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THE PHOTOLYSIS OF N_2O AT 1470A

by
Marcia C. Dodge and Julian Heicklen

December 30, 1970

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ABSTRACT

The photolysis of pure N_2O, N_2O and N_2, and N_2O and C_3H_6 mixtures at 1470 Å and room temperature has been studied to determine the relative importance of the primary processes. The results are

Reaction			Φ
$N_2O + h\nu$	→	$N_2(^1\Sigma) + O(^1D)$	0.515 ± 0.04
	→	$N_2(^3\Sigma) + O(^3P)$	0.084 ± 0.02
	→	$N_2(^1\Sigma) + O(^1S)$	0.38 ± 0.06
	→	$N(^2D) + NO(^2\Pi)$	
	→	$N_2(^1\Sigma) + O(^3P)$	0.02 ± 0.02
	→	$N(^4S) + NO(^2\Pi)$	

where $\Phi\{O(^1D)\} = 0.515$ represents both the $O(^1D)$ produced in the primary act and that produced by collisional quenching of $O(^1S)$, $\Phi\{N_2(^3\Sigma)\} = 0.084$ represents only that portion of $N_2(^3\Sigma)$ which dissociates N_2O on deactivation, and $\Phi\{O(^1S)\} = 0.38 - \Phi\{N(^2D)\}$ represents only that portion of $O(^1S)$ which enters into chemical reaction with N_2O.

If the reaction of $O(^1S)$ with N_2O yields only N_2 and O_2 as products, which seems likely from potential-energy curve considerations, then $\Phi\{O(^1S)\} = 0.135 \pm 0.06$ and $\Phi\{N(^2D)\} = 0.245 \pm 0.06$. Young et al[4] have found from spectroscopic observations that the total quantum yield of $O(^1S)$ is about 0.5. Thus it can be concluded that collisional removal of $O(^1S)$ by N_2O yields mainly $O(^1D)$ with chemical reaction being less important. Furthermore most of the $O(^1D)$ is produced this way and the true primary yield of $O(^1D)$ is about 0.15.

The metastable $N(^2D)$ is not deactivated by N_2O, but is removed by chemical reaction to produce N_2 and NO. The results further indicate that $N_2(^3\Sigma)$ dissociates N_2O at least 80% of the time during quenching. The relative efficiency of N_2O compared to N_2 is about 2 for the removal of $O(^1D)$. $O(^1S)$ is removed about 90 times as efficiently by C_3H_6 as by N_2O.

INTRODUCTION

The photolysis of N_2O at 1470A has been studied in some detail by a number of investigators. Zelikoff and Aschenbrand,[1] Groth and Schierholz,[2] and Yang and Servedio[3] have found the products of photolysis to be N_2, O_2, NO, and NO_2, and have measured their quantum yields.

The following primary processes are energetically possible in the photolysis of N_2O at 1470A.

$$N_2O + h\nu(1470A) \rightarrow N_2(^1\Sigma) + O(^1S) \quad 1$$

$$\rightarrow N_2(^1\Sigma) + O(^1D) \quad 2$$

$$\rightarrow N_2(^3\Sigma) + O(^3P) \quad 3$$

$$\rightarrow N(^2D) + NO(^2\Pi) \quad 4$$

$$\rightarrow N_2(^1\Sigma) + O(^3P) \quad 5$$

$$\rightarrow N(^4S) + NO(^2\Pi) \quad 6$$

Reactions 1-4 are spin allowed, but reactions 5 and 6 are spin forbidden. Young, Black, and Slanger[4] recently have measured the quantum yields of various metastable species formed in the photolysis by photometric techniques. They report quantum yields of 0.5, 0.55, and 0.08, respectively for $O(^1S)$, $O(^1D)$, and $N_2(^3\Sigma)$ production. However, the sum of their computed primary quantum yields exceeds unity.

In the present paper, we report product quantum yield measurements for the 1470A photolysis of pure N_2O, N_2O-N_2 mixtures, and N_2O-olefin mixtures. From the data obtained, we compute the quantum yields of each of the primary processes.

EXPERIMENTAL

A Raytheon microwave power generator Model PGM-10 was used to pass a microwave discharge through xenon as a source of 1470A radiation. The photolysis cell, about 15 cm in length and 2.5 cm in diameter, was equipped with a sapphire window to allow passage of the radiation. Absorbing gases could be introduced into a central compartment between the photolysis cell and the source to vary the intensity of the light reaching the photolysis cell. A side arm on the xenon lamp was immersed in liquid Ar during photolysis to trap out any impurities present in the lamp. The spectral purity of the lamp was determined by placing ethane, which absorbs 1470A radiation but no longer wavelengths, in the compartment between the photolysis cell (containing N_2O) and the lamp. Under these conditions no photolysis of N_2O could be detected. The intensity of the lamp was determined by carbon dioxide actinometry[5] where the quantum yield of CO formation is taken to be 1.0.

Matheson C.P. grade N_2O, trans-butene-2, and research grade C_3H_6 were purified by degassing at -196°C. The nitrogen used was Air Products research grade. It contained 5 ppm oxygen which necessitated a correction in determining the quantum yields of oxygen produced in experiments with N_2 present.

After irradiation the products were collected in a Toepler pump and compressed before gas chromatographic analysis on a 1/4" by 10 ft. long column packed with 5A molecular sieves of 60/80 mesh, and utilizing a Gow Mac Model 40-012 voltage regulator power supply with a Gow Mac Model 10677 thermistor detector. Either NO or O_2 was

detected, but not both. The NO and O_2 react before analysis so that only the gas present in excess is observed. Measurements with known mixtures of NO and O_2 done under identical conditions of an experiment showed that the NO and O_2 reacted quantitatively in a 4 to 1 ratio. Apparently, at the inlet to the chromatograph, the following reactions occur.

$$2NO + O_2 \rightarrow 2NO_2 \qquad 7$$

$$NO_2 + NO \rightarrow N_2O_3 \qquad 8$$

Therefore the measured quantum yield of O_2 formation, $\Phi_m\{O_2\}$, is related to the actual quantum yields by

$$\Phi_m\{O_2\} = \Phi\{O_2\} - (1/4)(\Phi\{NO\} - \Phi\{NO_2\}) \qquad a$$

Furthermore a mass balance requires that

$$\Phi\{N_2\} = 2\Phi\{O_2\} + (1/2)\Phi\{NO\} + (3/2)\Phi\{NO_2\} \qquad b$$

Combining equations a and b gives

$$\Phi\{O_2\} + (1/2)\Phi\{NO_2\} = (1/2)\Phi_m\{O_2\} + (1/4)\Phi\{N_2\} \qquad c$$

RESULTS

The quantum yields observed in the photolysis of N_2O at 1470A are listed in Table I. In most of these experiments the absorbed intensity, I_a, measured by CO_2 actinometry, was obtained before and after each run. The average value was used and is listed in the Table. The experiments are tabulated in the order of increasing percent decomposition, reported as 100 times the amount of N_2 produced divided by the N_2O pressure. Since about 0.75 molecules of N_2 are produced per N_2O decomposed, this ratio is about 3/4 of the percent decomposition, which varies between 0.05 and 1 percent.

Both the quantum yields of N_2 formation, $\Phi\{N_2\}$, and the measured quantum yield of O_2, $\Phi_m\{O_2\}$, are independent of N_2O pressure between 50 and 245 torr, but both yields increase with the percent decomposition. The average value for $\Phi\{N_2\}$ for all the runs in the table is 1.48 ± 0.07, whereas the average value for the first seven runs with low conversions is 1.41 ± 0.06. These two values agree within the experimental uncertainty, but the slight increase in $\Phi\{N_2\}$ with percent conversion is apparent. The reason for this increase is not known. The value of 1.41 for $\Phi\{N_2\}$ agrees extremely well with the previous work as shown in Table II and is adopted here. A value of 1.48 is too large to be consistent with the other investigations.

$\Phi_m\{O_2\}$ increases markedly with percent conversion, and the reason for this is quite clear. The formation of $N(^2D)$ atoms in the primary photolysis was demonstrated by the production of $^{30}N_2$ in the photolysis of $^{15}N^{14}NO$.[6] Since $N(^4S)$ does not react with N_2O,[6-8] the only way $^{30}N_2$ can be produced is by reaction of $^{15}N(^2D)$ with $^{15}N^{14}NO$

TABLE I

Quantum Yields in the Photolysis of N_2O
at 1470A and Room Temperature

$[N_2O]$, Torr	Irradiation Time, min	I_a, μ/min	$\frac{10^2[N_2]}{[N_2O]}$	$\Phi\{N_2\}$	$\Phi_m\{O_2\}$
245	60.0	1.03	0.038	1.50	0.139
103	30.0	1.43	0.058	1.39	0.132
100	60.0	0.73	0.064	1.45	0.146
98	60.0	1.03	0.098	1.50	0.145
61	60.0	1.28	0.168	1.33	0.130
50	60.0	1.15	0.194	1.40	0.135
53	60.0	1.28	0.194	1.34	0.134
60	60.0	1.57	0.237	1.51	0.162
101	60.0	3.16	0.284	1.51	0.190
99	60.0	3.16	0.303	1.59	0.200
69	120.0	1.43	0.38	1.50	0.161
77	60.0	3.72	0.46	1.58	0.197
107	320.0	1.47	0.70	1.59	0.202

$$N(^2D) + N_2O \rightarrow N_2 + NO \qquad 9$$

About 5 percent of the N_2 was of mass 30 and this represents a lower limit to the percent of N_2 arising from $N(^2D)$, since some of the $^{15}N(^2D)$ could react with N_2O to produce ^{15}NO. With about 1% of ^{15}NO added the percentage of $^{30}N_2$ increased thus indicating the following reactions

$$N(^2D) + NO \rightarrow N_2 + O(^3P) \qquad 10a$$

$$\rightarrow N(^4S) + NO \qquad 10b$$

$$N(^4S) + NO \rightarrow N_2 + O(^3P) \qquad 11$$

In our experiments at low conversions reaction 9 dominates and NO is produced. However, as NO is accumulated in the system, reaction 10 (10a + 10b) becomes more important. NO production is reduced, O_2 production is enhanced, and $\Phi_m\{O_2\}$ rises. The rate constants k_9 and k_{10} are known to be 3×10^{-12} and 1.8×10^{-10} cm^3/sec respectively.[9] Thus at 1 percent conversion about 25% of the $N(^2D)$ atoms are reacting with NO, which is sufficient to account for the observed trend in $\Phi_m\{O_2\}$. Therefore, the first seven runs in Table I, which correspond to low percent conversion, are used to obtain $\Phi_m\{O_2\} = 0.137 \pm 0.005$.

Values found for O_2 production from the previous studies are listed in Table II. Zelikoff and Aschenbrand[1] measured their products mass spectrometrically and found $\Phi\{O_2\}$ to be about 0.50 ± 0.09. They did not report NO_2, so presumably it was unimportant in their system. Both Groth and Schierholz[2] and Yang and Servedio[3] condensed their reaction mixture before analysis. Presumably in both experiments the NO was quantitatively converted to N_2O_3 before the O_2 was removed for analysis, though Yang and Servedio assumed that NO_2 rather than N_2O_3

TABLE II

Quantum Yields of Nitrogen and Oxygen

Product Yield	Zelikoff and Aschenbrand[1]	Groth and Schierholz[2]	Yang and Servedio[3]	Present Work
$\Phi\{N_2\}$	1.44 ± 0.11	1.40 ± 0.06	1.40 ± 0.02	1.41 ± 0.06
$\Phi_m\{O_2\}$	—	0.15 ± 0.01	0.19 ± 0.01	0.137 ± 0.005
$\Phi\{O_2\}+(1/2)\Phi\{NO_2\}$	0.50 ± 0.09	0.49 ± 0.04	0.45 ± 0.03[a]	0.42 ± 0.02

a) As recomputed by eqn. c.

was produced. Their analytical schemes should lead to the same observations as ours. Groth and Schierholz found $\Phi_m\{O_2\} = 0.15 \pm 0.01$ in excellent agreement with our result of 0.137 ± 0.005. The value of 0.19 ± 0.01 reported by Yang and Servedio apparently corresponds to percent conversions of 1-2% and agrees with our results for these conversions. However, this high value results from secondary reactions and can be discarded. (Actually Yang and Servedio do not report the precent decomposition in their paper for most of their runs. However, for the series in which the effect of the extent of conversion was studied, it was varied between about 1 and 62%. Presumably their low-conversion runs correspond to about 1 percent decomposition.) Groth and Schierholz also measured the NO_2 quantum yield to be 0.68 ± 0.05, so that $\Phi\{O_2\} + (1/2)\Phi\{NO_2\}$ can be computed directly. For both the Yang and Servedio experiments as well as in our work, this quantity is computed from eqn. c. The results of the four investigations agree within the experimental uncertainty. However, our result is the lowest and is to be preferred, both because it is the most precise and because it corresponds to the lowest percent decomposition.

Table III lists $\Phi_m\{O_2\}$ in the photolysis of N_2O in the presence of N_2. The ratio of $[N_2]$ to $[N_2O]$ was varied from 1.0 to 40 and $\Phi_m\{O_2\}$ increased with the ratio to an upper limiting value of about 0.375.

Table IV lists quantum yields in the photolysis of N_2O in the presence of C_3H_6. The ratio of $[N_2O]$ to $[C_3H_6]$ was varied between 1220 and 28. The ratio of extinction coefficients for C_3H_6 and N_2O is about 3 at 1470A,[10] so that even at the low ratio 90% of the radiation is absorbed by the N_2O, and the absorption due to the C_3H_6 is small. The

TABLE III

$\Phi_m\{O_2\}$ in the Photolysis of N_2O and N_2 Mixtures at 1470A and Room Temperature

$[N_2]/[N_2O]$	$[N_2O]$, Torr	$[N_2]$, Torr	Irradiation Time, min	I_a, μ/min	$\Phi_m\{O_2\}$
1.0	103	104	50	2.50	0.216
1.9	103	200	50	2.50	0.256
3.2	64	206	50	4.00	0.265
3.8	47	179	50	4.72	0.292
4.5	34	152	50	5.06	0.300
5.3	56	294	50	2.68	0.328
7.9	52	410	60	3.75	0.320
8.4	50	420	60	2.95	0.345
8.5	50	425	120	2.93	0.364
11.2	35	391	50	4.72	0.356
11.5	34	390	50	4.00	0.345
16.2	28	453	50	2.06	0.368
24.4	18	438	50	5.06	0.375
40.5	11	446	50	2.68	0.374

TABLE IV

Quantum Yields in the Photolysis of N_2O and C_3H_6 Mixtures at 1470A and Room Temperature

$[N_2O]/[C_3H_6]$	$[N_2O]$, Torr	$[C_3H_6]$, μ	Irradiation Time, min	I_a, μ/min	$\Phi\{N_2\}$	$\Phi_m\{O_2\}$	$\Phi_m\{NO\}$
1220	654	536	120	1.77	1.32	0.0425	-
1160	424	398	60	0.80	1.46	0.0396	-
734	537	730	120	0.82	1.56	0.0437	-
484	305	630	100	3.14	1.55	0.0440	-
286	98	342	60	3.50	1.49	0.0438	-
240	175	730	100	2.90	1.47	0.0417	-
155	85	550	100	2.90	1.35	0.0328	-
101	98	958	85	2.05	1.28	0.0324	-
100	71	710	100	3.80	1.28	0.0202	-
74	62	840	100	3.92	1.22	0.0153	-
73	38	520	100	2.18	1.14	0.0049	-
70	45	636	120	2.96	1.16	0.0045	-
53	43	810	100	2.90	1.17	-	0.0159
39	27	690	100	2.92	1.02	-	0.0288
38	30	800	110	2.24	1.01	-	0.0336
28	28	990	100	2.92	1.01	-	0.0411

quantum yields are a function of the ratio of reactant pressures. At ratios between 1220 and 240, $\Phi\{N_2\}$ is the same as in the absence of C_3H_6, whereas $\Phi_m\{O_2\}$ has dropped markedly to 0.0426 ± 0.0013, and is independent of either reactant pressure. As the ratio is lowered below 200 both $\Phi\{N_2\}$ and $\Phi_m\{O_2\}$ drop, the former to unity and the latter to zero. When O_2 is no longer detected, NO is observed and the measured quantum yield of NO, $\Phi_m\{NO\}$, is reported for those runs.

The reduction in $\Phi_m\{O_2\}$ when C_3H_6 is added in trace amounts is attributed to the scavenging of $O(^3P)$ by C_3H_6. However, this reaction can produce free radical intermediates which react with O_2 and NO, and thus might give misleading results. At the high total pressures used here, free radical production should be negligible.[11] To check this point, four runs were done with >300 torr of N_2O and < 750μ of trans-butene-2 to scavenge $O(^3P)$. Since trans-butene-2 is more complex than C_3H_6, free radical production as a result of $O(^3P)$ scavenging should be even less important with trans-butene-2.[11] The average measured value for $\Phi_m\{O_2\}$ in these runs was 0.0432 ± 0.0016 in excellent agreement with the C_3H_6-N_2O results.

DISCUSSION

The absorption of 1470A radiation by N_2O can lead to the six energetically permitted primary processes given by reactions 1-6. In order to understand the mechanistic details it is necessary to consider the fates of the reactive species produced in these reactions.

The atom $O(^1S)$ might react with N_2O

$$O(^1S) + N_2O \rightarrow N_2 + O_2 \qquad 12$$

$$\rightarrow 2NO \qquad 13$$

The rate constant for the total removal of $O(^1S)$ by N_2O has been found to be 1.6×10^{-11} $cm^3/sec.$[4] In addition to reactions 12 and 13, $O(^1S)$ could be deactivated to $O(^1D)$ or $O(^3P)$. However, these deactivations would be equivalent to $O(^1D)$ and $O(^3P)$ production by reactions 2 and 5, respectively. Therefore they need not be considered separately.

The $O(^1D)$ atom reacts with N_2O via

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

$$\rightarrow 2NO \qquad 15$$

These have been shown to be the only reactions of $O(^1D)$ with N_2O and the rate constant ratio k_{14}/k_{15} was found to be 0.59 ± 0.01.[12] Actually the spin conservation rules require that the O_2 product in reactions 12 and 14 be in a singlet state. However, there is no spectroscopic evidence to suggest that electronically excited O_2 is present in this system. If it is produced it must be deactivated before entering into chemical reactions different than those of ground state O_2.

The excited molecule $N_2(^3\Sigma)$ is deactivated by N_2O with a rate constant of 6×10^{-12} $cm^3/sec.$[4] A controversy exists concerning whether

quenching by N_2O does or does not dissociate the N_2O. For our purposes a non-dissociative quenching is equivalent to reaction 5 and need not be considered separately. Therefore it is only necessary for us to consider the step.

$$N_2(^3\Sigma) + N_2O \rightarrow 2N_2(^1\Sigma) + O(^3P) \qquad 16$$

Since the reaction of $O(^3P)$ with N_2O is immeasurably slow,[13] the fate of $O(^3P)$ is to produce O_2 and NO_2 via the reaction sequence

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad 17$$

$$O(^3P) + NO_2 \rightarrow NO + O_2 \qquad 18$$

As previously discussed the atoms $N(^2D)$ and $N(^4S)$ react respectively via

$$N(^2D) + N_2O \rightarrow N_2 + NO \qquad 9$$

$$N(^4S) + NO \rightarrow N_2 + O(^3P) \qquad 11$$

Determination of $\Phi\{O(^1D)\}$: The quantum yield of $O(^1D)$ production, $\Phi\{O(^1D)\}$, can be determined directly from the values of $\Phi_m\{O_2\}$ in pure N_2O and in the presence of a large excess of N_2. The presence of N_2 has no effect on $O(^1S)$, $N_2(^3\Sigma)$, or $N(^2D)$, as the rate constants for quenching of these species by N_2 are at least 500 times smaller than the respective quenching constants with N_2O.[9, 14] The ground state atoms $O(^3P)$ and $N(^4S)$ do not interact with N_2 at rates fast enough to be important in this system.[15] Therefore the only effect of adding N_2 is to quench $O(^1D)$[16]

$$N_2 + O(^1D) \rightarrow N_2 + O(^3P) \qquad 19$$

The addition of N_2 diminishes NO production, enhances O_2 production, and thus $\Phi_m\{O_2\}$ rises from 0.137 to about 0.375 as the $[N_2]/[N_2O]$ ratio is

raised from zero toward infinity. The data are plotted in Fig. 1. When $\Phi_m\{O_2\}$ is half way between its limits, or about 0.256, the rate of reaction 19 equals that of reactions 14 plus 15. This occurs when $[N_2]/[N_2O] \sim 2$ so that $(k_{14} + k_{15})/k_{19} \sim 2$, though this ratio might be as large as 4. This value is compared with that found by other investigations in Table V. Young et al.[17] report the ratio to be 3.6, while Preston and Cvetanović[18] found 4.2, and DeMore[19] obtained 5.2.

At the highest ratio of $[N_2]$ to $[N_2O]$ used in this study (i.e. 40), > 90% of the $O(^1D)$ atoms are quenched by N_2. Thus the limiting value of $\Phi_m\{O_2\}$ at high $[N_2]/[N_2O]$ might be expected to be slightly higher than the value of 0.375 observed. However in order to obtain enough product for significant measurements at these conditions, the conversion exceeded 1% and the reaction of $N(^2D)$ with NO should be significant as discussed earlier, thus tending to give larger values of $\Phi_m\{O_2\}$. The latter effect is more important than the former at the highest $[N_2]/[N_2O]$ ratios, and the value of 0.375 is too large. On the other hand, at $[N_2]/[N_2O]$ ratios of about 10, the percent conversion is about 0.2% and the results in Table I show that the latter effect is much less important than the fact that only about 80% of the $O(^1D)$ have been quenched. At this ratio $\Phi_m\{O_2\}$ was observed to be about 0.35, and this value must be less than the true limiting value at very large $[N_2]/[N_2O]$. Thus we conclude that the limiting value of the measured O_2 quantum yield, $\Phi_m^n\{O_2\}$, must be 0.365 ± 0.015.

The quantum yield of $O(^1D)$ production, $\Phi\{O(^1D)\}$, can be deduced to obey the relationship

$$\Phi\{O(^1D)\} = 2(\Phi_m^n\{O_2\} - \Phi_m^o\{O_2\})(k_{14} + k_{15})/(2k_{15} - k_{14}) \qquad d$$

TABLE V

Summary of Rate Constant Data at Room Temperature

Ratio	Value	Source
$(k_{14} + k_{15})/k_{19}$	2	Fig. 1
$(k_{14} + k_{15})/k_{19}$	3.6	Ref. 17
$(k_{14} + k_{15})/k_{19}$	4.2	Ref. 18
$(k_{14} + k_{15})/k_{19}$	5.2	Ref. 19
$k_{20}/(k_{12} + k_{13})$	$\sim$ 90	Fig. 2

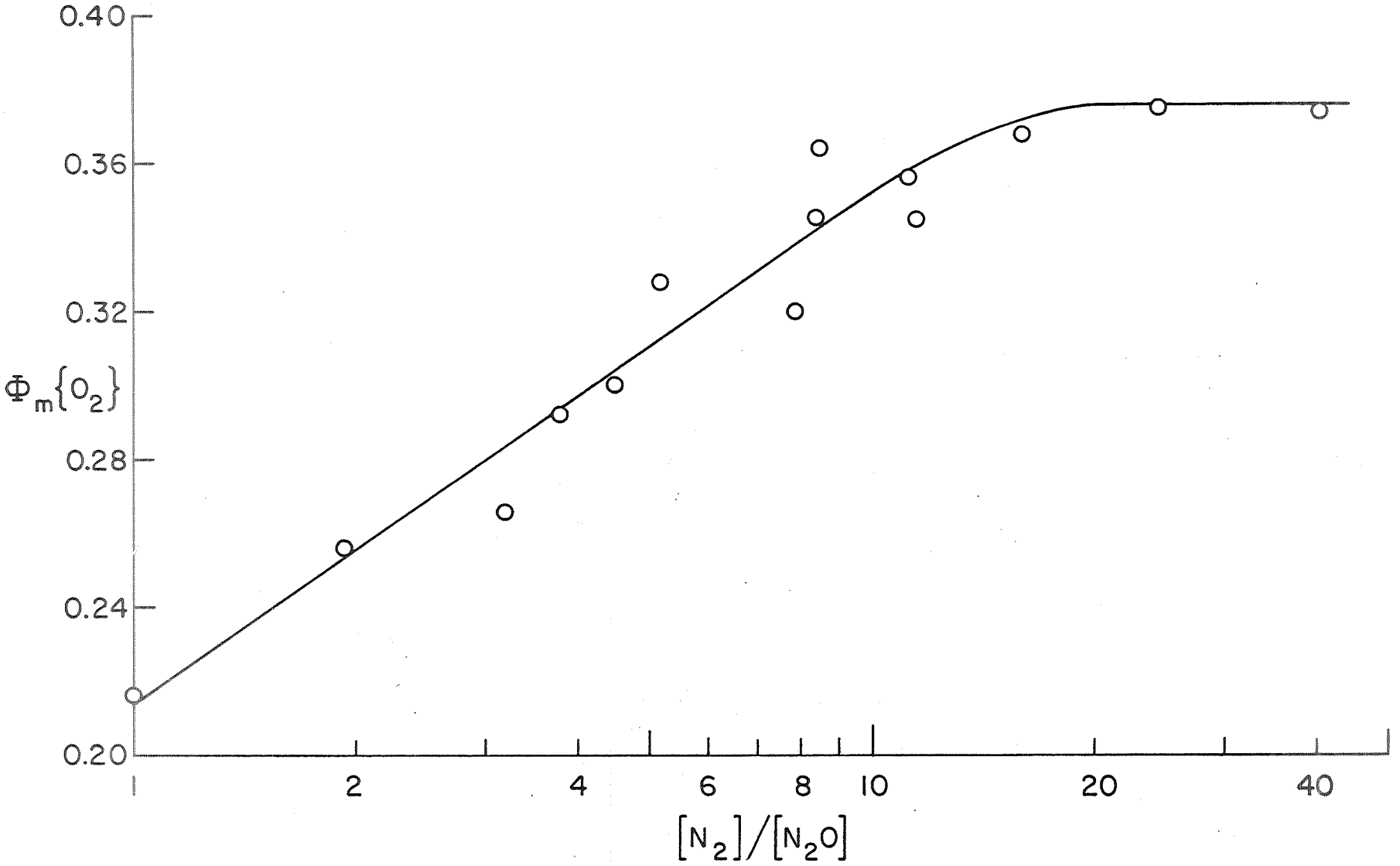

Figure 1 Plot of $\Phi_m\{O_2\}$ vs $[N_2]/[N_2O]$ in the photolysis of N_2O at 1470 A and room temperature in the presence of N_2.

where $\Phi_m^{\circ}\{O_2\}$ is the measured O_2 quantum yield in the absence of N_2, i.e., 0.137. Since k_{14}/k_{15} is accurately known to be 0.59,[12] $\Phi\{O(^1D)\}$ becomes 0.515 ± 0.04. This value is compared with that of Young et al.[4] in Table VI. Their value of 0.55 ± 0.03 agrees very well with our value. In both cases this value is the sum of the $O(^1D)$ produced directly in reaction 2 as well as any that may be produced in quenching $O(^1S)$ by N_2O.

Determination of $\Phi\{O(^3P)\}$: The total quamtum yield of $O(^3P)$ production, $\Phi\{O(^3P)\}$, can be obtained from the difference in $\Phi_m\{O_2\}$ in the absence and presence of C_3H_6. $\Phi\{O(^3P)\}$ includes the contribution to $O(^3P)$ production which may result from any process and is given by

$$\Phi\{O(^3P)\} = 2\Phi\{3\} + \Phi\{5\} + \Phi\{6\} \qquad e$$

where $\Phi\{3\}$, $\Phi\{5\}$, and $\Phi\{6\}$ are the quamtum yields of reactions 3, 5, and 6, respectively. Reaction 5 leads directly to $O(^3P)$. Reaction 6 also always produces $O(^3P)$ since $N(^4S)$ is always removed by reaction 11. Reaction 3 always produces two $O(^3P)$ atoms since reaction 3 only includes the $N_2(^3\Sigma)$ that is always removed via reaction 16. Any $N_2(^3\Sigma)$ that is quenched without dissociating N_2O is included as part of reaction 5. The other metastable states $O(^1S)$, $O(^1D)$, and $N(^2D)$ might also be deactivated to $O(^3P)$ (in the case of $N(^2D)$, deactivation to $N(^4S)$ is followed by reaction 11). Any fraction that is so deactivated is considered as if the excited precursor was never produced, and is therefore automatically included in reactions 5 and 6.

When C_3H_6 is added it might react with $N(^4S)$, $O(^3P)$, or any of the metastable species. The room-temperature rate constant for the reaction of $N(^4S)$ with C_3H_6 has been reported as 4.2×10^{-14} cm^3/sec

TABLE VI

Quantum Yields in N_2O Photolysis
at 1470A and Room Temperature

Φ	This work	Young et al. [4]
$O(^1D)$	0.515 ± 0.04 [a]	0.55 ± 0.03 [a]
$O(^3P)$	0.189 ± 0.012	-
$N_2(^3\Sigma)$	0.084 ± 0.02	0.08 ± 0.02
$\Phi\{5\} + \Phi\{6\}$	0.02 ± 0.02	0 [b]
$N(^2D)$	0.245 ± 0.06 [c]	~ 0.1 [b]
$O(^1S)$	0.135 ± 0.06 [c, d]	0.5 ± 0.1

a) Includes the $O(^1D)$ produced directly in a primary process as well as from deactivation of $O(^1S)$.

b) Assumed

c) Assumed $k_{12}/(k_{12} + k_{13}) \sim 1.0$.

d) Includes only that fraction of $O(^1S)$ which is not deactivated by N_2O to $O(^1D)$.

by Madhavan and Jones[20] and 1.5×10^{-14} cm^3/sec by Herron.[21] The rate constant k_{11} for the reaction $N(^4S)$ with NO is 2.2×10^{-11} cm^3/sec,[15] or at least 500 times larger than the rate constant for the $N(^4S) + C_3H_6$ reaction. For all of our experiments with added C_3H_6, the amount of NO at the end of a run exceeded 10% of the initial C_3H_6 pressure, and usually was about 30-50% of the initial C_3H_6 pressure. Consequently the reaction of $N(^4S)$ with C_3H_6 is unimportant and can be ignored.

With $O(^3P)$, exactly the opposite situation exists. The rate constant for the $O(^3P)$ reaction with C_3H_6 is 4.0×10^{-12} cm^3/sec,[11] whereas that for the reaction with NO, reaction 17, is 1.0×10^{-31} cm^6/sec with N_2 as a chaperone.[15] With N_2O as a chaperone the rate constant may be somewhat larger. However even at the most extreme conditions (large N_2O pressures and high $[NO]/[C_3H_6]$ ratios) used in this study, $O(^3P)$ is almost exclusively removed by C_3H_6.

The rate constants for the removal of the metastable species by N_2O are 1.6×10^{-11}, 2×10^{-10}, 6×10^{-12}, and 3×10^{-12} cm^3/sec for $O(^1S)$, $O(^1D)$, $N_2(^3\Sigma)$, and $N(^2D)$, respectively.[4,9] The rate constants for removal of these species by C_3H_6 are not known. However, they cannot exceed 10^{-9} cm^3/sec which corresponds to collision frequency. Thus at $[N_2O]/[C_3H_6]$ ratios of about 1000, removal by C_3H_6 should be unimportant. Table IV shows that $\Phi_m\{O_2\}$ rises with the ratio to a limiting value of 0.0426 ± 0.001 at ratios in excess of 240. Under these conditions the sole effect of C_3H_6 is to scavenge $O(^3P)$ atoms. Therefore $\Phi\{O(^3P)\}$ can be computed to be 0.189 ± 0.012 from the expression

$$\Phi\{O(^3P)\} = 2(\Phi_m{}^{O}\{O_2\} - \Phi_m{}^{P}\{O_2\}) \qquad f$$

where $\Phi_m^{\circ}\{O_2\}$ is the measured quantum yield of O_2 in the absence of C_3H_6 (i.e. 0.137) and $\Phi_m^{P}\{O_2\}$ is the measured quantum yield of O_2 production at $[N_2O]/[C_3H_6]$ ratios between 240 and 1220 (i.e. 0.0426).

The rate constant for quenching of metastables by C_3H_6 can be estimated from the fall-off in $\Phi\{N_2\}$ as $[N_2O]/[C_3H_6]$ is reduced. Figure 2 is a plot of this fall-off. At $[N_2O]/[C_3H_6] = 30$, $\Phi\{N_2\}$ has dropped to unity. Actually about 10 percent of the radiation has been absorbed by C_3H_6, so that $\Phi\{N_2\}$ is in fact about 1.1. Only about 25 percent of the $O(^1D)$ has been quenched by C_3H_6[12] so that the fall-off in $\Phi\{N_2\}$ is due to scavenging of the other metastables by C_3H_6. Since $O(^1S)$ is the most important of these species, its relative rate constant of removal is given approximately by the $[N_2O]/[C_3H_6]$ ratio when the fall-off is about 1/2 the full value. Thus $k_{20}/(k_{12} + k_{13})$ is about 90 where reaction 20 is

$$O(^1S) + C_3H_6 \rightarrow \text{removal of } O(^1S) \qquad 20$$

The value of about 90 for the ratio is similar to the value of 87 obtained by Filseth et al.[22] and ~150 obtained by Young et al[23] for the relative rates of C_2H_4 and N_2O in scavenging $O(^1S)$.

Determination of $\Phi\{N_2(^3\Sigma)\}$: The metastable state $N_2(^3\Sigma)$ is produced in reaction 3. Our computation for $\Phi\{N_2(^3\Sigma)\}$ emcompasses only that part of $N_2(^3\Sigma)$ which dissociates N_2O, any other fraction being equivalent to $N_2(^1\Sigma)$ production. $\Phi\{N_2(^3\Sigma)\}$ can be computed from the results of the photolysis of pure N_2O. The quantum yields for product formation are

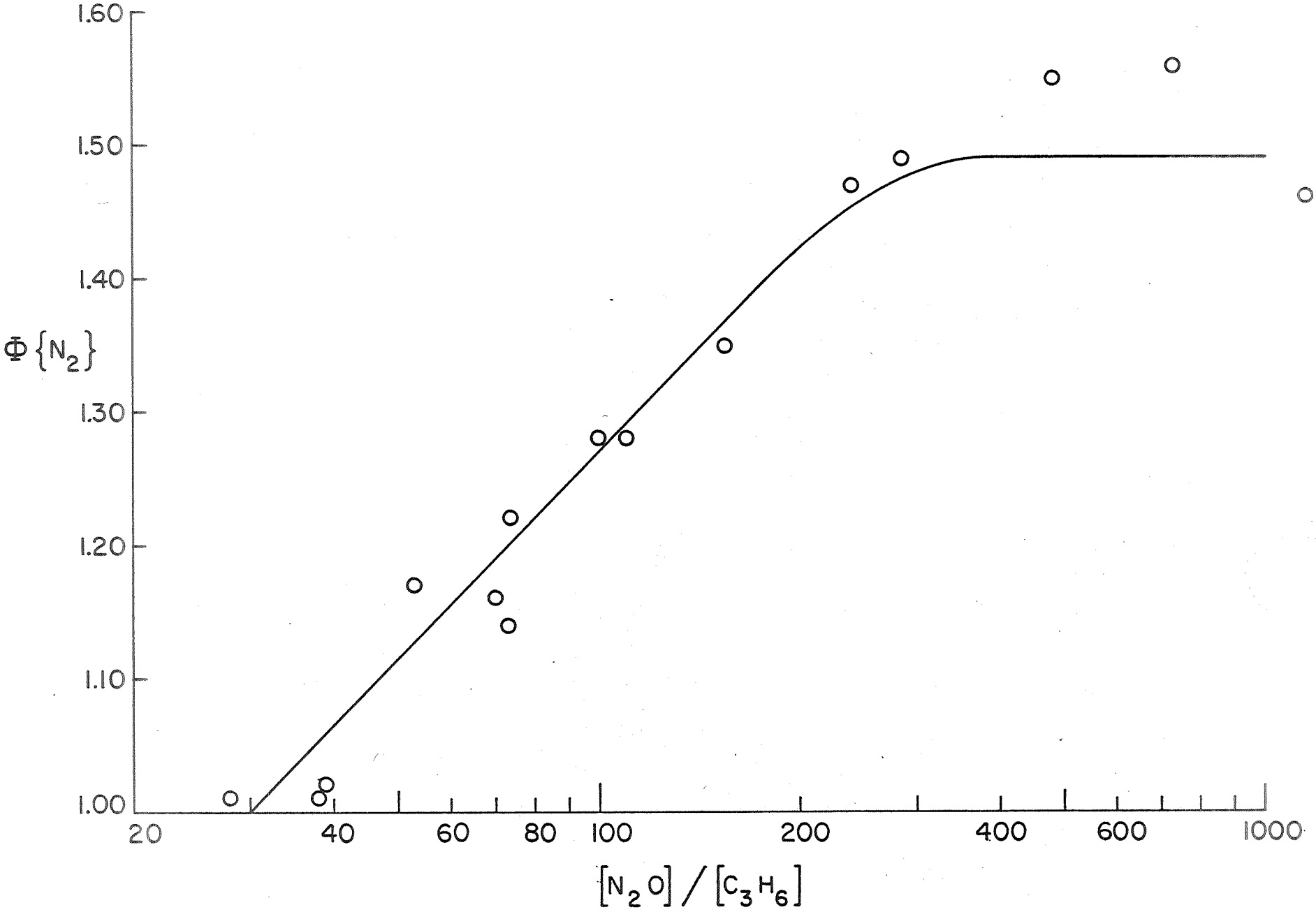

Figure 2 Plot of $\Phi\{N_2\}$ vs $[N_2O]/[C_3H_6]$ in the photolysis of N_2O at 1470 A and room temperature in the presence of C_3H_6.

$$\Phi\{N_2\} - 1 = \Phi\{O(^1S)\}k_{12}/(k_{12}+k_{13}) + \Phi\{O(^1D)\}k_{14}/(k_{14}+k_{15}) + \Phi\{N_2(^3\Sigma)\} \quad g$$

$$\Phi\{O_2\} + (1/2)\Phi\{NO_2\} = \Phi\{O(^1S)\}k_{12}/(k_{12}+k_{13}) + \Phi\{O(^1D)\}k_{14}/(k_{14}+k_{15})$$

$$+ (1/2)\,\Phi\{O(^3P)\} \quad h$$

Combining equations c, g, and h yields

$$\Phi\{N_2(^3\Sigma)\} = (3/4)\Phi\{N_2\} + (1/2)\Phi\{O(^3P)\} - (1/2)\,\Phi_m\{O_2\} - 1 \quad i$$

With the values of 1.41, 0.189, and 0.137, respectively, for $\Phi\{N_2\}$, $\Phi\{O(^3P)\}$, and $\Phi_m\{O_2\}$, $\Phi\{N_2(^3\Sigma)\}$ becomes 0.084. The experimental uncertainty in this number is ± 0.004 plus three quarters of the uncertainty in $\Phi\{N_2\}$. The uncertainty in $\Phi\{N_2\}$ is probably about 0.02 when all the separate investigations are combined. Thus we deduce that $\Phi\{N_2(^3\Sigma)\} = 0.084 \pm 0.02$ in excellent agreement with the value of 0.08 ± 0.02 found by Young et al.[4]

The above result when combined with eqn. e leads to the conclusion that $\Phi\{5\} + \Phi\{6\} = 0.02 \pm 0.02$. Thus the spin-forbidden processes are unimportant. Furthermore it follows that $O(^1S)$ and $O(^1D)$ are not deactivated by N_2O to $O(^3P)$, that $N(^2D)$ is not deactivated by N_2O to $N(^4S)$, and that $N_2(^3\Sigma)$ deactivation by N_2O results in the dissociation of N_2O at least 80% of the time. This conclusion is at variance with earlier findings that active nitrogen did not dissociate N_2O.[6-8] However Campbell and Thrush[24] have argued that the amount of decomposition expected would not have been detected. In a later paper[25] they have shown that $N_2(^3\Sigma)$ efficiently dissociates N_2O. Further support for this conclusion is given by Stedman et al.[26]

Young et al.[4] also concluded that $N_2(^3\Sigma)$ did not dissociate N_2O. This conclusion was based on the invariance of $\Phi\{O(^3P)\}$ when $N_2(^3\Sigma)$ was deactivated by N_2O and NO in two separate experiments. However the $NO(A^2\Sigma)$ produced from the quenching of $N_2(^3\Sigma)$ could have dissociated the N_2O, thus giving the same yield for $O(^3P)$ in both experiments.

Determination of $\Phi\{N(^2D)\}$ and $\Phi\{O(^1S)\}$: Since $\Phi\{2\} + \Phi\{3\} + \Phi\{5\} + \Phi\{6\} = 0.62$, then by difference $\Phi\{N(^2D)\} + \Phi\{O(^1S)\} = 0.38 \pm 0.06$, where our value of $\Phi\{O(^1S)\}$ includes only that fraction not deactivated by N_2O to $O(^1D)$. Doering and Mahan[6] found that about 5% of the N_2 produced in the photolysis of $^{15}N^{14}NO$ was $^{30}N_2$. With about 1% ^{15}NO added, this value increased to about 8% at short conversions. Furthermore the photolysis of $^{14}N^{15}NO$ in the presence of about 1% ^{15}NO gave about 3% $^{15}N_2$ at low conversions. From these results it can be concluded that at least 10% of the N_2 produced came from nitrogen atoms. Because the amount of $N(^4S)$ produced is negligible, this value corresponds entirely to $N(^2D)$ production. Since $k_{10}/k_9 = 60$ only about 1/3 of the $N(^2D)$ is reacting with NO and about 2/3 with N_2O for $[NO]/[N_2O] = 0.01$. The reaction of ^{15}N with either $^{15}N^{14}NO$ or $^{14}N^{15}NO$ can lead to $^{29}N_2$, so that considerably more than 10% of the N_2 could come from $N(^2D)$, and $\Phi\{N(^2D)\}$ should be about 0.2 - 0.3.

The value of $\Phi\{O(^1S)\}$ can be evaluated from either equation g or h if $k_{12}/(k_{12} + k_{13})$ is known. There is no experimental measurement of this ratio but Donovan and Husain[27] have pointed out that the only adiabatic path to products leads to $N_2 + O_2$ so that $k_{12}/(k_{12} + k_{13})$ should be close to unity. Since $k_{12}/(k_{12} + k_{13})$ cannot exceed one, the

assumption that it is one leads to the minimum value for $\Phi\{O(^1S)\}$. This value is 0.135 ± 0.06. By difference $\Phi\{N(^2D)\}$ becomes 0.245 ± 0.06. The difference between our value and that of Young et al.[4] for $\Phi\{O(^1S)\}$ corresponds to the portion deactivated by N_2O to $O(^1D)$.

REFERENCES

1. M. Zelikoff and L.M. Aschenbrand, J. Chem. Phys., 22, 1680 (1954).
2. W. E. Groth and H. Schierholz, Planet. Space Sci., 1, 333 (1959).
3. J. Y. Yang and F. M. Servedio, J. Chem. Phys., 47, 4817 (1967).
4. R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys., 49, 4769 (1968).
5. B. H. Mahan, J. Chem. Phys., 33, 959 (1960).
6. J. P. Doering and B. H. Mahan, J. Chem. Phys., 36, 1682 (1962).
7. G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys., 27, 1141 (1957).
8. F. Kaufman and J. R. Kelso, J. Chem. Phys., 28, 510 (1958).
9. G. Black, T. G. Slanger, G.A. St. John, and R. A. Young, J. Chem. Phys., 51, 116 (1969).
10. J. R. McNesbey and H. Okabe, Adv. Photochem., 3, 157 (1964).
11. R. J. Cvetanović, Adv. Photochem., 1, 115 (1963).
12. R. Greenberg and J. Heicklen, Int. J. Chem. Kinetics, 2, in press (1970).
13. F. Kaufman, Prog. Reaction Kinetics, 1, 1 (1961).
14. E. C. Zipf, Canad. J. Chem., 47, 1863 (1969).
15. DASA Reaction Rate Handbook (1967).
16. G. Paraskevopoulos and R. J. Cvetanović, J. Am. Chem. Soc., 91, 7572 (1969).
17. R. A. Young, G. Black and T. G. Slanger, J. Chem. Phys., 49, 4758 (1968).
18. K. F. Preston and R. J. Cvetanović, J. Chem. Phys., 45, 2888 (1966).
19. W. B. DeMore, J. Chem. Phys., 52, 4309 (1970).
20. N. Madhavan and W. E. Jones, J. Phys. Chem., 72, 1812 (1968).
21. J. Herron, J. Phys. Chem., 72, 2538 (1968).

22. S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys., 52, 239 (1970).

23. R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys., 50, 309 (1969).

24. I. M. Campbell and B. A. Thrush, Trans. Farad. Soc., 62, 3366 (1966).

25. I. M. Campbell and B. A. Thrush, Trans. Farad. Soc., 64, 1275 (1968).

26. D. D. Stedman, J. A. Meyer, and D. W. Setser, J. Am. Chem. Soc., 90, 6856 (1968).

27. R. J. Donovan and D. Husain, Chem. Rev., 70, 489 (1970).