.113	1.96	2.32$^{(a)}$
119.35	1.192	23.77	21.8	0.0918	1.93	2.20
120.40	1.211	23.77	22.5	0.0947	1.90	2.18
121.70	1.226	27.50	30.1	0.110	1.89	2.22
121.70	1.220	37.70	29.7	0.0788	1.87	2.10
135.25	1.368	18.60	29.9	0.161	1.73	2.21
151.00	1.528	18.60	34.1	0.183	1.56	2.07
175.10	1.767	18.60	40.0	0.215	1.37	1.91
220.65	2.233	18.60	68.2	0.333	1.14	1.93
255.00	2.573	18.60	70.6	0.380	1.01	1.87
298.40	3.020	18.60	111	0.541	0.91	2.45

TABLE 10 (cont.)

$[CH_4]$ (torr)	$R = \frac{[CH_4]}{[N_2O]}$	I_a (μ/min)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$	$\frac{\Phi\{C_2H_6\} + 2.205}{R}$	$\frac{k_{16}}{k_{14} + k_{15}}$
(B) 30 torr N_2O, 10 minutes irradiation						
32.80	1.080	13.65	9.5	0.0696	2.11	2.34
33.45	1.104	9.40	7.5	0.0798	2.07	2.34
41.90	1.378	9.40	14.1	0.150	1.71	2.17

(a) 30 minutes irradiation

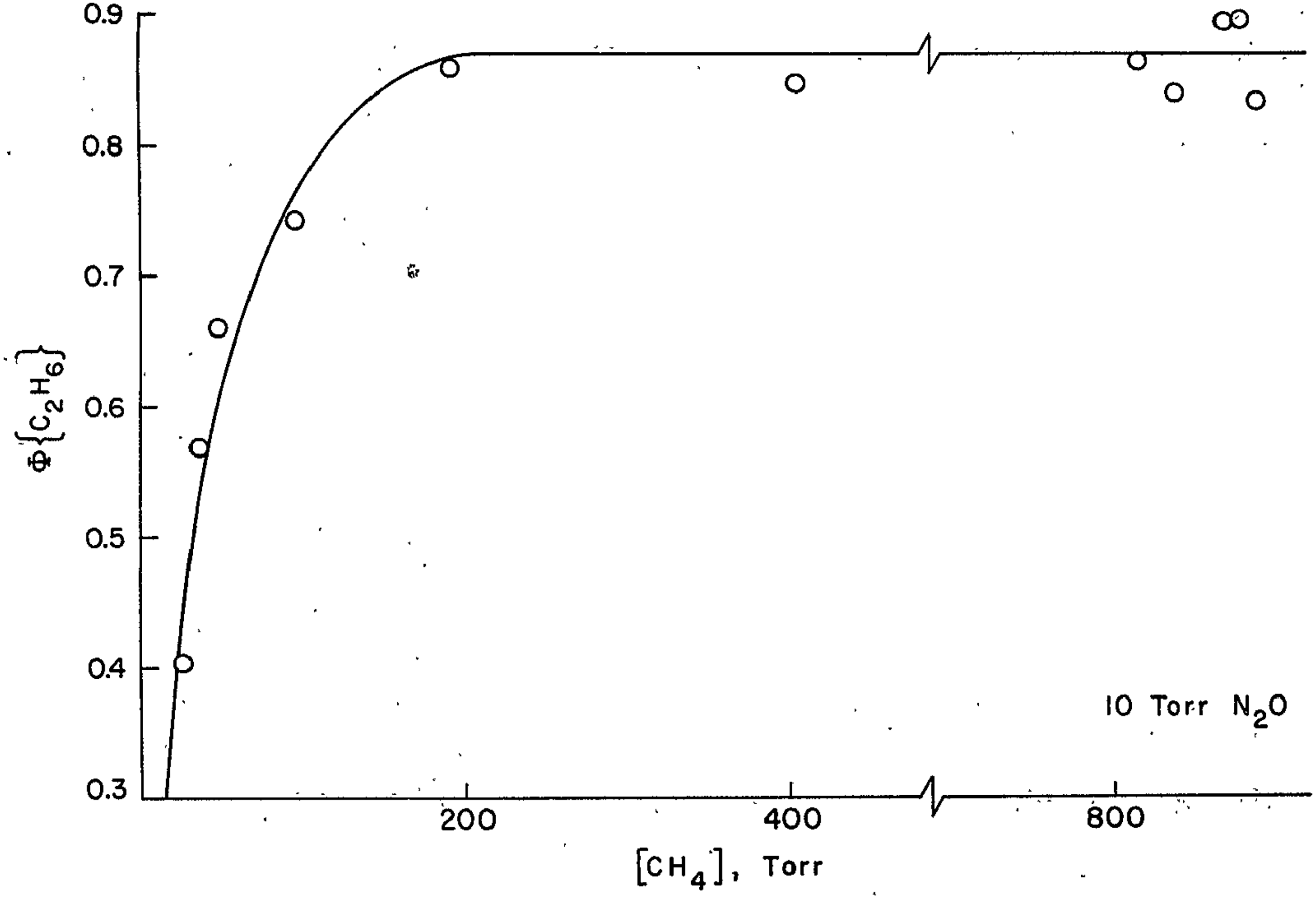

FIGURE 3

$\Phi\{C_2H_6\}$ AS A FUNCTION OF CH_4 PRESSURE $[N_2O]$ = 10 TORR

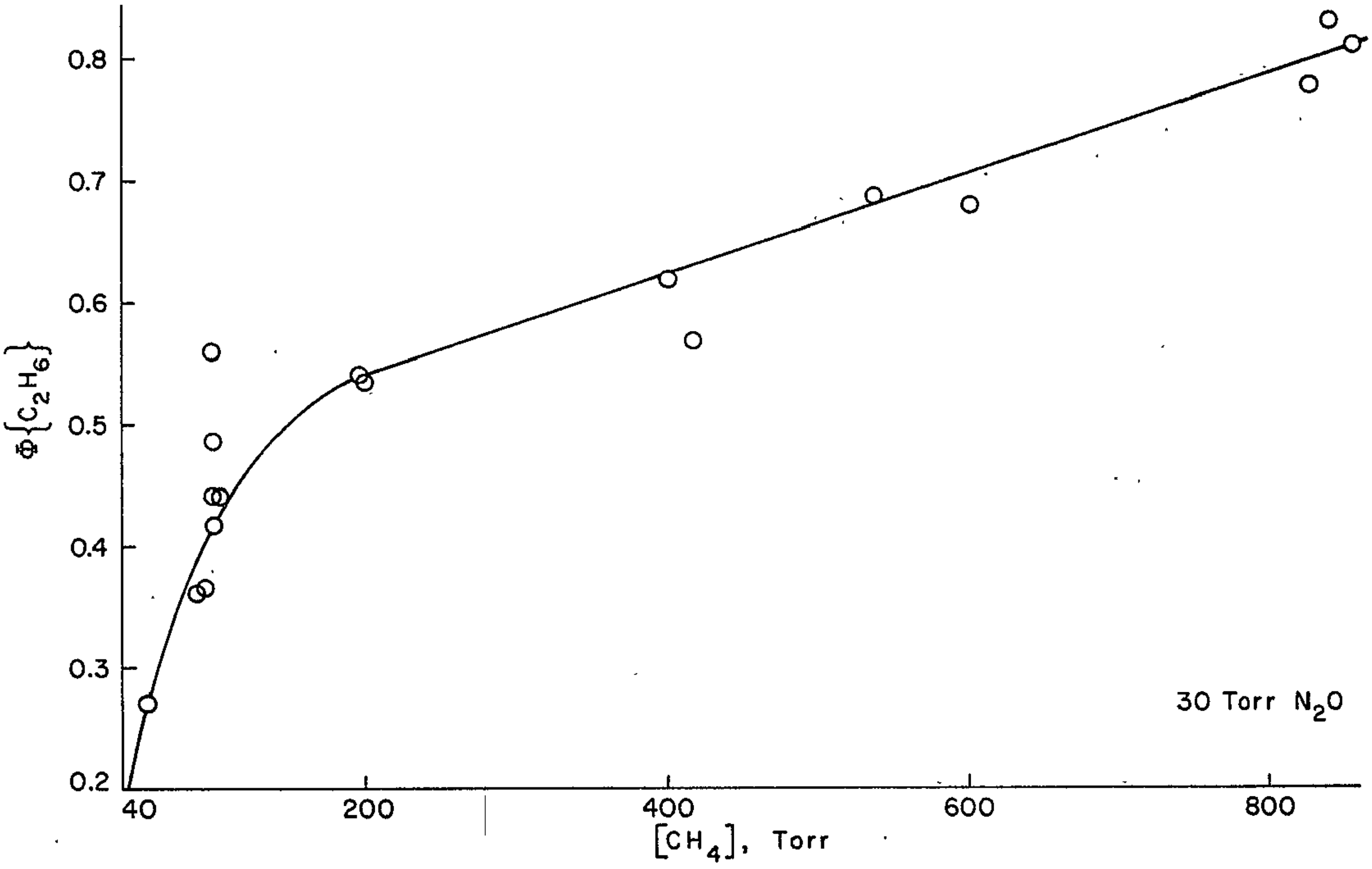

FIGURE 4

$\Phi\{C_2H_6\}$ AS A FUNCTION OF CH_4 PRESSURE $[N_2O] = 30$ TORR

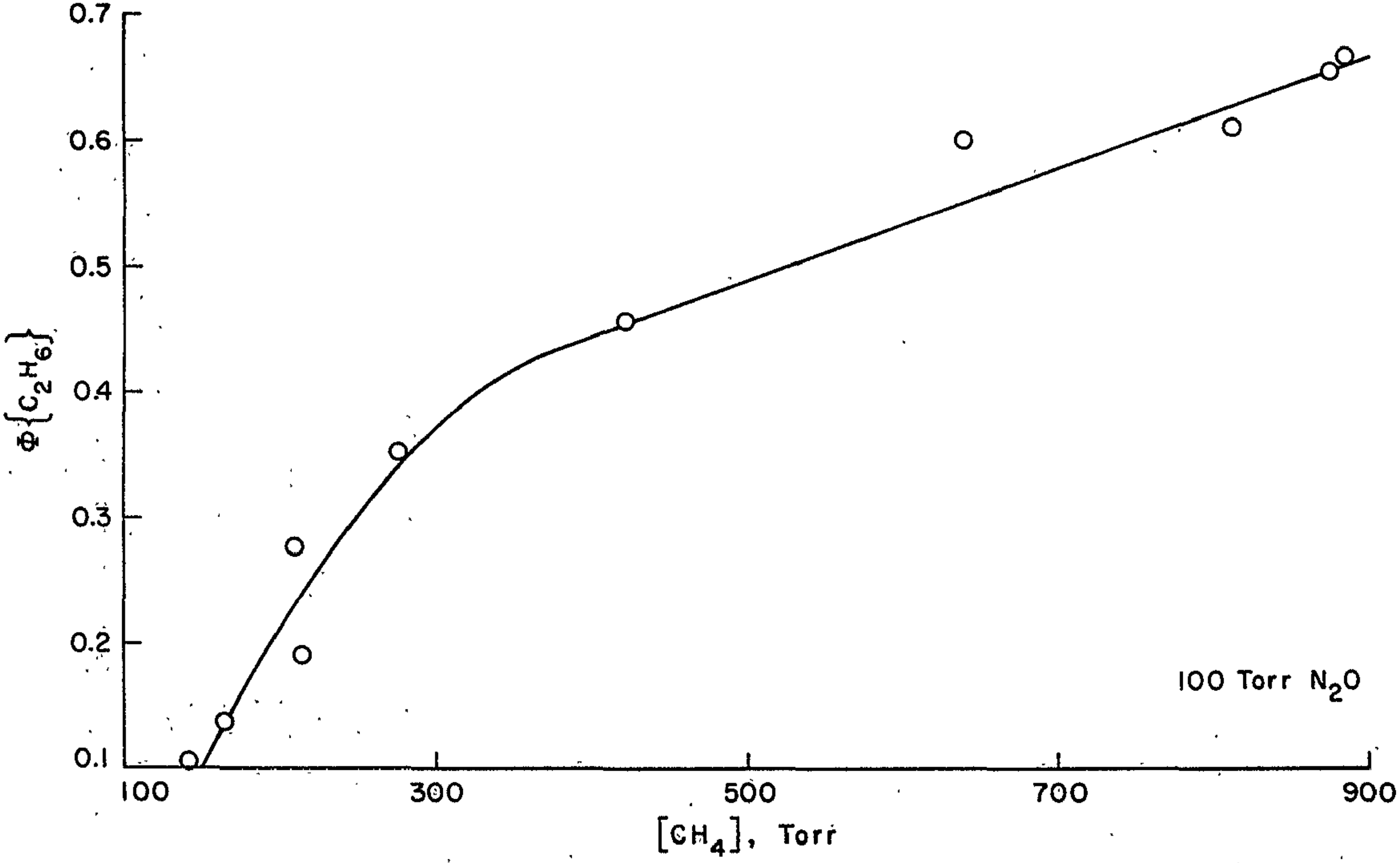

FIGURE 5

$\Phi\{C_2H_6\}$ AS A FUNCTION OF CH_4 PRESSURE, $[N_2O]$ = 100 TORR

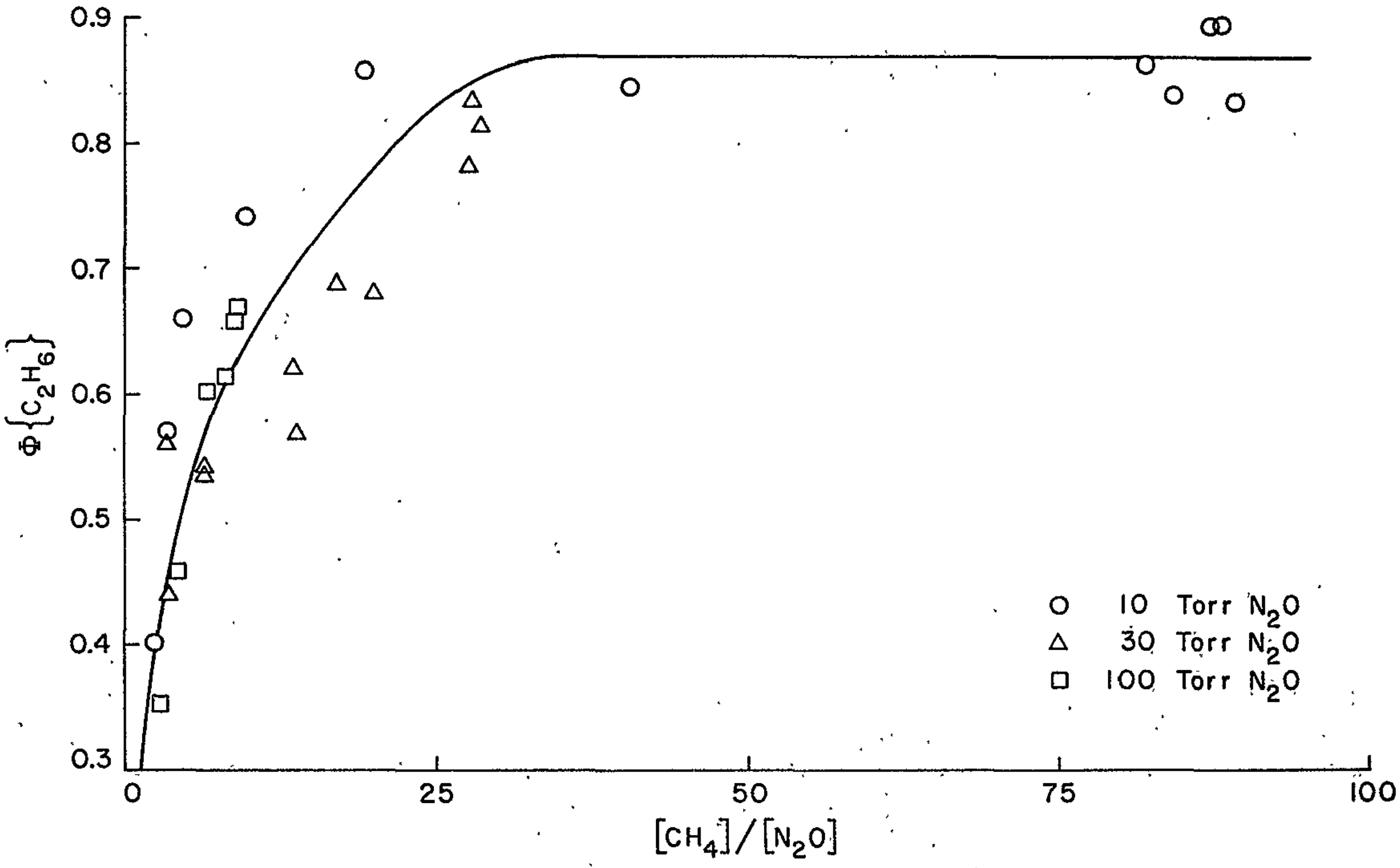

FIGURE 6

$\Phi\{C_2H_6\}$ AS A FUNCTION OF $[CH_4]/[N_2O]$

The CH_3OH could come from either

$$\cdot OH + CH_3 \rightarrow CH_3OH \qquad (34)$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \xrightarrow{CH_3} CH_3OH + CH_2O \qquad (28)$$

or

$$O(^1D) + CH_4 + M \rightarrow CH_3OH + M \qquad (17)$$

To unambiguously determine the route of CH_3OH formation, two experiments were done with 1.2 torr of NO added. The N_2O pressures were 28 and 9.1 torr, and the CH_4 pressures were 778 and 658 torr, respectively. The NO completely scavenges CH_3 radicals, so that the $\Phi\{CH_3OH\}$ should be reduced to zero if the CH_3 radical is the precursor, but should be unaffected if $O(^1D)$ inserts into CH_4. In both experiments CH_3OH formation was completely suppressed ($\Phi\{CH_3OH\} < 0.01$), from which it can be concluded that CH_3 is the precursor to CH_3OH production.

On the basis of the maximum $\Phi\{C_2H_6\} = 0.87$ and $\Phi\{CH_3OH\} = 0.06$, the maximum quantum yield of $O(^3P)$ production can be calculated. Each $O(^3P)$ formed reacts to form $(1/2)O_2$ which will scavenge one methyl radical:

$$\begin{array}{l} CH_4 + O(^1D) \rightarrow CH_4 + O(^3P) \\ \qquad\qquad\qquad\qquad\qquad\quad \hookrightarrow (1/2)O_2 \end{array} \qquad (27)$$

$$CH_3 + O_2 \xrightarrow{CH_3} \text{Products} \qquad (28)$$

In addition, two methyl radicals are lost from the two reactions:

$$O(^1D) + CH_4 \rightarrow CH_3 + OH \qquad (16)$$

$$OH + CH_4 \rightarrow H_2O + CH_3 \qquad (30)$$

Therefore each time $O(^1D)$ is deactivated by methane to form $O(^3P)$ atoms, three methyl radicals are lost. The maximum quantum yield of $O(^3P)$ production, $\max \Phi\{O(^3P)\}$, can be calculated to be equal to 0.05 ± 0.05. This value of 0.05 is a good estimate of the ratio of deactivation compared to reaction of the $O(^1D)$ atom with methane. DeMore and Raper[22] reported that deactivation of the $O(^1D)$ to $O(^3P)$ ground state accounts for 30% of the total reaction while no deactivation was reported by Paraskevopoulous and Cvetanović.[27] The result of this work that the deactivation is less than 5% is in good agreement with the later of the two observations but both contradict the result of DeMore and Raper, which were obtained in the liquid phase.

The other possible reactions are:

$$O(^1D) + CH_4 \rightarrow CH_2O + H_2 \qquad (18)$$

$$O(^1D) + CH_4 \rightarrow CH_2 + H_2O \qquad (19)$$

The possibility of the production of H_2 was investigated. No H_2 was detected; therefore it can be concluded that the quantum yield for the production of H_2, $\Phi\{H_2\}$ is less than 0.002 and probably zero.

If CH_2 is produced it would react in four ways:

$$CH_2 + CH_4 \rightarrow C_2H_6 \qquad (19a)$$

$$CH_2 + CH_4 \rightarrow 2CH_3 \tag{19b}$$

$$2CH_2 \rightarrow C_2H_4 \tag{19c}$$

$$CH_2 + CH_3 \rightarrow C_2H_5 \xrightarrow{CH_3} C_3H_8 \tag{19d}$$

No C_2H_4 or C_3H_8 ($\Phi\{C_3H_8\} < 0.02$) were found, so reactions (19c) and (19d) are unimportant. Reaction (19a) would occur only for singlet CH_2, which would not be scavenged by O_2 or NO. When NO was added, $\Phi\{C_2H_6\}$ fell to zero; therefore reaction (19a) also must be unimportant. Reaction (19b) cannot be eliminated as a possible path leading to the production of CH_3 radicals, but it is indistinguishable from reaction (16) followed by reaction (30), and need not be considered separately.

Since the method of chemical difference proved to be the best method in determining the ratio of rate constants k_{14}/k_{15} in the photolysis of N_2O by itself (Chapter 3), it was also found to be useful in this study. The results in the region where this method could be employed is shown in Tables 9 and 10. The data are separated in such a way that the results where the time effect is important is listed in Table 9 and the results where the time effect is negligible is shown in Table 10.

Simplified Mechanism

$O(^1D)$ atoms produced by the photolysis of N_2O at 2139 A are known to react with N_2O and the only important reactions were shown to be:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (12)$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (14)$$

$$O(^1D) + N_2O \rightarrow 2NO \qquad (15)$$

in the presence of CH_4 the $O(^1D)$ can react accordingly:

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \qquad (16)$$

$$OH + CH_4 \rightarrow H_2O + CH_3 \qquad (30)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (31)$$

$$O(^1D) + CH_4 \rightarrow O(^3P) + CH_4 \qquad (27)$$

The major fate of $O(^3P)$ is to produce O_2 by the reaction sequence:

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad (13)$$

$$O(^3P) + NO_2 \rightarrow O_2 + NO \qquad (14)$$

O_2 and NO are known radical scavengers of CH_3 radicals and the following reactions must be included:

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (28)$$

$$CH_3O_2 + CH_3 \rightarrow CH_3O_2CH_3 \qquad (38)$$

$$CH_3 + NO \rightarrow CH_3NO \qquad (29a)$$

$$CH_3NO + CH_3 \rightarrow (CH_3)_2NO \qquad (29b)$$

$$(CH_3)_2NO + CH_3 \rightarrow (CH_3)_2NO(CH_3) \qquad (29c)$$

Combining (29a), (29b) and (29c), the following reaction can be written:

$$CH_3 + NO \xrightarrow{2CH_3} (CH_3)_3NO \qquad (32)$$

At high values of $[CH_4]/[N_2O]$, reactions (14) and (15) will be small compared to the reactions of the $O(^1D)$ atom with methane. However, as the ratio of $[CH_4]/[N_2O]$ is lowered a competition for the reaction of the $O(^1D)$ between CH_4 and N_2O will occur. As a result of this competition occuring for low ratios $[CH_4]/[N_2O]$ ($6 < R \leq 10$; $R = [CH_4]/[N_2O]$) reactions (14) and (15) will be occurring extensively. Consequently, reactions (28) and (32) which are scavenging methyl radicals will become very important. As the $[CH_4]/[N_2O]$ ratio becomes smaller and smaller, reactions (28) and (32) will become more and more important and $\Phi\{C_2H_6\}$ will approach zero. In this region $\Phi\{C_2H_6\}$ will be a sensitive function of the ratio of $[CH_4]/[N_2O]$. The use of reactions (28) and (32) as radical scavenging paths is another example of the method of chemical difference.

Since each O_2 formed removes two methyl radicals and each NO formed removes three methyl radicals, an expression for the rate of production of ethane, $R\{C_2H_6\}$ can be written:

$$R\{C_2H_6\} = k_{16}[O(^1D)][CH_4] - (1/2)k_{27}[O(^1D)][CH_4] - k_{14}[O(^1D)][N_2O] - 3k_{15}[O(^1D)][N_2O]$$

From this expression the $\Phi\{C_2H_6\}$ is given by the equation:

$$\Phi\{C_2H_6\} = \frac{(k_{16} - (1/2)k_{27})[CH_4] - (k_{14} + 3\,k_{15})[N_2O]}{(k_{16} + k_{27})[CH_4] + (k_{14} + k_{15})[N_2O]}$$

rearranging this expression:

$$\frac{\Phi\{C_2H_6\} + b}{R} = a - c\,\Phi\,\{C_2H_6\} \qquad \text{(F)}$$

where

$$a = \frac{k_{16} - (1/2)k_{27}}{k_{14} + k_{15}}, \quad b = \frac{k_{14} + 3k_{15}}{k_{14} + k_{15}}, \quad c = \frac{k_{16} + k_{27}}{k_{14} + k_{15}}$$

$$\text{and } R = \frac{[CH_4]}{[N_2O]}$$

If it is assumed that $k_{14}/k_{15} = 0.66$ from the most recent result obtained in our laboratory,[28] b can be evaluated to be equal to 2.205. When $(\Phi\,\{C_2H_6\} + 2.205)/R$ is plotted versus $\Phi\{C_2H_6\}$ the intercept of the plot is equal to $(k_{16} - (1/2)k_{27})/(k_{14} + k_{15})$ and the slope is equal to $-(k_{16} + k_{27})/(k_{14} + k_{15})$. A plot of the data in the region where secondary reactions are negligible is shown in Figure 7. Secondary reactions of the following kind:

$$CH_3O + CH_2O \rightarrow CH_3OH + HCO \qquad (33)$$

were determined to be unimportant since the reactions of CH_2O

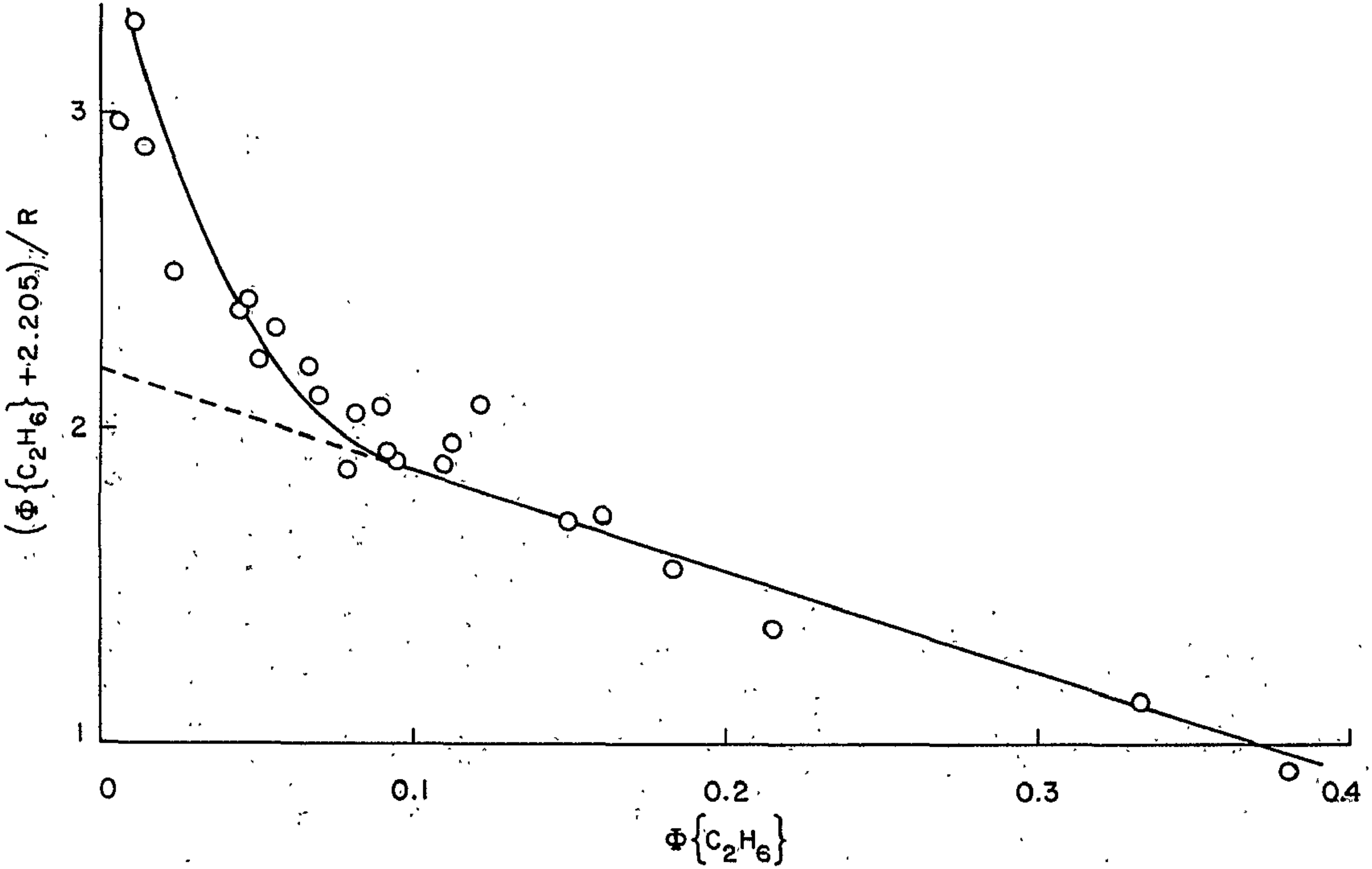

FIGURE 7

$(\Phi\{C_2H_6\} + 2.205)/R$ AS A FUNCTION OF $\Phi\{C_2H_6\}$

lead to CO. Under the conditions where no CO was detected it can be assumed that the secondary reactions of CH_2O must be unimportant.

The linear portion of the plot has an intercept of 2.18 and a slope of -3.2. Substituting these values into the expression for a and c respectively the two equations can be solved simultaneously:

$$\frac{k_{16}}{k_{14} + k_{15}} = 2.5$$

$$\frac{k_{27}}{k_{16} + k_{27}} = 0.18$$

The analysis is quite sensitive for $k_{16}/(k_{14} + k_{15})$, but relatively insensitive to $k_{27}/(k_{16} + k_{27})$. From the product analysis it was determined that $k_{27}/(k_{16} + k_{27}) = 0.05 \pm 0.05$. With this value, the expression for a gives $k_{16}/(k_{14} + k_{15}) = 2.2$. Utilizing the known value of $(k_{14} + k_{15}) = 1.1 \times 10^{11}$ $M^{-1} sec^{-1}$,[28] $k_{16} = 2.4 \times 10^{11}$ M^{-1} sec^{-1}.

The non-linear portion of the plot in Figure 7 cannot be explained on the basis of this simple mechanism but can be explained on the basis of the more complete mechanism which will be given in the next section of this chapter. This deviation can be attributed to the reaction of CH_3O with NO. The NO will scavenge less methyl radicals than predicted in reaction (32) and $\Phi\{C_2H_6\}$ will be larger, as is shown in Figure 7.

Complete Mechanism and Computer Results

The complete mechanism will include in addition to reactions (12), (14), (15), (16), (27), (28), (30), (31) and (32) as given in the simplified mechanistic scheme:

$$CH_3 + OH \rightarrow CH_3OH \qquad (34)$$

the reaction of ground state, $O(^3P)$ atoms:

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad (35)$$

$$O(^3P) + NO_2 \rightarrow O_2 + NO \qquad (26)$$

$$NO_2 + CH_3 \rightarrow CH_3NO_2 \qquad (36)$$

CH_3O_2 can react with itself and with other radicals:

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2 \qquad (37)$$

$$CH_3O_2 + CH_3 \rightarrow CH_3OOCH_3 \qquad (38)$$

$$CH_3O_2 + CH_3O \rightarrow CH_3O_2H + CH_2O \qquad (39)$$

$$CH_3O_2 + NO \rightarrow CH_3O_2NO \qquad (48)$$

$$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2 \qquad (49)$$

CH_3O can react via:

$$CH_3O + NO \rightarrow CH_3ONO \qquad (40a)$$

$$CH_3O + NO \rightarrow CH_2O + HNO \tag{40b}$$

$$CH_3O + CH_3 \rightarrow CH_3OCH_3 \tag{41a}$$

$$CH_3O + CH_3 \rightarrow CH_3O + CH_4 \tag{41b}$$

$$CH_3O + CH_3O \rightarrow \text{Product} \tag{42}$$

$$CH_3O + NO_2 \rightarrow CH_3ONO_2 \tag{43}$$

Finally, the reactions of HNO must be included:

$$HNO + CH_3 \rightarrow CH_4 + NO \tag{44}$$

$$HNO + CH_3O \rightarrow CH_3OH + NO \tag{45}$$

$$HNO + CH_3O_2 \rightarrow CH_3O_2H + NO \tag{46}$$

$$HNO + HNO \rightarrow H_2O + N_2O \tag{47}$$

The value of all known and estimated rate constants are listed in Table 11.

Steady state equations can be written for each of the radical intermediates:

$$[O(^1D)] = \frac{I_a}{(k_{14} + k_{15})[N_2O] + (k_{16} + k_{27})[CH_4]} . \tag{G}$$

$$[OH] = \frac{k_{16}[O(^1D)]}{k_{30}} \tag{H}$$

TABLE 11

RATE CONSTANTS AT 25°C(a)

Reaction	k	Reference
(14) $O(^1D) + N_2O \rightarrow N_2 + O_2$	1.1×10^{11}	Young et al.[29]
(15) $O(^1D) + N_2O \rightarrow 2NO$		
(16) $O(^1D) + CH_4 \rightarrow OH + CH_3$	-	-
(26) $O(^3P) + NO_2 \rightarrow O_2 + NO$	1.7×10^{10}	DASA[30]
(27) $O(^1D) + CH_4 \rightarrow O(^3P) + CH_4$	-	-
(28) $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	3×10^{10}	McMillen and Calvert[31]
(30) $OH + CH_4 \rightarrow H_2O + CH_3$	6.2×10^6	Wilson and Westenberg[32]
(31) $CH_3 + CH_3 \rightarrow C_2H_6$	2.4×10^{10}	Basco et al.[33]
(32) $CH_3 + NO \xrightarrow{2CH_3} CH_3NO(CH_3)_2$	2.4×10^9	Basco et al.[33]
(34) $CH_3 + OH \rightarrow CH_3OH$	2×10^9	Estimate

TABLE 11 (cont.)

Reaction	k	Reference
(35) $O(^3P) + NO + M \rightarrow NO_2 + M$	3.6×10^{10}	DASA[30]
(36) $CH_3 + NO_2 \rightarrow CH_3NO_2$	3.0×10^{9}	Heicklen and Cohen[34]
(37) $CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	1.5×10^{10}	Heicklen[35]
(38) $CH_3 + CH_3O_2 \rightarrow CH_3OOCH_3$	8×10^{8}	Heicklen[35]
(39) $CH_3O + CH_3O_2 \rightarrow CH_3O_2H + CH_2O$	1.6×10^{9}	Heicklen and Cohen[34]
(40a) $CH_3O + NO \rightarrow CH_3O\,NO$	3×10^{7}	Wiebe[36]
(40b) $CH_3O + NO \rightarrow CH_2O + H\,NO$	6×10^{6}	McGraw and Johnston[37], Wiebe[36]
(41a) $CH_3 + CH_3O \rightarrow CH_3OCH_3$	1.6×10^{10}	Heicklen[35]
(41b) $CH_3 + CH_3O \rightarrow CH_2O + CH_4$		
(42) $CH_3O + CH_3O \rightarrow$ product	1×10^{10}	Heicklen[35]
(43) $CH_3O + NO_2 \rightarrow CH_3ONO_2$	6.0×10^{7}	Wiebe[36]
(44) $CH_3 + HNO \rightarrow CH_4 + NO$	$1 + 10^{8}$	Estimate

TABLE 11 (cont.)

	Reaction	k	Reference
(45)	$CH_3 + HNO \rightarrow CH_3OH + NO$	1×10^8	Estimate
(46)	$CH_3O_2 + HNO \rightarrow CH_3O_2H + NO$	1×10^8	Estimate
(47)	$HNO + HNO \rightarrow H_2O + N_2O$	1×10^6	Estimate
(48)	$CH_3O_2 + NO \rightarrow CH_3O_2NO$	3.0×10^7	Spicer[38]
(49)	$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	3.0×10^7	Spicer[38]

(a) units of moles, liters, and seconds

$$[O_2] = \frac{k_{14}[O(^1D)][N_2O] + k_{37}[CH_3O_2]^2 + k_{26}[O(^3P)][NO_2]}{k_{28}[CH_3][M]} \tag{I}$$

$$[O(^3P)] = \frac{k_{27}[O(^1D)][CH_4]}{k_{35}[NO][M] + k_{26}[NO_2]} \tag{J}$$

$$\begin{aligned}[NO] = {} & \Big(2k_{15}[O(^1D)][N_2O] + k_{26}[O(^3P)][NO_2] + k_{44}[CH_3][HNO] \\ & + k_{45}[CH_3O][HNO] + k_{46}[CH_3O_2][HNO] \Big) \Big/ \Big(k_{32}[CH_3] \\ & + (k_{40a} + k_{40b})[CH_3O] + k_{35}[O(^3P)][M] + k_{48}[CH_3O_2] \Big)\end{aligned} \tag{K}$$

$$\begin{aligned}[CH_3O_2] = {} & \Big(k_{28}[CH_3][O_2][M] \Big) \Big/ \Big(k_{38}[CH_3] + 2k_{37}[CH_3O_2] \\ & + k_{39}[CH_3O] + k_{46}[HNO] + k_{48}[NO] + k_{49}[NO_2] \Big)\end{aligned} \tag{L}$$

$$\begin{aligned}[CH_3O] = {} & \Big(2k_{37}[CH_3O_2]^2 \Big) \Big/ \Big((k_{40a} + k_{40b})[NO] + k_{41}[CH_3] \\ & + 2k_{42}[CH_3O] + k_{45}[HNO] + k_{43}[NO_2] + k_{39}[CH_3O_2] \Big)\end{aligned} \tag{M}$$

$$\begin{aligned}[NO_2] = {} & \Big(k_{35}[O(^3P)][NO][M] \Big) \Big/ \Big(k_{36}[CH_3] + k_{43}[CH_3O] \\ & + k_{26}[O(^3P)] + k_{49}[CH_3O_2] \Big)\end{aligned} \tag{N}$$

$$[HNO] = \frac{k_{40b}[CH_3O][NO]}{k_{44}[CH_3] + k_{45}[CH_3O] + k_{46}[CH_3O_2] + 2k_{47}[HNO]} \qquad (O)$$

$$[CH_3] = \left(2k_{16}[O(^1D)][CH_4]\right) \Big/ \Big(2k_{31}[CH_3] + k_{28}[O_2][M] + 3k_{32}[NO] + k_{34}[OH] + k_{36}[NO_2] + k_{41}[CH_3O] + k_{38}[CH_3O_2] + k_{44}[HNO]\Big) \qquad (P)$$

From reaction (31):

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (31)$$

the following expression can be written:

$$\Phi\{C_2H_6\} = \frac{k_{31}(CH_3)^2}{I_a}$$

rearranging:

$$(CH_3)^2 = \frac{\Phi\{C_2H_6\} I_a}{k_{31}}$$

k_{31} and I_a are known and $\Phi\{C_2H_6\}$ was measured for each experiment; as a result, the concentration of methyl radicals can be calculated for each experimental run. Now the $[CH_3]$ is no longer unknown and the steady state equation for CH_3 expression (P) can be rewritten as an equation to solve for the value of k_{16}.

These 10 steady state equations can be reduced to six non-linear equations; equations (M), (O) and

$$\begin{aligned}[CH_3O_2] = {} & \left(k_{14}C_1[N_2O] + k_{37}[CH_3O_2]^2 + C_1C_2[NO_2]\right) \Big/ \\ & \left(k_{38}[CH_3] + 2k_{37}[CH_3O_2] + k_{39}[CH_3O] + k_{46}[HNO] \right. \\ & \left. + k_{48}[NO] + k_{49}[NO_2]\right)\end{aligned}$$

$$\begin{aligned}[NO] = {} & \left(2k_{15}\, C_1[N_2O] + C_1C_2[NO_2] + k_{44}[CH_3][HNO] \right. \\ & \left. + k_{45}[CH_3O][HNO] + k_{46}[CH_3O_2][HNO]\right) \Big/ \left(k_{32}[CH_3] \right. \\ & \left. + (k_{40a} + k_{40b})[CH_3O] + C_1C_3 + k_{48}[CH_3O_2]\right)\end{aligned}$$

$$[NO_2] = \frac{C_1C_3[NO]}{k_{36}[CH_3] + k_{43}[CH_3O] + C_1C_2 + k_{49}[CH_3O_2]}$$

$$\begin{aligned}k_{16} = {} & \left(2k_{31}[CH_3]^2 + k_{14}\, C_1[N_2O] + k_{37}[CH_3O_2]^2 + C_1C_2[NO_2] \right. \\ & + 3k_{32}[CH_3][NO] + k_{34}k_{16}\, C_1[CH_3] \,/\, k_{30} + k_{36}[NO_2][CH_3] \\ & \left. + k_{41}[CH_3O][CH_3] + k_{38}[CH_3O_2][CH_3] + k_{44}[HNO][CH_3]\right) \Big/ \\ & 2C_1[CH_4]\end{aligned}$$

where

$$C_1 = \frac{I_a}{(k_{14} + k_{15})[N_2O] + (k_{16} + k_{27})[CH_4]}$$

$$C_2 = \frac{k_{28}k_8[CH_4]}{k_{35}[NO][M] + k_{26}[NO_2]}$$

$$C_3 = \frac{k_{27}k_{35}[M][CH_4]}{k_{35}[NO][M] + k_{26}[NO_2]}$$

The ten steady state equations have been reduced to six non-linear equations involving seven parameters:

CH_3O, HNO, CH_3O_2, NO, NO_2, k_{16} and k_{27}.

Of these six were unknown, but the ratio k_{27}/k_{16} was set equal to 0.05 based on the experiments performed at high $[CH_4]/[N_2O]$ ratios.

A computer program was written to solve these six equations in six unknowns by an iterative process. The program is a Fortran IV (Watfor) Program and it is tabulated in the Appendix. The computer was fed the following information:

1. Six non-linear steady state equations.
2. Values of all rate constants from Table 11.
3. Initial guesses for all the radical intermediates as listed in Table 12.
4. An initial guess for the value of k_{16}.
5. A value of $k_{14}/k_{15} = 0.66$ based on the most recent result obtained in our laboratory.[28]
6. Data cards for each experimental run that was listed in Table 10. The information listed on the data cards is shown in Table 13.

TABLE 12

INITIAL GUESSES OF THE RADICAL CONCENTRATIONS

Radical	Concentration (Moles/Liter)
CH_3O_2	1.7×10^{-10}
NO_2	1.17×10^{-9}
CH_3O	1.1×10^{-9}
HNO	2.5×10^{-9}
NO	4.5×10^{-8}

TABLE 13

DATA AS LISTED FOR THE COMPUTER WORK[(a)]

$[CH_4]$ ($\times 10^{-3}$ $\frac{\text{moles}}{\text{liter}}$)	$[N_2O]$ ($\times 10^{-3}$ $\frac{\text{moles}}{\text{liter}}$)	I_a ($\times 10^{-8}$ $\frac{\text{moles}}{\text{liter-sec}}$)	$[CH_3]$ ($\times 10^{-10}$ $\frac{\text{moles}}{\text{liter}}$)	$[M]$ ($\times 10^{-2}$ $\frac{\text{moles}}{\text{liter}}$)
(A) 100 torr N_2O, 10 minutes irradiation				
3.789	5.617	2.50	1.03	0.941
4.060	5.453	3.38	0.91	0.951
4.227	5.502	2.12	1.08	0.973
4.784	5.370	2.13	1.38	1.015
4.972	5.330	2.29	2.03	1.030
5.072	5.362	2.12	1.89	1.043
5.168	5.300	2.12	2.13	1.047
5.384	5.410	2.12	2.34	1.079
5.545	5.392	2.13	2.15	1.094
5.585	5.494	2.13	2.03	1.108
5.962	5.330	2.31	3.30	1.129

TABLE 13 (cont.)

$[CH_4]$ $(\times 10^{-3} \frac{\text{moles}}{\text{liter}})$	$[N_2O]$ $(\times 10^{-3} \frac{\text{moles}}{\text{liter}})$	I_a $(\times 10^{-8} \frac{\text{moles}}{\text{liter-sec}})$	$[CH_3]$ $(\times 10^{-10} \frac{\text{moles}}{\text{liter}})$	$[M]$ $(\times 10^{-2} \frac{\text{moles}}{\text{liter}})$
6.067	5.445	0.78	0.94	1.151
6.392	5.402	0.28	1.11	1.179
6.419	5.384	2.13	2.74	1.180
6.475	5.346	2.13	2.79	1.182
6.545	5.338	2.47	3.22	1.188
6.545	5.367	3.38	3.20	1.191
7.274	5.316	1.67	3.21	1.259
8.121	5.316	1.67	3.43	1.344
9.417	5.330	1.67	3.71	1.475
11.87	5.314	1.67	4.62	1.718
13.71	5.330	1.67	4.94	1.904
16.05	5.314	1.67	5.89	2.136

TABLE 13 (cont.)

$[CH_4]$ (x 10^{-3} $\frac{\text{moles}}{\text{liter}}$)	$[N_2O]$ (x 10^{-3} $\frac{\text{moles}}{\text{liter}}$)	I_a (x 10^{-8} $\frac{\text{moles}}{\text{liter-sec}}$)	$[CH_3]$ (x 10^{-10} $\frac{\text{moles}}{\text{liter}}$)	$[M]$ (x 10^{-2} $\frac{\text{moles}}{\text{liter}}$)
(B) 30 torr N_2O, 10 minutes irradiation				
1.764	1.630	1.22	1.81	0.339
1.799	1.630	0.84	1.61	0.343
2.253	1.635	0.84	2.21	0.389

(a) refers to the data in Table 10

The computer calculated new values of the six unknowns iteratively until a set tolerance between two successive iterations were met. The computed values for $k_{16}/(k_{14} + k_{15})$ for each run are listed in Table 10. If the values corresponding to the three lowest values of $\Phi\{C_2H_6\}$ are discarded then the values for $k_{16}/(k_{14} + k_{15})$ lie between 1.87 and 2.55 even though $\Phi\{C_2H_6\}$ varies by a factor of 23. The average value of $k_{16}/(k_{14} + k_{15})$ with its standard deviation is 2.28 ± 0.20 in good agreement with the result obtained from the simplified mechanism.

The value of k_{14}/k_{15} was changed from 0.66 to 0.59, the original value obtained in this work (from Chapter 3); $k_{16}/(k_{14} + k_{15})$ increased from 2.28 to 2.33. This change is insignificant.

In addition, the value of $k_{16}/(k_{14} + k_{15})$ that was calculated was independent of the following possible variations:

1. Initial guesses of the steady state concentrations.
2. The initial starting value of k_{27}/k_{16} between 0.00 and 0.20 as is shown in Table 14.
3. The value of the following rate constants which were varied over a factor of 100 (a factor of 10 greater and 10 smaller of the value listed in Table 11):

   k_{26}, k_{28}, k_{30}, k_{34}, k_{35}, k_{36}, k_{37}, k_{38},
   k_{39}, k_{40b}, k_{42}, k_{43}, k_{45}, k_{46}, k_{47}, k_{49}

Table 15 lists the effect on the average value of $k_{16}/(k_{14} + k_{15})$ with its standard deviation over a factor of 100 variation in all the

TABLE 14

EFFECT OF VARYING RATIO k_{27}/k_{16} on $k_{16}(k_{14} + k_{15})$

Value of k_{27}/k_{16}	$k_{16}/(k_{14} + k_{15})$
0.000	2.20 ± 0.21
0.030	2.23 ± 0.20
0.053	2.28 ± 0.20
0.100	2.36 ± 0.18
0.150	2.47 ± 0.16
0.200	2.59 ± 0.14

TABLE 15

EFFECT ON AVERAGE VALUE OF $k_{16}/(k_{14} + k_{15})$ BY VARYING THE VALUE OF THE RATE CONSTANT[(a)]

k	$k_{16}/(k_{14} + k_{15})$
$k_{26} = 1.7 \times 10^{9}$	2.18 ± 0.20
$k_{26} = 1.7 \times 10^{11}$	2.31 ± 0.20
$k_{28} = 3.0 \times 10^{9}$	2.28 ± 0.20
$k_{28} = 3.0 \times 10^{11}$	2.28 ± 0.20
$k_{30} = 6.2 \times 10^{5}$	2.28 ± 0.20
$k_{30} = 6.2 \times 10^{7}$	2.28 ± 0.20
$k_{31} = 2.6 \times 10^{9}$	1.88 ± 0.20
$k_{31} = 2.6 \times 10^{11}$	11.6 ± 7.4[(b)]
$k_{32} = 6.0 \times 10^{7}$	1.47 ± 0.11
$k_{32} = 2.4 \times 10^{8}$	1.82 ± 0.12
$k_{32} = 6.0 \times 10^{8}$	2.06 ± 0.15
$k_{32} = 2.4 \times 10^{10}$	2.38 ± 0.23
$k_{34} = 2.0 \times 10^{8}$	2.28 ± 0.20
$k_{34} = 2.0 \times 10^{10}$	2.28 ± 0.20

TABLE 15 (cont.)

k	$k_{16}/(k_{14} + k_{15})$
$k_{35} = 3.6 \times 10^9$	2.31 ± 0.20
$k_{35} = 3.6 \times 10^{11}$	2.18 ± 0.20
$k_{36} = 3.0 \times 10^8$	2.31 ± 0.20
$k_{36} = 3.0 \times 10^{10}$	2.19 ± 0.20
$k_{37} = 1.5 \times 10^9$	2.16 ± 0.18
$k_{37} = 1.5 \times 10^{11}$	2.33 ± 0.21
$k_{38} = 8.0 \times 10^7$	2.28 ± 0.20
$k_{38} = 8.0 \times 10^9$	2.26 ± 0.21
$k_{39} = 1.6 \times 10^8$	2.30 ± 0.20
$k_{39} = 1.6 \times 10^{10}$	2.17 ± 0.20
$k_{40a} = 3.0 \times 10^6$	2.30 ± 0.21
$k_{40a} = 3.0 \times 10^8$	2.07 ± 0.15
$k_{40b} = 6.0 \times 10^5$	2.28 ± 0.20
$k_{40b} = 6.0 \times 10^7$	2.27 ± 0.19

TABLE 15 (cont.)

	$k_{16}/(k_{14} + k_{15})$
$k_{41} = 1.6 \times 10^{9}$	2.14 ± 0.21
$k_{41} = 1.6 \times 10^{11}$	2.55 ± 0.24
$k_{42} = 1.0 \times 10^{9}$	2.34 ± 0.19
$k_{42} = 1.0 \times 10^{11}$	2.22 ± 0.21
$k_{43} = 6.0 \times 10^{6}$	2.28 ± 0.20
$k_{43} = 6.0 \times 10^{8}$	2.27 ± 0.20
$k_{44} = 1.0 \times 10^{7}$	2.28 ± 0.20
$k_{44} = 1.0 \times 10^{9}$	2.28 ± 0.20
$k_{45} = 1.0 \times 10^{7}$	2.28 ± 0.20
$k_{45} = 1.0 \times 10^{9}$	2.28 ± 0.20
$k_{46} = 1.0 \times 10^{7}$	2.28 ± 0.20
$k_{46} = 1.0 \times 10^{9}$	2.28 ± 0.20
$k_{47} = 1.0 \times 10^{5}$	2.28 ± 0.20
$k_{47} = 1.0 \times 10^{7}$	2.28 ± 0.20

TABLE 15 (cont.)

k	$k_{16}/(k_{14} + k_{15})$
$k_{48} = 3.0 \times 10^6$	2.31 ± 0.21
$k_{48} = 3.0 \times 10^8$	2.01 ± 0.14
$k_{49} = 3.0 \times 10^6$	2.27 ± 0.20
$k_{49} = 3.0 \times 10^8$	2.17 ± 0.20

(a) first three runs from Table 10 omitted in averaging

(b) a number of the runs did not converge in 100 iterations rate constants. The effect in the majority of the cases is less than 1-2% change in $k_{16}/(k_{14} + k_{15})$.

The value of $k_{16}/(k_{14} + k_{15})$ computed did depend on the values of the rate constants: k_{31}, k_{32}, k_{40a}, k_{41}, and k_{48}. For reactions (40a), (41) and (48) the effect results in less than 12% change in the $k_{16}/(k_{14} + k_{15})$. The value of $k_{16}/(k_{14} + k_{15})$ did depend significantly on the value of k_{32}; lowering k_{32} to 6.0×10^7 reduced $k_{16}/(k_{14} + k_{15})$ to 1.47 ± 0.11.

Lowering k_{31} by a factor of 10 only reduced $k_{16}/(k_{14} + k_{15})$ to 1.88 ± 0.20 but raising k_{31} by a factor of 10 increased $k_{16}/(k_{14} + k_{15})$ to 11.6 ± 7 with a large number of the individual runs not converging in 100 iterations. The very large scatter in the data is a good indication that k_{31} cannot be so large. Furthermore, the value of k_{31} is very accurately known (< 10% uncertainty), so that the high result need not be considered.

The reliability of this method depends on the validity of the steady state assumptions. For the steady state assumption to be valid, it is necessary that the steady state concentrations be much less than the $O(^1D)$ produced (93-377μ). The final steady state concentrations given in the last iteration of the computer output are listed in Table 16. The results in Table 16 indicate that the steady state concentrations are all negligibly small (< 1μ) except for possibly the O_2 steady state values for the first three runs.

The values of $k_{16}/(k_{14} + k_{15})$ equal to 3.10, 2.70 and 2.77 are exceptionally high, these represent the points in Figure 7 which deviate most from the linear position and are the runs under which the quantum yields of ethane measured were very low. Under

TABLE 16

STEADY STATE CONCENTRATIONS AS LISTED IN THE LAST ITERATION OF THE COMPUTER CALCULATION

$\frac{k_{16}}{k_{14}+k_{15}}$	10^9x [NO] M	10^9x [NO_2] M	10^{10}x [CH_3O_2] M	10^{10}x [CH_3O] M	10^{10}x [HNO] M	10^{17}x [$O(^1D)$] M	10^{13}x$^{(a)}$ [OH] M	10^{10}x$^{(b)}$ [$O(^3P)$] M	10^8x$^{(c)}$ [O_2] M	10^7x$^{(d)}$ [CH_3NO] M
3.10	33.67	4.60	4.23	4.34	8.96	1.39	6.95	0.45	21.12	20.20
2.70	51.49	7.01	4.87	4.99	13.94	1.90	8.65	0.39	32.11	30.89
2.77	27.15	3.83	3.90	4.00	7.14	1.19	5.32	0.46	16.43	16.29
2.48	21.30	3.14	3.91	3.96	5.42	1.19	4.78	0.57	12.32	12.28
2.55	15.08	2.29	4.03	3.94	3.54	1.23	5.03	0.87	8.60	9.05
2.49	15.09	2.31	3.88	3.81	3.58	1.14	4.57	0.80	8.49	9.05
2.49	13.13	2.04	3.86	3.73	3.00	1.13	4.52	0.91	7.37	7.88
2.51	11.77	1.88	3.84	3.65	2.61	1.08	4.37	0.99	6.42	7.06
2.36	13.07	2.09	3.87	3.73	2.99	1.11	4.23	0.89	7.02	7.84
2.37	13.92	2.24	3.88	3.77	3.24	1.10	4.18	0.82	7.38	8.35
2.50	8.45	1.44	3.90	3.46	1.64	1.10	4.44	1.48	4.46	5.07
2.31	3.82	0.64	1.39	1.30	0.82	0.14	0.52	0.39	1.60	2.29

TABLE 16 (cont.)

$\frac{k_{16}}{k_{14}+k_{15}}$	10^9x [NO] M	10^9x [NO_2] M	10^{10}x [CH_3O_2] M	10^{10}x [CH_3O] M	10^{10}x [HNO] M	10^{17}x [$O(^1D)$] M	10^{13}x$^{(a)}$ [OH] M	10^{10}x$^{(b)}$ [$O(^3P)$] M	10^8x$^{(c)}$ [O_2] M	10^7x$^{(d)}$ [CH_3NO] M
2.32	3.11	0.54	1.37	1.23	0.62	0.13	0.50	0.47	1.52	1.87
2.20	9.77	1.69	3.80	3.50	2.04	1.05	3.73	1.12	4.89	5.86
2.18	9.59	1.66	3.80	3.48	1.98	1.05	3.71	1.14	4.80	5.75
2.22	9.40	1.65	4.05	3.65	1.88	1.19	4.28	1.16	4.70	5.64
2.10	13.52	2.33	4.82	4.51	2.91	1.71	5.77	1.27	6.69	8.11
2.21	5.92	1.11	3.24	2.75	1.06	0.75	2.67	1.40	2.82	3.55
2.07	5.37	1.07	3.19	2.66	0.92	0.72	2.42	1.46	2.41	3.22
1.91	4.72	1.03	3.13	2.52	0.76	0.69	2.12	1.54	1.95	2.83
1.93	3.11	0.81	2.90	2.07	0.40	0.57	1.76	2.09	1.15	1.86
1.87	2.66	0.77	2.80	1.91	0.32	0.52	1.55	2.24	0.91	1.60
2.45	1.53	0.53	2.45	1.42	0.13	0.36	1.41	3.57	0.53	0.92
2.34	8.81	0.55	2.93	2.78	1.95	2.05	7.73	2.22	15.38	5.29

TABLE 16 (cont.)

$\frac{k_{16}}{k_{14}+k_{15}}$	10^9 x [NO] $\underline{M}$	10^9 x [NO_2] $\underline{M}$	10^{10} x [CH_3O_2] $\underline{M}$	10^{10} x [CH_3O] $\underline{M}$	10^{10} x [HNO] $\underline{M}$	10^{17} x [$O(^1D)$] $\underline{M}$	10^{13} x$^{(a)}$ [OH] $\underline{M}$	10^{10} x$^{(b)}$ [$O(^3P)$] $\underline{M}$	10^8 x$^{(c)}$ [O_2] $\underline{M}$	10^7 x$^{(d)}$ [CH_3NO] $\underline{M}$
2.34	6.74	0.43	2.42	2.27	1.45	1.39	5.25	1.99	11.66	4.04
2.17	4.45	0.32	2.33	2.01	0.82	1.24	4.35	2.76	6.90	2.67

(a) calculated from Equation (H)

(b) calculated from Equation (J)

(c) calculated from Equation (I)

(d) calculated on the basis of $k_{29a} = 4 \times 10^7 \ \underline{M}^{-1} sec^{-1}$

these conditions the steady state assumption for CH_3NO collapses. Exact steady state values for CH_3NO cannot be obtained because only a lower limit to k_{29a} is known: $k_{29a} \geq 4 \times 10^7$.[33] An upper limit for CH_3NO is listed in Table 16. These values are significant and could easily account for the large values of $k_{16}/(k_{14} + k_{15})$ computed for these runs. For the other runs the limiting steady state values are between 1 and 10% of the total $O(^1D)$ produced and the steady state assumption is valid.

It was hoped that an estimate of k_{27}/k_{16} could be obtained from the computer work. However, as was stated previously the value that was calculated for $k_{16}/(k_{14} + k_{15})$ was independent of the initial starting value of k_{27}/k_{16}. Therefore, an estimate of the value of k_{27}/k_{16} was not possible from the computer work.

CHAPTER 5

THE TRANSLATIONALLY HOT $O(^1D)$ ATOMS

Introduction

In Chapter 3 it was reported that for the photolysis of N_2O at 2139 A the $O(^1D)$ atoms react:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (12)$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (14)$$

$$O(^1D) + N_2O \rightarrow 2NO \qquad (15)$$

The ratio $k_{14}/k_{15} = 0.66 \pm 0.06$ was determined by the method of chemical difference. In addition Goldman, Greenberg, and Heicklen,[39] determined this ratio in the photolysis of O_3-N_2O mixtures and found $k_{14}/k_{15} = 0.59 \pm 0.08$ at 2537 A and $k_{14}/k_{15} = 0.50 \pm 0.07$ at 2288 A. However, Preston[40] has also measured k_{14}/k_{15} using several sources of $O(^1D)$ atoms: photolysis of N_2O-NO_2 mixtures at 2288 A and 2400 A gave $k_{14}/k_{15} = 1.01 \pm 0.06$, flash photolysis of N_2O-O_3 mixtures gave $k_{14}/k_{15} = 0.99 \pm 0.06$, and the photolysis of N_2O at 2288 A gave $k_{14}/k_{15} = 1.08 \pm 0.19$. The discrepancy between the two laboratories is outside the claimed experimental errors. The difference between the work from this laboratory and that of Preston will be discussed in terms of the excess translational energy of the $O(^1D)$ atoms, which will in turn depend on the source of the $O(^1D)$ atom. Some common sources of the $O(^1D)$ atom and the excess energy available are shown in Table 17.

TABLE 17

SOURCE OF O(^{1}D) AND EXCESS ENERGY AVAILABLE

Source	λ	energy kcal/mole
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	2139 A	48.1
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	2288 A	45.0
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2288 A	31.8
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2537 A	20.3
$NO_2 + h\nu \rightarrow NO + O(^1D)$	2288 A	5.6

Furthermore, the excess translational energy of the $O(^1D)$ atom will be shown to be important in the reactions of the $O(^1D)$ atom in the N_2O-CH_4 system.

Helium was chosen as a third body to remove the excess translational energy of the $O(^1D)$ because helium is known to quench only the excess translational energy of the $O(^1D)$ but not deactivate it to the $O(^3P)$ ground state.

Results

The results of added helium in the photolysis of N_2O by itself with 2139 A radiation is shown in Table 18. A plot of $\Phi_m\{O_2\}$ as a function of added helium pressure is shown in Figure 8.

The stoichiometry of the $NO + O_2$ reaction was checked in the presence of added helium under identical conditions as described in Chapter 3 except that approximately 200 torr of helium was added to the reaction cell before the sample was collected and analyzed. The results of the two stoichiometric experiments performed are:

NO/O_2 Consumed: 3.76 and 4.11

Average: 3.94 ± 0.18

This is in excellent agreement with the value of 3.96 ± 0.20 obtained in the absence of helium. Therefore, reaction (21) is still valid:

$$4NO + O_2 \rightarrow 2N_2O_3 \qquad (21)$$

The data in Figure 8 are badly scattered; however, a definite effect of the added third body is apparent. From $\Phi_m\{O_2\}$ at high helium pressures, the average value of $\Phi_m\{O_2\} = 0.182 \pm 0.02$. The

TABLE 18

PHOTOLYSIS OF 10 TORR N_2O AT 2139A IN THE PRESENCE OF ADDED HELIUM

[He] (torr)	$\Phi_m\{O_2\}$
0	0.090
0	0.080
0	0.070
29	0.12
72	0.17
101.5	0.18
124	0.17
159.5	0.21
193	0.17
216	0.16
239	0.15
248	0.23
253	0.17
339	0.20

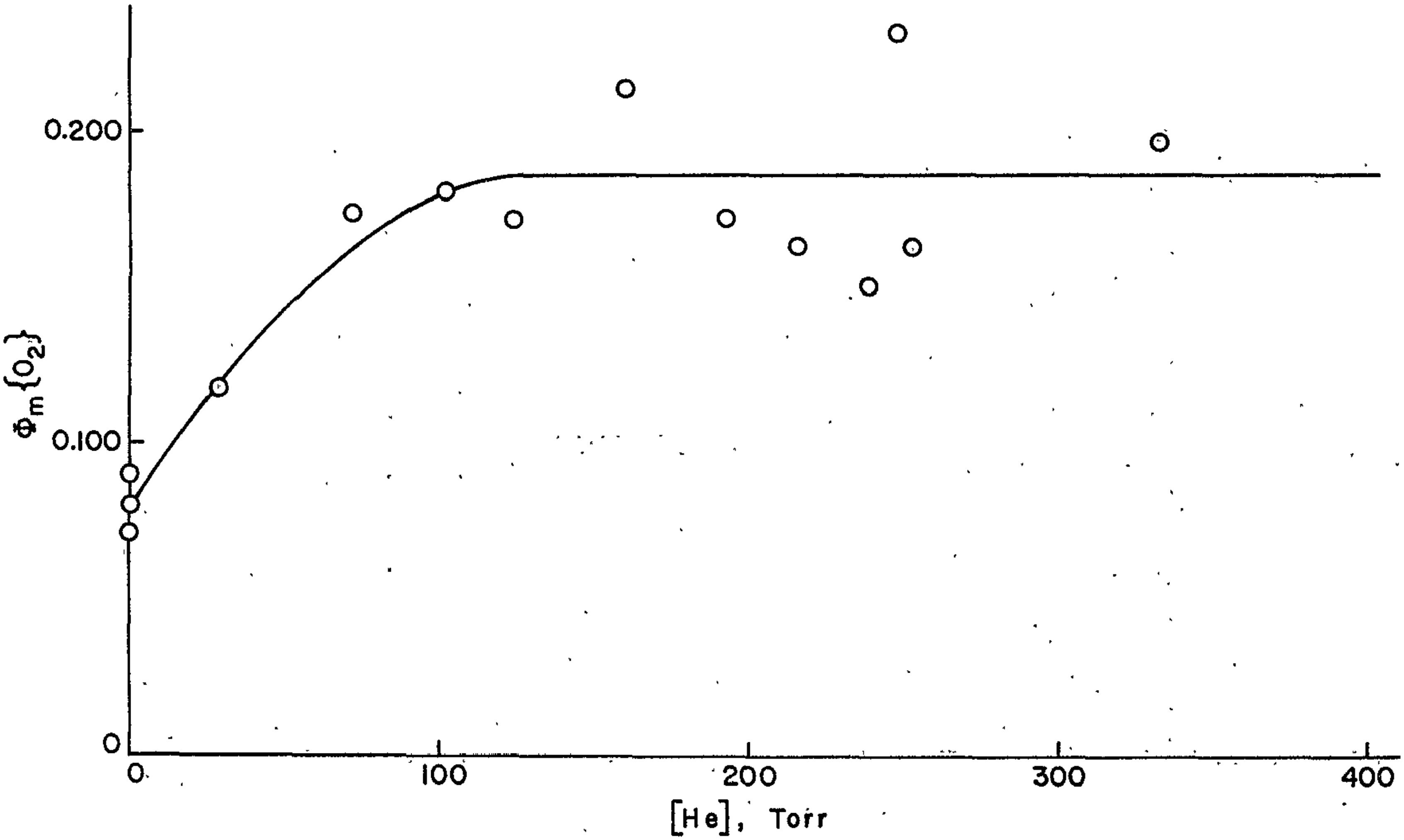

FIGURE 8

$\Phi_m\{O_2\}$ AS A FUNCTION OF ADDED HELIUM value of k_{14}/k_{15} can be calculated from expression (E) derived in Chapter 3.

$$\frac{k_{14}}{k_{15}} = \frac{0.5 + \Phi_m\{O_2\}}{1 - \Phi_m\{O_2\}} \qquad \text{(E)}$$

$$k_{14}/k_{15} = 0.85 \pm 0.05$$

A more detailed study of the effect of added helium in the photolysis of N_2O by itself at 2139 A and 1849 A has been made in this laboratory.[39]

The affect of added helium in the photolysis of CH_4 - N_2O mixtures was determined by the use of a computer program. The experimental conditions and the results of the measurement of $\Phi\{C_2H_6\}$ is shown in Table 19 and the information that was listed on the data cards is given in Table 20. The value of $k_{14}/k_{15} = 0.66$ was used in the calculation of $k_{16}/(k_{14} + k_{15})$. The average for the ratio of rate constants $k_{16}/(k_{14} + k_{15})$ at 330 torr and 760 torr helium are respectively 2.04 ± 0.08 and 1.89 ± 0.10. The final steady state concentrations as given in the last iteration of the computer outputs are listed in Table 21.

It was necessary to determine the effect of using different weight factors of the helium pressure in the third body term, M, of the mechanistic scheme. The results of this study are shown in Table 22. From these measurements it can be concluded that the values of $k_{16}/(k_{14}+k_{15})$ are independent of the fraction of the helium pressures weighted into the M term.

TABLE 19

EFFECT OF ADDED HELIUM IN THE PHOTOLYSIS OF N_2O-CH_4 MIXTURES

$[CH_4]$ (torr)	[He] (torr)	$R = \frac{[CH_4]}{[N_2O]}$	I_a (μ/min)	$[C_2H_6]$ (μ)	$\Phi\{C_2H_6\}$	$\frac{k_{16}}{(k_{14}+k_{15})}$ (a)
(a) 100 torr N_2O, 10 minutes irradiation, ~330 torr helium added						
106.15	356	1.062	33.8	12.1	0.0358	2.16
111.75	317	1.115	33.8	15.7	0.0464	2.12
119.85	325	1.209	33.8	15.2	0.0450	1.94
120.10	320	1.215	25.6	15.6	0.0609	2.01
132.65	349	1.337	25.6	24.3	0.0949	1.97
(B) 100 torr N_2O, 10 minutes irradiation, ~760 torr helium added						
109.70	791	1.104	33.8	11.5	0.0340	2.05
120.55	758	1.223	33.8	13.6	0.0402	1.89
135.05	788	1.366	25.6	19.2	0.0750	1.84
144.70	712	1.438	25.6	21.9	0.0855	1.78

(a) based on helium weighted 1/3 into M term and $k_2/k_3 = 0.66$

TABLE 20

ADDED HELIUM DATA IN THE PHOTOLYSIS OF N_2O-CH_4 MIXTURES AS LISTED FOR THE COMPUTER WORK$^{(a)}$

$[CH_4]$ (x 10^{-3} $\frac{\text{moles}}{\text{liter}}$)	$[N_2O]$ (x 10^{-3} $\frac{\text{moles}}{\text{liter}}$)	I_a (x 10^{-8} $\frac{\text{moles}}{\text{liter-sec}}$)	$[CH_3]$ (x 10^{-10} $\frac{\text{moles}}{\text{liter}}$)	$[M]^{(b)}$ (x 10^{-2} $\frac{\text{moles}}{\text{liter}}$)
(A) 100 torr N_2O, 10 minutes irradiation, ~330 torr helium added				
5.709	5.375	3.03	2.04	1.747
6.010	5.392	3.03	2.33	1.708
6.446	5.330	3.03	2.29	1.760
6.459	5.322	2.29	2.32	1.752
7.134	5.335	2.29	2.89	1.873
(B) 100 torr N_2O, 10 minutes irradiation, ~760 torr helium added				
5.900	5.343	3.03	1.99	2.542
6.483	5.303	3.03	2.16	2.538

TABLE 20 (cont.)

$[CH_4]$ ($\times 10^{-3}$ $\frac{\text{moles}}{\text{liter}}$)	$[N_2O]$ ($\times 10^{-3}$ $\frac{\text{moles}}{\text{liter}}$)	I_a ($\times 10^{-8}$ $\frac{\text{moles}}{\text{liter-sec}}$)	$[CH_3]$ ($\times 10^{-10}$ $\frac{\text{moles}}{\text{liter}}$)	$[M]^{(b)}$ ($\times 10^{-2}$ $\frac{\text{moles}}{\text{liter}}$)
7.263	5.319	2.29	2.57	2.671
7.782	5.413	2.29	2.75	2.596

(a) refers to the data in Table 16

(b) based on helium pressure weighted a factor of 1/3

TABLE 22

HELIUM PRESSURE WEIGHTED INTO THE THIRD BODY TERM

Fraction of Helium Pressure Weighted into M	$k_{16}/(k_{14} + k_{15})$[(a)]	
	[He] = 330 torr	[He] = 760 torr
0	2.05 ± 0.08	1.91 ± 0.10
1/3	2.04 ± 0.08	1.89 ± 0.10
1/2	2.03 ± 0.08	1.88 ± 0.10
1	2.02 ± 0.08	1.86 ± 0.10

(a) based on $k_2/k_3 = 0.66$

TABLE 21

STEADY STATE CONCENTRATIONS AS LISTED IN THE LAST ITERATION OF THE COMPUTER CALCULATION FOR THE CH_4-N_2O-He DATA[a]

$\frac{k_{16}}{k_{14}+k_{15}}$	$10^8 \times$ [NO] M	$10^{10} \times$ [NO_2] M	$10^{10} \times$ [CH_3O_2] M	$10^{10} \times$ [CH_3O] M	$10^{10} \times$ [HNO] M	$10^{17} \times$ [$O(^1D)$] M	$10^{18} \times$[b] [OH] M	$10^{11} \times$[c] [$O(^3P)$] M	$10^8 \times$[d] [O_2] M
2.16	2.00	4.33	4.64	4.61	4.87	1.65	5.75	5.40	6.71
2.12	1.74	3.74	4.62	4.52	4.08	1.62	5.51	6.37	5.95
1.94	1.77	3.87	4.62	4.53	4.17	1.64	5.13	6.10	5.87
2.01	1.29	2.87	3.99	3.83	2.92	1.21	3.92	6.37	4.33
1.97	0.99	2.36	3.93	3.60	2.05	1.14	3.62	7.94	3.12
2.05	2.06	5.57	4.63	4.60	5.02	1.68	5.54	3.80	4.71
1.89	1.88	5.12	4.62	4.55	4.49	1.67	5.07	4.18	4.31
1.84	1.14	3.33	3.95	3.71	2.47	1.19	3.51	5.04	2.50
1.78	1.05	3.05	3.93	3.65	2.22	1.15	3.30	5.60	2.38

(a) $k_{14}/k_{15} = 0.66$ and He weighted 1/3 in M

(b) calculated from Equation (4)

(c) calculated from Equation (J)

(d) calculated from Equation (I)

Discussion

This work has shown a significant effect of the removal of excess translational energy in both the photolysis of N_2O by itself and in the photolysis of N_2O - CH_4 mixtures. The difference between the value obtained for k_{14}/k_{15} in this work (0.66) and that obtained by Preston (1.00) can be explained in terms of the excess translational energy of the $O(^1D)$. For if the excess translational energy of the $O(^1D)$ atom is removed the new value of k_{14}/k_{15} calculated is 0.85 in much better agreement with the value obtained by Preston.

However, according to the results of Preston there is no indication that excess translational energy affects the ratio of rate constants k_{14}/k_{15}. The addition of excess SF_6 in the photolysis of O_3 - N_2O mixtures had no effect on the ratio k_{14}/k_{15}. The apparent discrepancy can be explained on the basis that the method of chemical difference is a sensitive tool in measuring small changes in the ratio k_{14}/k_{15}. This can be confirmed since the effect of the removal of the excess translational energy of the $O(^1D)$ atom was investigated in the photolysis of O_3 - N_2O mixtures. No effect of added helium was found. Therefore, it can be concluded that the only method sensitive enough to determine small changes in k_{14}/k_{15} is the method of chemical difference.

From the hard sphere model for atomic collisions, the average amount of translational energy removed from the $O(^1D)$ atom after a collision with helium is given by:[41]

$$E_T' = E_T \cdot \frac{M_{O(^1D)}^2 + M_{He}^2}{(M_{O(^1D)} + M_{He})^2}$$

where

E_T' = excess translational energy after collision

E_T = excess translational energy before collision

Substituting in the values for the masses of the $O(^1D)$ and He, $E_T'/E_T = 0.68$; thus 32% of the excess translational energy is removed by each collision with helium.

The number of times that an average $O(^1D)$ atom will collide with a helium atom before colliding with a nitrous oxide molecule is given by the ratio:

$$\frac{\sigma^2_{He-O}\,[He]}{\sigma^2_{N_2O-O}\,[N_2O]}$$

where $\sigma^2_{N_2O-O}$ and σ^2_{He-O} are the collision cross sections of $O(^1D)$ atom with nitrous oxide and helium respectively. Table 23 contains the values of σ_i,

$$\sigma^2_{1-2} = \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2$$

for the various species of interest. From the values in Table 23, the ratio of collision cross sections can be calculated:

$$\frac{\sigma^2_{N_2O-O}}{\sigma^2_{He-O}} = 2.25$$

TABLE 23

VALUES OF $\sigma^{(a)}$

Species	σ, (A)	Reference
$O(^1D)^{(b)}$	2.9	Suehla[42]
He	2.18	Kennard[41]
N_2O	4.71	Benson[43]
CH_4	4.14	Kennard[41]

(a) from viscosity data

(b) value of $O(^1D)$ assumed to be the same as for $O(^3P)$.

If it is assumed that the excess energy available is distributed evenly between the $O(^1D)$ atom and the molecular fragment, the excess translation energy of the $O(^1D)$ atom will be 24.2 kcal/mole. For a $[He]/[N_2O]$ ratio of 20/1, the relative number of collisions of $O(^1D)$ with He to that with N_2O is 8.9. Under these conditions of high $[He]/[N_2O]$ ratios, the excess translation energy is reduced to less than 1 kcal/mole. Therefore, the ratio $k_{14}/k_{15} = 0.85 \pm 0.05$ can be assumed to be the value for the completely thermalized $O(^1D)$ atom.

Similar arguments and calculations can be made for the $CH_4 - N_2O$ system. The number of times that an average $O(^1D)$ atom will collide with a helium atom before colliding with a methane molecule is given by the ratio:

$$\frac{\sigma^2_{He-O}\,[He]}{\sigma^2_{CH_4-O}\,[CH_4]}$$

From the values in Table 23, the ratio of collision cross sections can be calculated:

$$\frac{\sigma^2_{CH_4-O}}{\sigma^2_{He-O}} = 1.92$$

The number of times that an average $O(^1D)$ atom will collide with a helium atom before colliding with either a nitrous oxide or methane molecule is given by:

$$\frac{\sigma^2_{He-O}\,[He]}{\sigma^2_{N_2O-O}\,[N_2O] + \sigma^2_{CH_4-O}\,[CH_4]}$$

rearranging:

$$\left(\frac{\sigma^2_{N_2O-O}\,[N_2O]}{\sigma^2_{He-O}\,[He]} + \frac{\sigma^2_{CH_4-O}\,[CH_4]}{\sigma^2_{He-O}\,[He]} \right)^{-1}$$

evaluating this expression at 330 and 760 torr He, the values 0.73 and 1.7 are obtained. Using these results, the excess translational energy can be calculated to be equal to 18.3 and 12.7 kcal/mole, respectively.

For the CH_4-N_2O-He runs listed in Table 19 the He present is not sufficient to remove all the translational energy in the $O(^1D)$ atoms. Thus k_{14}/k_{15} must lie between 0.59 and 0.85. The results of varying k_{14}/k_{15} does introduce a slight effect as shown in Table 24.

Table 25 gives the experimental results of $k_{16}/(k_{14} + k_{15})$ as a function of the excess translational energy of the $O(^1D)$ atom. The value of infinite helium pressure ($E_T = 0$) is obtained by extrapolation as shown in Figure 9. Because of the extrapolation and the estimates required in obtaining E_T, the uncertaintly in this value is rather large. However, the value of $k_{16}/(k_{14} + k_{15}) = 1.35 \pm 0.3$ can be assumed to be the value for the completely thermalized $O(^1D)$ atoms. This agrees with the value of 1.22 found by Young et. al.[29] who worked with excess Ar, which also removes translational energy without quenching $O(^1D)$ to $O(^3P)$.

TABLE 24

EFFECT OF THE VALUE OF k_{14}/k_{15} ON $k_{16}/(k_{14} + k_{15})$ IN THE PRESENCE OF He$^{(a)}$

k_{14}/k_{15}	$k_{16}/(k_{14} + k_{15})$	
	[He] = 330 torr	[He] = 760 torr
0.59	2.09 ± 0.09	1.94 ± 0.11
0.66	2.04 ± 0.08	1.89 ± 0.10
0.75	1.99 ± 0.08	1.84 ± 0.10
0.85	1.94 ± 0.08	1.79 ± 0.09

(a) He weighted a factor of 1/3 in M

TABLE 25

COMPUTER CALCULATED VALUES OF $k_{16}/k_{14} + k_{15})$ AS A FUNCTION OF ADDED HELIUM

[He] (torr)	E_T (kcal/mole)	$k_{16}/(k_{14} + k_{15})$
0	24.2	2.28
330	18.3	2.01
760	12.7	1.84
∞	0.0	1.35[(a)]

(a) extropolated

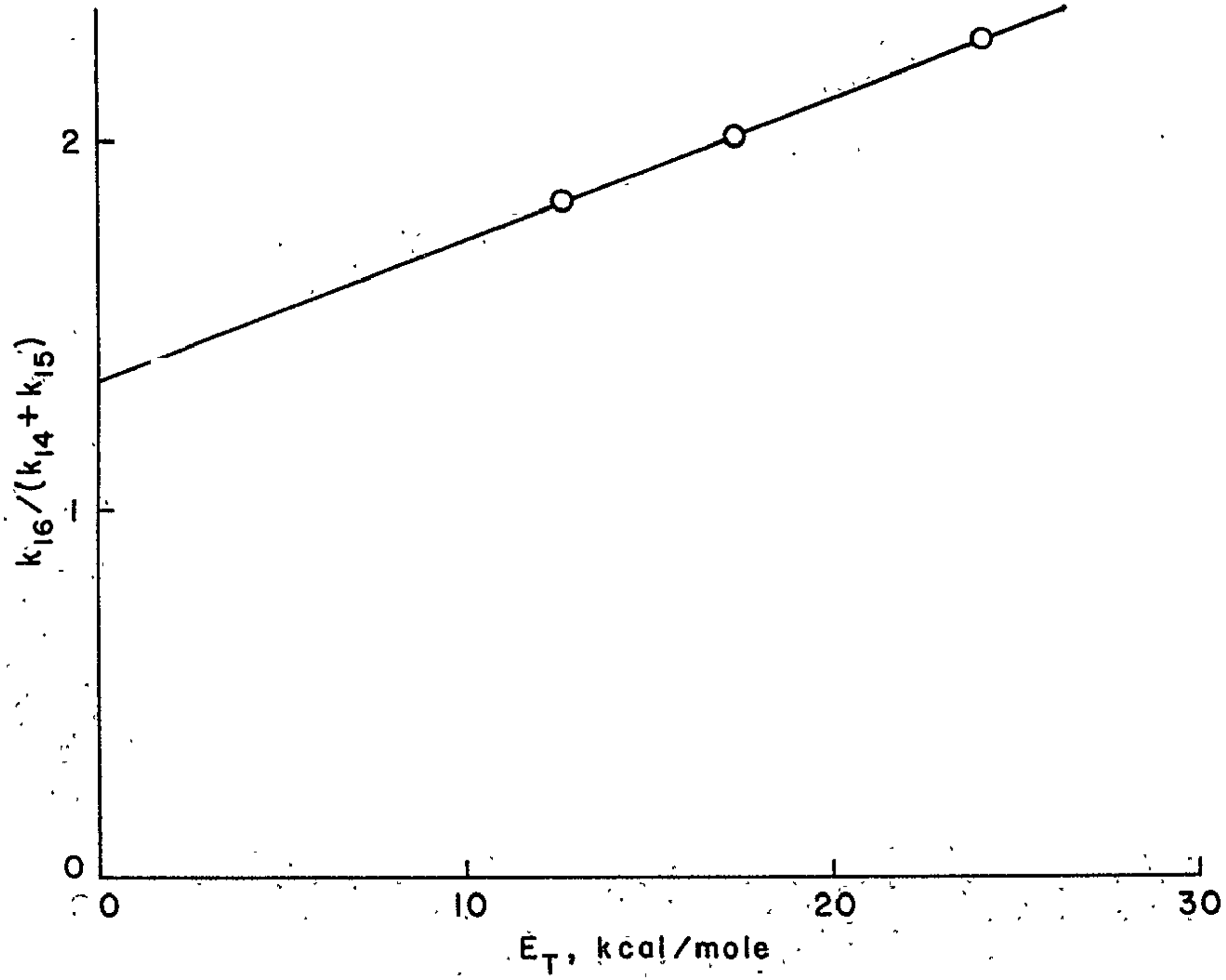

FIGURE 9

$k_{16}/(k_{14} + k_{15})$ AS A FUNCTION OF THE EXCESS TRANSLATIONAL ENERGY

In conclusion, the removal of the excess translational energy increases the ratio of rate constants k_{14}/k_{15} while the value for $k_{16}/(k_{14} + k_{15})$ decreases. In the photolysis of N_2O by itself the increase in the value of k_{14}/k_{15} can be understood physically if reaction (15) has a small activation energy. The decrease in the ratio of $k_{16}/(k_{14} + k_{15})$ in the photolysis of N_2O - CH_4 mixtures can be understood physically if reaction (16) has a greater activation energy than the sum of the activation energies for reaction (14) and (15).

CHAPTER 6

SUMMARY AND CONCLUSIONS

This study investigates the reactions of $O(^1D)$ atoms both translationally hot and thermally equilibrated in two systems:

(1) The photolysis of N_2O at 2139 A

(2) The photolysis of N_2O-CH_4 mixtures at 2139 A

The relative rate constants ratio for the reactions

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \tag{14}$$

$$O(^1D) + N_2O \rightarrow 2NO \tag{15}$$

was determined, $k_{14}/k_{15} = 0.59 \pm 0.01$, by the use of a new technique; the method of chemical difference, an in situ chemical titration technique.

In the photolysis of N_2O-CH_4 mixtures, the detailed mechanism was elucidated and relative rate constants were determined by the method of chemical difference with the aid of a computer program:

$$O(^1D) + CH_4 \rightarrow CH_3 + OH \tag{16}$$

$$O(^1D) + CH_4 \rightarrow O(^3P) + CH_4 \tag{27}$$

where

$$k_{16}/(k_{14} + k_{15}) = 2.28 \pm 0.20$$

$$k_{27}/(k_{16} + k_{27}) = 0.05 \pm 0.05$$

From the results of the experiments with added helium, it was found that the O(^{1}D) atom possesses translational energy in excess of that obtained from thermal equilibrium. This excess translational energy has been shown to affect the values of the ratios of rate constants k_{14}/k_{15} and $k_{16}/(k_{14} + k_{15})$. This effect explains to some extent the discrepancies in many of the previous investigations of the ratio k_{14}/k_{15}.

The results of this work, indicate the importance of the translational energy possessed by the O(^{1}D) atom in its reactions. Furthermore, this effect of excess translational energy should not be overlooked in other possible atom reactions.

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APPENDIX

FORTRAN IV (WATFOR) PROGRAM

```
C     THIS PROGRAM ATTEMPTS TO SOLVE ITERATIVELY A SET OF
C     SIX NON-LINEAR SIMULTANEOUS EQUATIONS INVOLVING SIX
C     UNKNOWNS.
C     10/21/70 -- R. L. DIVANY
      IMPLICIT REAL*4 (A-I,K-Z)
      REAL*4 CH3O2(2),NO(2),NO2(2),CH3O(2),
     1HNO(2),K16(2),V(12),K27(2),W(6)
      EQUIVALENCE (V(1),CH3O2),(V(3),NO)
      EQUIVALENCE (V(5),NO2),(V(7),CH3O),(V(9),HNO)
      EQUIVALENCE (V(11),K16),(W(1),ICH3O2),(W(2),INO)
      EQUIVALENCE (W(3),INO2),(W(4),ICH3O),(W(5),IHNO)
      EQUIVALENCE (W(6),IK16)
C     K16 AND K27 ARE BOTH UNKNOWNS BUT K27 IS CALCULATED
C     FROM K16.
      TOL=0.001
      JIT=100
      DIFF=1000.
C     DIFF IS THE FACTOR BY WHICH A VARIABLE MAY GO HIGH OR
C     LOW BEFORE IT MUST BE CONSTRAINED.
      K14=4.0E+10
      K15=6.0E+10
      K30=6.2E+06
      K31=2.6E+10
      K28=3.0E+10
      K32=2.4E+09
      K34=2.0E+09
      K35=3.6E+10
      K40A=3.0E+07
      K40B=6.0E+06
      K36=3.0E+09
      K41=1.6E+10
      K38=8.0E+08
      K37=1.5E+10
      K42=1.0E+10
      K43=6.0E+07
      K26=1.7E+10
      K39=1.6E+09
      K44=1.0E+08
      K45=1.0E+08
      K46=1.0E+08
      K47=1.0E+06
      K48=3.0E+07
      K49=3.0E+07
      DO 90 J=1,50
```

```
      CH302(1)=1.7E-10
      NO(1)=4.5E-08
      NO2(1)=1.17E-09
      CH30(1)=1.1E-09
      HNO(1)=2.5E-09
      K16(1)=2.4E+11
      K27(1)=0.053*K16(1)
      ICH302=CH302(1)
      INO=NO(1)
      INO2=NO2(1)
      ICH30=CH30(1)
      K27(1)=0.053*K16(1)
      ICH302=CH302(1)
      INO=NO(1)
      INO2=NO2(1)
      ICH30=CH30(1)
      IHNO=HNO(1)
      IK16=K16(1)
      READ, CH4,N2O,IA,CH3,M
      PRINT,'CH4 =',CH4,'   N2O =',N2O,'   IA =',IA,' CH3 ='
     1  ,CH3,'      M =',M
      PRINT 102
102   FORMAT (/////' ',6X'NO'9X'NO2'7X'CH302'7X
     1          'CH30',8X'HNO'8X'K16',8X'K27'/)
      JKOUNT=0
      J2=1
      PRINT 100,NO(J2),NO2(J2),CH302(J2)
     1,CH30(J2),HNO(J2),K16(J2),K27(J2)
10    J1=1
      J2=2
C     J1 INDICATES PRESENT VALUE.
C     J2 INDICATES NEW PREDICTED VALUE.
15    C1=IA/((K14+K15)*N2O+(K16(J1)+K27(J1))*CH4)
      C2=K26*K27(J1)*CH4/(K35*NO(J1)*M+K26*NO2(J1))
      C3=K27(J1)*K35*M*CH4/(K35*NO(J1)*M+K26*NO2(J1))
      CH30(J2)=2.0*K37*CH302(J1)*CH302(J1)/((K40A+K40B)*
     1NO(J1)+K41*CH3+2.0*K42*CH30(J1)+K43*NO2(J1)+K39*
     2CH302(J1)+K45*HNO(J1))
      HNO(J2)=K40B*CH30(J1)*NO(J1)/(K44*CH3+K45*CH30(J1)+
     1K46*CH302(J1)+2.0*K47*HNO(J1))
      CH302(J2)=(C1*K14*N2O+K37*CH302(J1)*CH302(J1)+C2*
     1NO2(J1)*C1)/(K38*CH3+2.0*K37*CH302(J1)+K39*CH30(J1)+
     2K46*HNO(J1)+K48*NO(J1)+K49*NO2(J1))
      NO(J2)=(2.0*K15*N2O*C1+C1*C2*NO2(J1)+K44*CH3*HNO(J1)+
     1K45*HNO(J1)*CH30(J1)+K46*CH302(J1)*HNO(J1))/(K32*
     2CH3+(K40A+K40B)*CH30(J1)+C3*C1+K48*CH302(J1))
      NO2(J2)=C3*NO(J1)*C1/(K36*CH3+K43*CH30(J1)+C2*C1+
     1K49*CH302(J1))
      K16(J2)=(2.0*K31*CH3*CH3+3.0*K32*NO(J1)*CH3+K34*
     1K16(J1)*C1*CH3/K30+K14*N2O*C1+K37*CH302(J1)*CH302(J1)+
```

```
     2C2*NO2(J1)*C1+K36*NO2(J1)*CH3+K41*CH30(J1)*CH3+K38*
     3CH302(J1)*CH3+K44*HNO(J1)*CH3)/(2.0*CH4*C1)
      K27(J2)=K16(J2)*0.053
      JSTART=J2
      JSTOP=J2+10
      JW=1
      DO 30 JIND=JSTART,JSTOP,2
      IF(V(JIND).GT. W(JW)/DIFF) GO TO 24
      V(JIND)=W(JW)/DIFF
      GO TO 38
24    IF(V(JIND).LT. W(JW)*DIFF) GO TO 30
      V(JIND)=W(JW)*DIFF
      GO TO 38
30    JW=JW+1
38    PRINT 100,NO(J2),NO2(J2),CH302(J2),
     1CH30(J2),HNO(J2),K16(J2),K27(J2),C1,C2,C3
100   FORMAT(' ',1P11E11.3)
      JKOUNT=JKOUNT+1
      JTEMP=J1
      J1=J2
      J2=JTEMP
      DO 40 JJ=1,11,2
      IF(ABS(V(JJ)-V(JJ+1)).GT. TOL*V(JJ)) GO TO 45
40    CONTINUE
      GO TO 90
45    IF(JKOUNT.LT.JIT) GO TO 15
      PRINT 101,JIT
101   FORMAT ('3DID NOT CONVERGE IN',I4,' ITERATIONS')
90    CONTINUE
      STOP 1
      END
```