The Mercury-Sensitized Photodecomposition of Nitrous Oxide in the

Presence of Mixtures of Carbon Monoxide and Methane

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The mercury-photosensitized decomposition of N_2O in the presence of $CO-CH_4$ mixtures was studied at 548°K. From the competition between CO and CH_4 for $O(^3P)$, the ratio k_1/k_2 was found to be 2.0, where the reactions are (1) $O(^3P) + CO \rightarrow CO_2$ and (2) $O(^3P) + CH_4 \rightarrow CH_3 + HO$. Reaction 1 is second order at the pressures used in this study (>250 Torr, mainly N_2O). Furthermore, the HO radical produced in reaction 2 can react with either CO (HO + CO → H + CO_2, reaction 3) or CH_4 (HO + CH_4 → H_2O + CH_3, reaction 4). An approximate value of $k_4/k_3 = 1.0$ was obtained. A reexamination of the determination of k_2 suggests that its value at 548°K is about one-tenth as large as previously reported. In runs in the absence of CO or CH_4, the $O(^3P)$ produced in the primary process appears as O_2, but there is a noticeable induction period in O_2 formation. Experiments with added CH_4 have established that the oxygen atoms are efficiently adsorbed by the wall of the quartz reaction vessel. Thus because of the inhomogeneity of the light absorption, $O(^3P)$ atoms can be removed by the walls even in the presence of an $O(^3P)$ scavenger. Furthermore, results with two different mercury resonance lamps are quantitatively different, because of the difference in pressure broadening of the incident radiation.

Introduction

Recently[1] we have examined the reaction of $O(^3P)$

$$O(^3P) + CO \longrightarrow CO_2 \qquad (1)$$
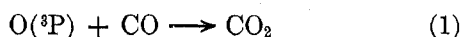
with CO at 298–472°K by studying the competition between CO and 2-trifluoromethylpropene for oxygen atoms produced in the mercury-photosensitized decomposition of N_2O. We found this reaction to be intermediate between second and third order at pressures of 200–800 Torr with N_2O as the principal gas. Furthermore, at any pressure the reaction became more second order as the temperature was raised. The limiting low- and high-pressure rate constants were found to fit the expressions $k_0 = 1.29 \times 10^9 \exp(-4070/RT)$ M^{-2} sec^{-1} and $k_\infty = 3.40 \times 10^6 \exp(-2930/RT)$ M^{-1} sec^{-1}.

In view of the unusual behavior found for the rate constant and the discrepancies found in the literature[2,3] with regard to the rate constant and the order of the reaction, it seemed appropriate to examine reaction 1 in a different system. In this paper the same technique for generating oxygen atoms is used at 548°K, but the competing gas was CH_4 rather than 2-trifluoromethylpropene, so that reaction 1 was studied in competition with reaction 2

$$O(^3P) + CH_4 \longrightarrow HO + CH_3 \qquad (2)$$

Since HO radicals are produced in reaction 2, it was

hoped that, in addition to obtaining k_1/k_2, it also would be possible to measure k_3/k_4

$$HO + CO \longrightarrow H + CO_2 \qquad (3)$$

$$HO + CH_4 \longrightarrow H_2O + CH_3 \qquad (4)$$
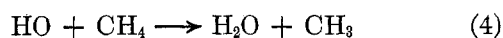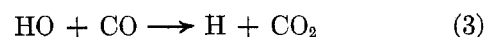
Measuring the competition between reactions 3 and 4 is difficult because reaction 1 produces CO_2 which complicates the analysis of the data. Nevertheless, an estimate for k_3/k_4 could be made.

As the study was in progress, it became apparent that some of the oxygen atoms were being removed by a reaction other than reaction 2. Thus it was necessary to study this route of oxygen atom disappearance. This was done in several series of runs with CO absent, and those results are also reported here.

Experimental Section

Most of the experiments utilized conventional static photochemical techniques. Matheson CP grade N_2O was purified in several ways. For some runs the N_2O was passed over ascarite and degassed at −196°. In other runs the N_2O was distilled at −160°, and the

(1) R. Simonaitis and J. Heicklen, *J. Chem. Phys.*, in press.

(2) D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, "High Temperature Reaction Rate Data," No. 1, Department of Physical Chemistry, Leeds University, 1968.

(3) N. Cohen and J. Heicklen, "Comprehensive Chemical Kinetics," C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, to be published in Vol. 6.

middle fraction was used. A third procedure was to preirradiate N_2O–Hg mixtures and then to degas at $-196°$. All three methods of purification gave N_2O free of impurities (<10 ppm) as determined by both gas chromatography and mass spectrometry. Specifically NO, O_2, N_2, and hydrocarbons were absent. Furthermore, the photochemical results were the same regardless of the methods of purification, except with N_2O alone at 275°. For these runs a different cylinder of N_2O was used, and the oxygen quantum yields were lower if the N_2O was distilled at $-160°$ to remove any NO_2.

Matheson "ultrapure" methane was purified by repeated degassing at $-196°$ and distillation at $-186°$. The remaining impurities were N_2 (100 ppm), O_2 (<10 ppm), and C_2H_6 (<20 ppm). At high pressures of CH_4 a small correction for the presence of these impurities was made. However, for most runs the correction was negligible.

Matheson CP grade CO was purified by passage over glass beads at $-196°$, degassing at $-196°$, and distillation from liquid argon. The O_2 impurity was reduced to <10 ppm, but 190 ppm N_2 remained.

The reactants were saturated with mercury vapor before being mixed in the reaction vessel which was a cylindrical quartz cell 5 cm in diameter and 10 cm long. The reaction vessel was jacketed in a wire-wound aluminum furnace with quartz windows. Irradiation was from a Hanovia flat-spiral, low-pressure mercury resonance lamp. The radiation passed through a Corning 9-54 filter before entering the reaction cell to remove all radiation below 2200 Å. For some runs without CO present, a North American Phillips Model 93109E low-pressure mercury resonance lamp was used.

After irradiation the cell contents were condensed in a trap at $-196°$. The noncondensables (N_2, H_2, CO, and O_2) were collected in a Toepler pump and analyzed for N_2 and O_2 by gas chromatography using a 0.25-in. diameter by 10-ft long 5A molecular sieve column operating at 25°. Corrections for background N_2 were made in computing the rate of N_2 formation, $R\{N_2\}$. The fraction condensable at $-196°$ was analyzed for C_2H_6 and CO_2 on a 0.25-in. diameter by 20-ft long Porapak Q column at 25°.

Some experiments were done using electron paramagnetic resonance spectroscopy to follow continuously the rate of production of O_2 in situ in the mercury-sensitized decomposition of N_2O alone. The 25-cc photolysis cell used consisted of a length of Suprasil quartz tubing placed in the X-band cavity of a Varian 4502 epr spectrometer and extending about 15 cm below it. A 50-W spiral low-pressure mercury lamp, obtained from Ultra-violet Products, Inc., was placed around the extension immediately below the cavity. A Corning 7-54 filter could be inserted between the quartz tubular cell and the spiral lamp to eliminate the 1849-Å mercury spectral line.

Results

CO Absent. Initially, the mercury-sensitized photodecomposition of 100 Torr N_2O at 23° was studied as a function of irradiation time. The results are listed in Table I for N_2 and O_2 productions. Since $\Phi\{N_2\} = 1.00$, the ratio of O_2 to N_2 is $\Phi\{O_2\}$.

Table I: Effect of Irradiation Time on the Mercury-Photosensitized Decomposition of N_2O

Irradiation time, min	$10^8 \times R\{N_2\}$, mol/l. sec	$\Phi\{O_2\}$
$T = 23°$, $[N_2O] = 100$ Torr, Phillips 93109E Lamp		
60.0	0.108	0.200
63.0	0.127	0.236
64.0	0.117	0.254
180.0	0.115	0.339
398.0	0.152	0.414
600.0	0.118	0.337
1200.0	0.064	0.221
$T = 275°$, $[N_2O] = 53$ Torr, Hanovia Lamp		
33.0	0.42	0.038
210.0	0.64	0.20

The irradiation time was varied from 60 to 1200 min. For about 600 min the rate of N_2 production, $R\{N_2\}$, was nearly constant, where $R\{N_2\}$ is computed as the N_2 produced divided by the irradiation time. For 1200-min exposure, $R\{N_2\}$ dropped noticeably indicating that HgO was formed, which inhibited the reaction. The production of HgO in the later part of the reaction is attributed to the sequence of steps

$$O + O_2 + M \longrightarrow O_3 + M$$

$$O_3 + Hg \longrightarrow HgO + O_2$$
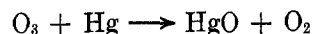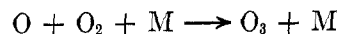
The measured quantum yield of O_2 formation is very much less than 0.5 for short irradiation times and increases with exposure time, reaching a maximum value of about 0.42 for about 400-min exposure. Further irradiation decreases the yield. Our peak value of $\Phi\{O_2\} \simeq 0.42$ occurs for a total N_2 production of 36 μmol/l. Cvetanović[4] obtained $\Phi\{O_2\} = 0.47$ for a total N_2 production of 6-50 μmol/l. Our results compare favorably even though Cvetanović's intensity was about five to ten times ours. The falloff of $\Phi\{O_2\}$ as the irradiation time increases is due to the O_2 consumption via the above reactions. The low values for $\Phi\{O_2\}$ at short exposures were unexpected and indicate that some of the oxygen atoms have formed products other than O_2.

At 275°, the induction period in oxygen formation is even more pronounced. For the 210-min run almost 1 Torr of oxygen atoms is missing.

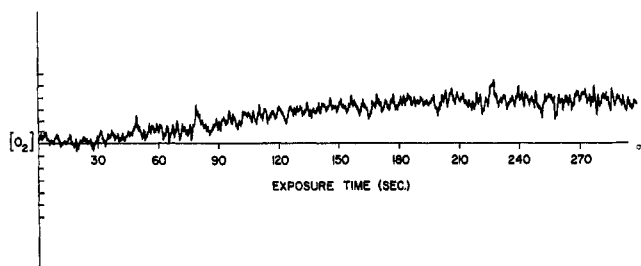(4) R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1203 (1955).

Figure 1. Plot of $[O_2]$ vs. time as obtained by epr spectroscopy during the mercury-sensitized photolysis of 20 Torr N_2O at 25°. The intensity of the $K = 11$, $J = 12 \rightarrow 10$, $M_s = -2 \rightarrow -1$ transition of O_2 was monitored. This transition occurred at a magnetic field of 5961.4 G with a klystron frequency of 9208.5 MHz.

To check the induction period in O_2 formation, epr experiments were done so that O_2 could be monitored continuously. The $K = 11$, $J = 12 \rightarrow 10$, $M_s = -2 \rightarrow -1$ transition at X-band frequencies is useful for this type of experiment. The cell was filled with 20 Torr N_2O and irradiated in the absence of mercury vapor and with no filter. Under these conditions the direct photolysis of N_2O produces $O(^1D)$ which reacts with N_2O and produces O_2 instantaneously; the epr signal appears with no delay. With the filter in place O_2 is not detected.
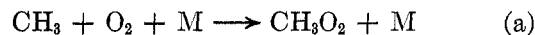
When the cell is filled with 20 Torr N_2O and allowed to stand overnight over a small amount of mercury, the spectrum of O_2 appears with an induction period upon irradiation with filtered light from the spiral lamp. The curve of growth is shown in Figure 1. After a 30-sec induction period the O_2 grows at a rate of 2.34×10^{-8} mol/l. sec until it levels off and reaches a constant value of 3.5 μmol/l. The limiting value can be attributed to HgO formation which was observed on the surface of the mercury pool at the bottom of the cell. The induction period represents a loss of 1.4 μmol/l. or 26 μ of oxygen atoms.

We looked for the epr signal due to NO with no success. However, the epr spectrum of O_2 is so intense in the region where the NO transitions are expected to occur that they may be obscured. This problem could be circumvented by using a cavity with a Stark modulation system rather than Zeeman modulation. A search for the signal due to $O(^3P_2)$ yielded negative results, thus indicating a steady-state pressure of $O(^3P_2)$ of $\leq 1 \mu$.

Table II shows the results of the mercury-photosensitized decomposition of N_2O at 275° in the presence of CH_4. The products measured were C_2H_6, CO_2, and CO. No oxygen was found. Methane is very much less efficient than N_2O in scavenging $Hg(6^3P_1)$.[5a] However to be certain that $\Phi\{N_2\}$ remained 1.00 in the presence of CH_4, a few runs were done with a few Torr of C_3H_6 present (to scavenge the oxygen atoms) with CH_4 both present and absent. The rate of N_2 formation was unaffected. In the $N_2O–CH_4$ system the oxygen atom can react with CH_4 leading to

$$O + CH_4 \longrightarrow CH_3 + OH \qquad (2)$$

$$OH + CH_4 \longrightarrow H_2O + CH_3 \qquad (4)$$
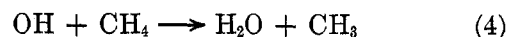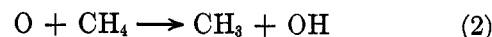
If any O_2 is produced, it is scavenged by CH_3

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \qquad (a)$$

$$CH_3O_2 + CH_4 \longrightarrow CH_3O_2H + CH_3 \qquad (b)$$

An alternate fate of CH_3O_2 could be self-annihilation. However, since its rate constant[5b] is about 10^{10} M^{-1} sec^{-1}, this reaction will be unimportant in our system if $k_b > 10^2$ M^{-1} sec^{-1}. Our results are consistent with this hypothesis. The CH_3OOH presumably decomposes to H_2O and CH_2O, the latter being further oxidized to CO and CO_2. Thus, for every oxygen atom reacting with CH_4, one molecule of C_2H_6 is produced.

The ethane yield, $\Phi\{C_2H_6\}$, increases from 0.12 to 0.57 as the CH_4 pressure is raised from 5 to 99 Torr. However, $\Phi\{C_2H_6\}$ is almost independent of a 30-fold change in N_2O pressure or a 300-fold change in $R\{N_2\}$ (i.e., the absorbed intensity, I_a).

Most of the runs were done for similar conversions. However, two runs were done at greatly reduced conversions (the 2- and 10-min runs). $\Phi\{C_2H_6\}$ decreased from 0.35 to 0.22 as the irradiation time increased from 2 to 66 min for otherwise identical runs. The reason for the drop may be that at longer conversions more O_2 is produced which enhances reaction a and thus leads to some loss of CH_3 via reaction a followed by self-annihilation of CH_3O_2. However, the drop in $\Phi\{C_2H_6\}$ is not very pronounced considering the 33-fold variation in extent of conversion. At any rate, all the other runs are for similar conversions and should be directly comparable.

The effect of conversion was further checked under other conditions. These results are shown in Table III. A ninefold variation in the extent of conversion had no noticeable effect on $\Phi\{C_2H_6\}$.

Another series of runs was made to test the effect of N_2O pressure and these results are shown in Table IV. Contrary to the results in Table II where the N_2O pressure had almost no effect, the results in Table IV show that $\Phi\{C_2H_6\}$ noticeably drops as $[N_2O]$ increases. The effect is more pronounced with 9.8 Torr CH_4 than with 110 Torr CH_4. However, even in the former case, the effect is much less than linear, a 35-fold increase in $[N_2O]$ gives only a 4.3-fold drop in $\Phi\{C_2H_6\}$. The difference between the two sets of experiment listed in Tables II and IV is that two different types of mercury resonance lamp were used. These results were carefully checked, and the different results caused by the two types of lamps are real.

Table V contains another set of experiments illustrating that $\Phi\{C_2H_6\}$ increases with $[CH_4]$. $\Phi\{C_2H_6\}$

(5) (a) R. J. Cvetanović, Progr. React. Kinet., 2, 39 (1964); (b) J. Heicklen, Advan. Chem. Ser., No. 76, 23 (1968).

Table II: Mercury-Photosensitized Decomposition of N_2O-CH_4 Mixtures at 275° with a Hanovia Flat-Spiral, Low-Pressure Mercury Resonance Lamp

[N₂O], Torr	[CH₄], Torr	Irradiation time, min	$10^8 \times R\{N_2\}$, mol/l. sec	$\Phi\{C_2H_6\}$	$\Phi\{CO_2\}$	$\Phi\{CO\}$
30.0ᵃ	5.00	65.00	0.50	0.120	...	0.165
615	5.00	65.00	0.55	0.103	0.068	...
32.0	5.05	66.00	0.43	0.128	0.080	0.118
610	5.10	65.00	0.57	0.080	...	...
30.0	5.90	4.00	6.5	0.133	0.043	...
600	9.80	1010.00	0.041	0.204	...	...
660	9.80	4.00	9.9	0.089	...	...
20.0	10.0	65.00	0.43	0.217	...	...
615	10.0	65.00	0.58	0.165	...	...
635	10.0	65.00	0.57	0.160	0.050	0.124
220	10.1	65.00	0.58	0.202	0.033	...
22.0	10.1	66.00	0.43	0.224	0.065	...
22.3	10.2	10.00	0.44	0.27	...	...
22.3	10.2	2.00	0.44	0.35	...	...
614	13.5	65.00	0.56	0.213	0.045	0.119
642	23.0	4.00	8.4	0.214	...	...
630	25.0	840.00	0.032	0.262	0.146	0.042
604	56.0	4.00	9.9	0.37	0.028	...
540	99.0	65.00	0.56	0.57	0.027	...

ᵃ 390 Torr CF_4 also present.

Table III: Effect of Irradiation Time on the Mercury-Photosensitized Decomposition of N_2O-CH_4 Mixtures at 275°; Phillips 93109E Lamp

[N₂O], Torr	[CH₄], Torr	Irradiation time, min	$10^8 \times R\{N_2\}$, mol/l. sec	$\Phi\{C_2H_6\}$	$\Phi\{CO_2\}$
100	102	12.0	0.326	0.61	...
97	103	14.0	0.348	0.54	0.025
100	100	30.0	0.346	0.59	0.014
100	97	81.0	0.286	0.63	0.012
100	98	155.0	0.224	0.61	0.011

Table IV: Effect of N_2O Pressure on the Mercury-Photosensitized Decomposition of N_2O-CH_4 Mixtures at 275°; Phillips 93109E Lamp

[N₂O], Torr	$10^8 \times R\{N_2\}$, mol/l. sec	$\Phi\{C_2H_6\}$	$\Phi\{CO_2\}$
[CH₄] = 110 ± 10 Torr, Irradiation Time = 30 min
13.5	0.195	0.81	0.17
17	0.214	0.82	0.025
30	0.214	0.85	0.12
100	0.347	0.60	0.014
112	0.337	0.67	0.011
117	0.325	0.61	0.011
244	0.438	0.62	...
[CH₄] = 9.8 ± 0.2 Torr, Irradiation Time = 60 min
13.0	0.063	0.57	...
54.0	0.172	0.33	...
123	0.235	0.25	...
228	0.302	0.198	...
310	0.34	0.193	...
460	0.47	0.132	...

Table V: Effect of CH_4 Pressure on the Mercury-Photosensitized Decomposition of N_2O-CH_4 Mixtures at 275°; Phillips 93109E Lamp

[N₂O], Torr	[CH₄], Torr	Irradiation time, min	$10^8 \times R\{N_2\}$, mol/l. sec	$\Phi\{C_2H_6\}$	$\Phi\{CO_2\}$
80	5.0	15.0	0.393	0.062	...
75	5.5	30.0	0.426	0.060	...
54	9.8	60.0	0.172	0.295	...
42	13.0	64.0	0.180	0.39	...
31	19	30.0	...	0.23	...
45	23.0	60.0	0.146	0.51	...
27	29	30.0	...	0.30	...
60	36	30.5	0.390	0.44	...
80	62	30.0	0.344	0.60	...
100	100	870.0	0.0087	0.49	0.002
100	100	1080.0	0.0096	0.47	0.037
45	112	30.0	0.271	0.64	...
51	316	30.0	0.366	0.79	0.012
57	354	30.0	0.406	0.80	0.009
53	374	30.0	0.424	0.68	0.008
51	434	30.0	0.424	0.87	0.009

increases from 0.06 to 0.87 as [CH₄] is raised from 5.0 to 434 Torr.

CO Present. When the mercury-photosensitized decomposition of N_2O is studied in the presence of mixtures of CO and CH_4 at 548°K, the products of the reaction are N_2, C_2H_6, CO_2, H_2, and presumably H_2O. The first four products were found, but no effort was made to find H_2O. Oxygen was not produced under our reaction conditions.

The present study was complicated by the occurrence of a heterogeneous dark reaction between N_2O and CO

to give CO_2 and N_2 at high pressures of CO. It was also observed that this dark reaction became more important as the cell aged. Therefore, the rates of formation of CO_2 and N_2 were not useful at high CO pressures. Actinometry had to be done in separate runs in which CO was not present. For the experiments at low pressures of CO, which were also the first to be performed, the dark reaction was negligible. This dark reaction also became more important as the temperature was raised above 548°K, thus prohibiting us from performing experiments at more elevated temperatures.

A further complication was the disappearance of H_2 in the dark. Over a period of 1-2 hr 30-50% of a known amount of H_2 (~30 μ) introduced into the cell in the presence of reactants at 548°K disappeared; over a period of 12 hr, all the H_2 vanished. Thus the rate of H_2 formation could not be measured reliably. Fortunately C_2H_6 is unaffected in the dark in the presence of the reactants at 548°K.

The best regime to study the competition between reactions 1 and 2 is at high [CO]/[CH₄] where the quantum yield of ethane formation, $\Phi\{C_2H_6\}$, is small (see Discussion). Results of experiments at high [CO]/[CH₄] at 548°K with two different radiation sources are given in Table VI. For the runs with CO present, the CO pressure was varied from 7.6 to 204 Torr; the CH₄ pressure, from 4.80 to 182 Torr; and the N_2O pressure, from 146 to 652 Torr. In all the runs the relative amounts of N_2O, CH₄, and CO were such that at least 90% of the excited mercury atoms were scavenged by N_2O as computed from the known quenching constants.[5a] The ratio [CO]/[CH₄] ranged from 0.084 to 20; $\Phi\{C_2H_6\}$ dropped regularly as the ratio was raised and was reduced to 0.020 at the highest ratio. Two runs were done with the intensity reduced by a factor of 47, and $\Phi\{C_2H_6\}$ was only slightly altered.

At lower ratios of [CO] to [CH₄], the relative importance of reaction 1 compared to reaction 2 is reduced, and the competition between reactions 3 and 4 can be studied. Results at reduced values of [CO]/[CH₄] are shown in Table VII. The pressure of CO was varied from 3.4 to 9.3 Torr; of CH₄, from 94 to 379 Torr; and of N_2O, from 22 to 465 Torr. As for the studies listed in Table VI, the gas pressures were such that at least 90% of quenching of the excited mercury atom was done by N_2O. The ratio [CH₄]/[CO] was changed by a factor of 4 in these experiments, and two runs were done at very reduced intensities. Neither the quantum yield of C_2H_6 nor CO_2 was much influenced by the variation in experimental parameters. $\Phi\{C_2H_6\}$ remained between 0.49 and 0.75. $\Phi\{CO_2\}$ showed slightly more variation, ranging from 0.052 to 0.160.

Discussion

CO Absent. It is clear from our results that there is a considerable delay in O_2 production in the mercury-sensitized photolysis of pure N_2O. Furthermore, the

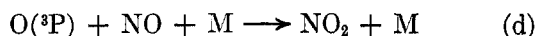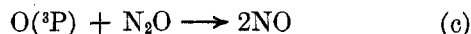**Table VI:** Mercury-Photosensitized Decomposition of N_2O at 548°K in the Presence of CH₄ and High Pressures of CO

[CO], Torr	[CH₄], Torr	[N₂O], Torr	Irradiation time, min	$10^7 I_a$, einsteins/ l. min	$\Phi\{C_2H_6\}$
		Hanovia Lamp			
0.0	4.90	146	66.0	3.30	0.127
53	4.80	167	89.0	3.30	0.029
53	182	184	68.0	3.30	0.61
57	9.70	161	69.0	3.30	0.068
58	4.85	162	67.0	3.30	0.037
59	9.75	287	75.0	3.30	0.055
60	10.00	652	67.0	3.30	0.041
61	165	574	67.0	3.30	0.49
103	10.00	617	1245.0	0.0745	0.055
105	9.80	290	65.0	3.30	0.041
108	9.90	623	66.0	3.30	0.035
186	11.00	600	1257.0	0.0745	0.035
196	9.75	584	65.0	3.30	0.020
		Phillips Lamp			
0.0	19.0	306	60.0	2.31	0.31
0.0	26.5	370	60.0	2.63	0.31
7.6	90.0	496	60.0	2.63	0.53
13.0	34.0	567	60.0	2.63	0.28
19.0	19.0	290	60.0	2.22	0.137
27.0	75.0	515	60.0	2.63	0.37
37.5	26.5	560	60.0	2.63	0.147
50	16.5	585	60.0	2.63	0.070
51	11.0	552	60.0	2.63	0.048
51	38.0	588	60.0	2.63	0.204
53	8.0	294	60.0	2.31	0.055
73	26.0	565	60.0	2.63	0.12
95	19.5	290	60.0	2.43	0.084
104	26.0	305	60.0	2.43	0.092
127	27.5	592	60.0	2.63	0.076
137	26.0	562	60.0	2.63	0.062
204	26.0	594	60.0	2.63	0.044

Table VII: Mercury-Photosensitized Decomposition of N_2O at 548°K with the Phillips Lamp in the Presence of CH₄ and Low Pressures of CO

[CO], Torr	[CH₄], Torr	[N₂O], Torr	Irradiation time, min	$10^7 I_a$, einsteins/ l. min	$\Phi\{C_2H_6\}$	$\Phi\{CO_2\}$
3.4	126	92	30.0	2.11	0.54	0.052
4.4	117	190	30.0	2.22	0.48	0.057
4.5	112	44	30.0	1.58	0.64	0.073
5.7	212	22	60.0	1.59	0.75	0.056
6.2	96	287	60.0	1.95	0.56	0.110
6.2	181	351	60.0	2.32	0.68	0.088
6.3	94	95	966.0	0.070	0.61	0.120
6.3	101	465	60.0	1.91	0.52	0.130
6.5	98	186	60.0	2.40	0.49	0.085
7.5	94	32	970.0	0.050	0.54	0.110
8.2	203	106	30.0	2.31	0.62	0.086
8.9	104	350	60.0	1.94	0.49	0.160
9.3	379	128	30.0	2.75	0.69	0.065

amount of unaccounted for oxygen atoms is sufficiently large to eliminate the possibility of reaction with either

Hg or an impurity since their initial pressures are less than a few microns. An apparent explanation is given by the sequence of steps

$$O(^3P) + N_2O \longrightarrow 2NO \qquad (c)$$

$$O(^3P) + NO + M \longrightarrow NO_2 + M \qquad (d)$$

$$O(^3P) + NO_2 \longrightarrow NO + O_2 \qquad (e)$$

The initial product of the reaction is NO, which conforms to Cvetanović's[4] finding that oxides of nitrogen are produced. The best values[6] for the rate constants k_d and k_e at room temperatures are $k_d = 3.6 \times 10^{10}$ M^{-2} sec^{-1} with O_2 as a chaperone and $k_e = 2.6 \times 10^9$ M^{-1} sec^{-1}. Even if reaction d is more efficient with N_2O than with O_2, which is likely, k_2 is still sufficiently large so that $[NO_2]/[NO]$ is always much less than unity for all our experiments; the steady-state approximation on NO_2 is valid.

An approximate value for k_c can be estimated from the expression $k_c = k_d[NO]$ when the rates of reaction c and d are equal. The results indicate that this occurs for $[NO] \sim 10\ \mu$. Then $k_c \sim 2 \times 10^4\ M^{-1}$ sec^{-1} at room temperature.

Reaction c has been studied in the shock tube by several investigators at temperatures of 1000–2000°.[7] The best rate constant is $2.3 \times 10^{10}\ \exp(-24,100/RT)$ M^{-1} sec^{-1}, which gives $1.3 \times 10^{-10}\ M^{-1}$ sec^{-1} when extrapolated to 300°K. This value is 14 orders of magnitude smaller than estimated above. Furthermore, it is not clear why the reaction of $O(^3P)$ with N_2O should give only NO at room temperature and not O_2 plus N_2, as it does at higher temperatures.[7] Also, attempts to find NO by both gas chromatography and mass spectrometry were unsuccessful.

Other difficulties with this mechanism come from the results with CH_4 present. The reaction of oxygen atoms with N_2O would lead to products which will scavenge CH_3 radicals, thus leading to a strong dependence of $\Phi\{C_2H_6\}$ on $[N_2O]$ contrary to our findings. Finally, if NO were produced, it should scavenge CH_3 ultimately to produce CH_2NOH.[8] Therefore, we conclude that the oxygen atoms are not reacting with N_2O, contrary to an earlier report by us.[9]

The only remaining possibility is that the oxygen atoms are being removed by adsorption on the walls of the reaction vessel.

$$O \xrightarrow{\text{wall}} O_{ads} \qquad (5)$$

The mechanism would then predict

$$\Phi\{C_2H_6\}^{-1} - 1 = k_5/k_2[CH_4] \qquad (I)$$

Figure 2 is a log–log plot of this expression using the data of Table II with the two low conversion points omitted. The slight effect of N_2O pressure is observed, the low-pressure points lying below those at high pressure. The best straight line of unit slope is drawn through the high-pressure points, and the intercept
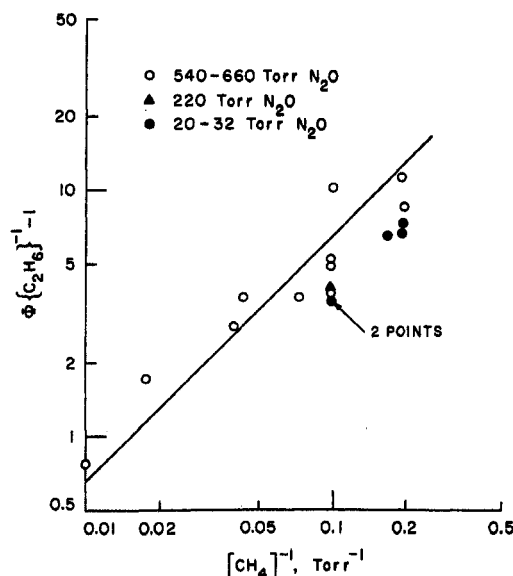
Figure 2. Plot of $\Phi\{C_2H_6\}^{-1} - 1$ vs. $[CH_4]^{-1}$ in the mercury-photosensitized decomposition of N_2O–CH_4 mixtures at 275°, using a Hanovia flat-spiral, low-pressure mercury resonance lamp.

yields $k_5/k_2 = 65$ Torr. The three points lying furthest above the line are those at highest intensity. Under these conditions some methyl radicals might be removed by interaction with oxygen atoms[10,11]

$$O + CH_3 \longrightarrow CH_2O + H$$
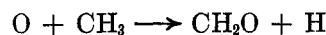
thus yielding low values for $\Phi\{C_2H_6\}$.

There are two apparent difficulties with the wall removal mechanism. First, diffusion from the interior of the reaction vessel is much too slow to compete with reaction 2 which has a rate constant of $5.1 \times 10^6\ M^{-1}$ sec^{-1} at 275°.[12] Second, the diffusion rate should vary inversely with the total pressure, whereas we observe only a slight pressure dependence.

Both of these apparent discrepancies can be explained by the fact that the absorption of radiation is non-uniform and occurs mainly near the front window of the reaction cell; thus diffusion distances are small. In fact, because of pressure broadening the absorption occurs nearer the window at higher pressures, and this effect apparently compensates for the reduced diffusion rates.

(6) "DASA Reaction Rate Handbook," 1967.

(7) D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "High Temperature Reaction Rate Data," No. 4, Department of Physical Chemistry, Leeds University, 1969.

(8) J. Heicklen and N. Cohen, Advan. Photochem., 5, 157 (1968).

(9) R. Simonaitis, J. Heicklen, M. M. Maguire, and R. Bernheim, Ionosphere Research Laboratory Scientific Report No. 340, The Pennsylvania State University, 1969.

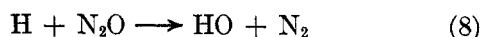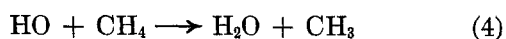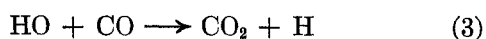(10) H. Niki, E. E. Daby, and B. Weinstock, 12th Symposium (International) on Combustion, 1969, p 277.
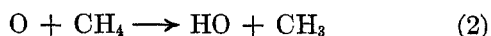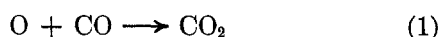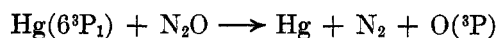
(11) J. T. Herron and R. D. Penzhorn, J. Phys. Chem., 73, 191 (1969).

(12) J. T. Herron, Int. J. Chem. Kinet, 1, 527 (1969).

The experimental results tend to verify the above arguments. The Hanovia lamp operates at relatively low temperatures, and the incident mercury radiation is sharp. Measurements of $R\{N_2\}$ as a function of [N₂O] show that about 75% of the radiation is absorbed at 20 Torr and essentially all the radiation is absorbed above 50 Torr of N₂O. Only a small effect of N₂O pressure on k_5 is observed. On the other hand, the Phillips lamp operates at higher temperatures and thus the incident mercury radiation is considerably broader. $R\{N_2\}$ increases markedly with N₂O pressure, and even at 600 Torr of N₂O, all the radiation is not absorbed. Thus, at low pressure more of the radiation is absorbed in the interior of the vessel, k_5 is correspondingly reduced, and $\Phi\{C_2H_6\}$ is enhanced as shown in Table IV.

The efficient removal of oxygen atoms by adsorption on the walls of the vessel has also been shown to be the case in the vacuum ultraviolet photolysis of CO_2,[13] thus accounting for the oxygen deficiency in that system. A very recent publication[14] has shown that Pyrex surfaces efficiently adsorb oxygen atoms and that these atoms do not combine to form O_2. Our results with N₂O are consistent with these findings.

CO Present. The reaction scheme is certainly the following

$$Hg + h\nu \ (2537 \ \text{Å}) \longrightarrow Hg(6^3P_1)$$

$$Hg(6^3P_1) + N_2O \longrightarrow Hg + N_2 + O(^3P)$$

$$O + CO \longrightarrow CO_2 \tag{1}$$

$$O + CH_4 \longrightarrow HO + CH_3 \tag{2}$$

$$HO + CO \longrightarrow CO_2 + H \tag{3}$$

$$HO + CH_4 \longrightarrow H_2O + CH_3 \tag{4}$$

$$O \longrightarrow wall \tag{5}$$

$$2CH_3 \longrightarrow C_2H_6 \tag{6}$$

$$H + CH_4 \longrightarrow H_2 + CH_3 \tag{7}$$

$$H + N_2O \longrightarrow HO + N_2 \tag{8}$$

All of the listed reactions, except reaction 5, are well known and have been reported in numerous studies. As shown above, reaction 5 occurs in our reaction vessel, and with experiments using the Hanovia lamp, k_5/k_2 is 65 Torr at 548°K. Another radical–molecule reaction which might be considered is

$$HO + N_2O \longrightarrow HO_2 + N_2$$

No evidence has ever been advanced for this reaction, though it is exothermic and conserves spin. In the absence of CO, the rate of N₂ formation is not enhanced in the mercury-photosensitized decomposition of N₂O at 548°K by introducing HO radicals into the system. Thus this reaction must be slow and can be neglected.
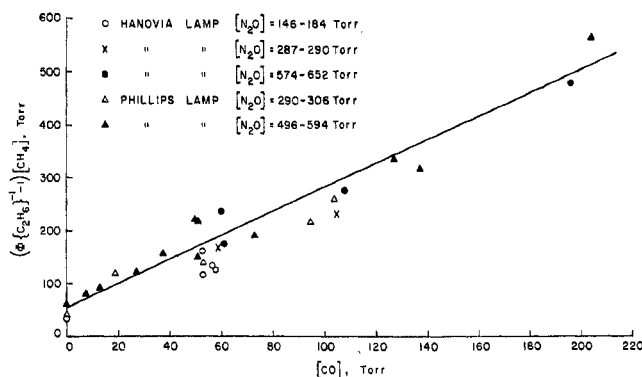
Radical–radical reactions involving O, HO, and H

Figure 3. Plot of $(\Phi\{C_2H_6\}^{-1} - 1)[CH_4]$ vs. [CO] in the mercury-photosensitized decomposition of N₂O at 548°K in the presence of CH₄ and high pressures of CO.

have also been neglected in the above scheme. If such reactions were important, then a reduction in intensity would reduce their relative importance, and $\Phi\{C_2H_6\}$ should increase. The runs at reduced intensity gave slightly higher values for $\Phi\{C_2H_6\}$, but considering the factor of 47 change in I_a, this increase is minor. Consequently, competitions between radical–radical and radical–molecule reactions cannot be important. This is not true at lower temperatures where experiments were also attempted. At 475°K and below, there is a pronounced intensity effect which prohibited meaningful experiments from being done at those temperatures.

Determination of k_1/k_2. The mechanism leads to the following rate law for C_2H_6 production

$$(\Phi\{C_2H_6\}^{-1} - 1)[CH_4] = k_5/k_2 + k_1[CO]/k_2 \tag{II}$$

Figure 3 is a plot of the left-hand side of the equation vs. [CO] for the data in Table VI. In spite of the significant scatter, the plot can reasonably be fitted by a straight line, showing that reaction 1 is second order as expected from the results at lower temperatures.[1] The intercept of 65 Torr corresponds to the value of k_5/k_2 found with the Hanovia lamp above. The data with the Phillips lamp are for high total pressures, and pressure broadening is sufficient to ensure complete absorption of the radiation. Thus the differences between the two lamps are negligible (as seen from Tables II and IV at total pressures above 200 Torr) and the data from the two lamps fit the same plot. The slope of 2.0 corresponds to k_1/k_2. Close examination of Figure 3 reveals that the data points at high N₂O pressures lie slightly higher than those at low N₂O pressures, thus indicating that k_1 may be just into the pressure-falloff region.

Value of k_2. The value of k_2 has been reported by many investigators, and the results were recently reviewed by Herron.[12] Most of the investigators measured

(13) T. G. Slanger, *J. Chem. Phys.*, **45**, 4127 (1966).

(14) J. A. Riley and C. F. Giese, *ibid.*, **53**, 146 (1970).

Table VIII: Rate Constants of Importance in the Reaction of $O(^3P)$ with CH_4; Units of M^{-1} sec^{-1}
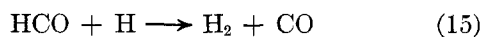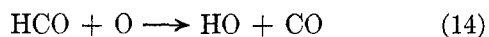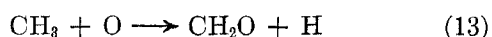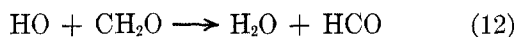
Rate constant expression	Value at 548°K	Reference
$k_4 = 2.9 \times 10^{10} \exp(-5000/RT)$	2.9×10^8	Wilson and Westenberg[a]
$k_7 = 12.6 \times 10^{10} \exp(-11,900/RT)$	2.19×10^6	Walker[b]
$k_9 = 1.3 \times 10^{10}$	1.3×10^{10}	Baulch, et al.[c]
$k_{10} = 10^{10} \exp(-3300/RT)$	4.8×10^8	McNesby, et al.[d]
$k_{11} = \sim 10^{10} \exp(-3500/RT)$	3.9×10^8	e
$k_{12} = 4.0 \times 10^{10}$	4.0×10^{10}	f

[a] Reference 17. [b] R. W. Walker, *J. Chem. Soc. A*, 2391 (1968). [c] D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, "High Temperature Reaction Rate Data," No. 3, Department of Physical Chemistry, Leeds University, 1969. [d] J. R. McNesby, M. D. Scheer, and R. Klein, *J. Chem. Phys.*, **32**, 1814 (1960). [e] Preexponential factor assumed equal to that of k_{10}. Activation energy determined from value of $k_{11} = 2.6 \times 10^7$ at 300°K [W. R. Brennan, I. D. Gay, G. P. Glass, and H. Niki, *J. Chem. Phys.*, **43**, 2569 (1965)]. [f] Hoare[18] found $k_{12}/k_4 = 33 \pm 6$ at 525°K. Thus 4.0×10^{10} is an upper limit to k_{12} at 548°K.

the loss of oxygen atoms in a flow tube experiment and, between 350 and 2000°K, their results fit the expression

$$-d[O]/dt[O][CH]_4 =$$

$$8.0 \times 10^{10} \exp(-9050/RT) \; M^{-1} \sec^{-1} \quad (III)$$

Westenberg and deHaas[15] measured the ratio of oxygen atom to CH_4 consumption and found a ratio of 3.8 ± 0.4. On this basis the rate constant for reaction 2 was assumed to be given by the right-hand side of expression III divided by 3.8. However the stoichiometry was not measured under the same conditions as the rate experiments. Herron[12] has pointed out that the stoichiometric factor should be higher. Even if the stoichiometric factor is correct, the conclusion that the rate constant is the rate divided by the stoichiometric factor will only be valid if CH_4 is removed exclusively by oxygen atoms and not by other species. In fact, this is not the case, and the complete mechanism is

$$O + CH_4 \longrightarrow HO + CH_3 \quad (2)$$

$$HO + CH_4 \longrightarrow H_2O + CH_3 \quad (4)$$

$$H + CH_4 \longrightarrow H_2 + CH_3 \quad (7)$$

$$HO + O \longrightarrow O_2 + H \quad (9)$$

$$O + CH_2O \longrightarrow HO + HCO \quad (10)$$

$$H + CH_2O \longrightarrow H_2 + HCO \quad (11)$$

$$HO + CH_2O \longrightarrow H_2O + HCO \quad (12)$$

$$CH_3 + O \longrightarrow CH_2O + H \quad (13)$$

$$HCO + O \longrightarrow HO + CO \quad (14)$$

$$HCO + H \longrightarrow H_2 + CO \quad (15)$$
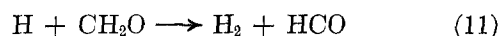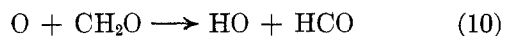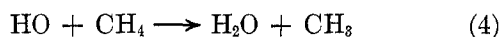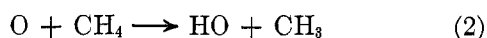
Both O_2 and H atoms were found as products of the reaction, but CH_2O was not. For this reason all the investigators rejected reaction 13, though it since has been shown to be important.[11,16] Since $k_9 \gg k_4$, then under the conditions of the experiments, the rate of reaction 4 is small compared to that for reaction 9 and can be neglected, for simplicity. If reaction 12 is also neglected, and the steady-state assumption is made for

HO, CH_3, HCO, and CH_2O, the above mechanism leads to the prediction

$$-d[O]/dt = \{(3 + 2\alpha + 2\beta)k_2[O] +$$

$$(1 + 2\alpha + 2\beta)k_7[H]\} [CH_4] \quad (IV)$$

where

$$\alpha \equiv k_{10}[O]/(k_{10}[O] + k_{11}[H]) \quad (V)$$

$$\beta \equiv k_{14}[O]/(k_{14}[O] + k_{15}[H]) \quad (VI)$$

The values for k_{14} and k_{15} are not known, but they should be similar. Values for the other pertinent rate constants are listed in Table VIII.

Let us first consider the erroneous assumptions that reaction 7 is unimportant. Reaction 7 can only be unimportant if $[H]/[O]$ is sufficiently small. Under these conditions, reactions 11 and 15 are also unimportant; α and β both become 1; and eq IV reduces to

$$k_{obsd} = -d[O]/dt[O][CH_4] = 7k_2 \quad (VII)$$

Thus, even for these assumptions, $k_2 = k_{obsd}/7$ and not $k_{obsd}/3.8$.

Actually, reaction 7 cannot be negligible as hydrogen atoms are seen as a product of the reaction. To have made meaningful measurements, most of the oxygen atoms must have been consumed and $[H] \sim [O]$; k_2 would be even smaller than deduced from eq VII.

The above conclusions are consistent with the assumption that reaction 12 is less important than reactions 10 plus 11 at 548°K if $[CH_4] \leq 300 \, \mu$ pressure, which was generally the case. Furthermore, the steady-state value for $[CH_2O]$ becomes less than 10^{-2}. $[CH_4]$, which is below the detection limit of the analytical schemes and explains why CH_2O was not found as a product.

From an extrapolation of our previous work,[1] the high-pressure limiting value of k_1 is computed to be

(15) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **46**, 490 (1967).

(16) H. Niki, E. E. Daby, and B. Weinstock, *ibid.*, **48**, 5279 (1968).

$1.05 \times 10^6 \ M^{-1} \sec^{-1}$. Thus k_2 should be about $5 \times 10^5 \ M^{-1} \sec^{-1}$ at 548°K, since $k_1/k_2 = 2.0$.

Determination of k_3/k_4. The mechanism consisting of steps 1–8 leads to the prediction

$$\left(\frac{\Phi\{CO_2\}}{\Phi\{C_2H_6\}} - \frac{k_1[CO)}{k_2[CH_4)} \right)^{-1} =$$

$$\frac{k_7[CH_4]}{k_7[CH_4] + k_8[N_2O]} + \frac{k_4[CH_4]}{k_3[CO]} \quad (VIII)$$

For the data in Table VII, the left-hand side of eq VIII is always much greater than unity, whereas the first term on the right-hand side of the equation necessarily must be less than 1 and can be neglected. A plot of the left-hand side of eq VIII *vs.* [CH₄]/[CO] is shown in Figure 4. The data are badly scattered owing to the fact that the ordinate is a small difference of two similar numbers. Nevertheless, the log–log plot is fitted by the best line of slope 1 and yields an approximate value for $k_4/k_3 = 1.0$, with an uncertainty of about a factor of 2.

The value of k_3 can be obtained from the expression $k_3 = 4.2 \times 10^8 \exp(-1080/RT) \ M^{-1} \sec^{-1}$ given by Baulch, *et al.*,[2] to be $1.56 \times 10^8 \ M^{-1} \sec^{-1}$ at 548°K. Using the value[17] of 2.9×10^8 for k_4 at 548°K gives $k_4/k_3 = 1.86$. Within the experimental uncertainty our results give the same value. However, k_4/k_3 was measured directly by Hoare[18] at 400–650°. An extrapolation of his data gives $k_4/k_3 = 0.25$ at 548°K, considerably lower than our value.
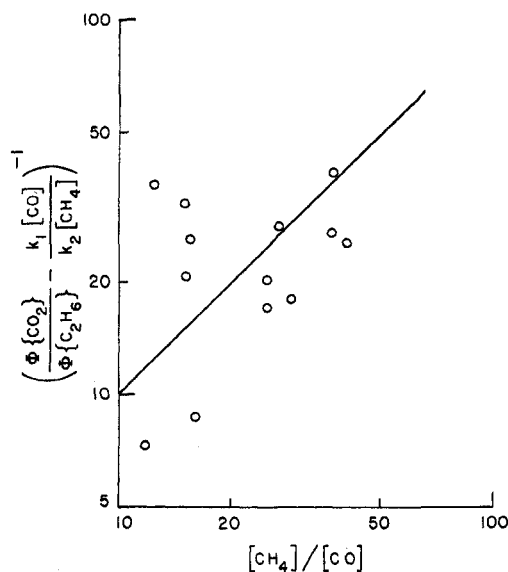

Figure 4. Log–log plot of $(\Phi\{CO_2\}/\Phi\{C_2H_6\} - k_1[CO]/k_2[CH_4])^{-1}$ *vs.* [CH₄]/[CO] in the mercury-photosensitized decomposition of N₂O at 548°K in the presence of CH₄ and low pressures of CO.

(17) W. E. Wilson and A. A. Westenberg, 11th Symposium (International) on Combustion, 1967 p 1143.
(18) D. E. Hoare, *Proc. Roy. Soc., Ser. A*, **291**, 73 (1966).