

THE REACTIONS OF O(¹D) AND HO WITH CH₃OH

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Summary

N₂O was photolyzed at 2139 Å in the presence of CH₃OH and CO. The O(¹D) produced in the photolysis could react with CH₃OH to produce HO radicals, and thus the reactions of both O(¹D) and HO could be studied. The reaction of O(¹D) with CH₃OH was found to give HO 46 ± 10% of the time and O(³P) < 5% of the time. Presumably the remainder of the reaction produced CH₃O₂H or CH₂O plus H₂O. The relative rate coefficient for O(¹D) reacting with CH₃OH compared to N₂O was found to be 5.5 ± 2.0 at both 25 and 72 °C. The relative rate coefficient for HO reacting with CH₃OH compared to CO is 0.63 ± 0.10 at 25 °C and 0.98 ± 0.20 at 72 °C.

Introduction

Apparently the reactions of CH₃OH with O(¹D) and HO have not been studied. We report here relative rate coefficients for both reactions. The reaction with O(¹D) is studied in competition with N₂O, whereas that with HO is studied in competition with CO. The O(¹D) was produced from the photolysis of N₂O at 2139 Å and HO was produced in the reaction of O(¹D) with CH₃OH.

Experimental

A conventional high-vacuum line using greased ground-glass stopcocks and Teflon stopcocks with Viton "O" rings was used. The reaction vessels were two cylindrical quartz cells 10 cm long and 5 cm in diameter. The cells were enclosed in wire-wound aluminum block furnaces. A Powerstat variable autotransformer, connected to each furnace, was set at the voltage which would give the steady state temperature desired.

The N₂O and CO used were Matheson C.P. grade. The N₂O was purified by passage over ascarite and degassed at -196 °C. The CO was purified by a modification of the procedure used by Millikan [1]. It was passed through 4 ft. of ¼ in. o.d. copper tubing packed with 8 - 14 mesh activated alumina which was immersed in a dry ice/acetone bath, and through 10 ft. of ½ in.

o.d. copper tubing containing copper wool, which was immersed in liquid nitrogen. The CO thus purified was found to be free of CO₂ but contained 0.028% N₂. The experimental results were corrected for this N₂, and this was usually less than a 10% correction.

Certified A.C.S. spectroanalyzed methanol was obtained from Fisher Scientific Company. Some runs were done in which the methanol was just degassed at -196 °C, most of the runs were done with methanol that was distilled *in vacuo* from -46 ° to -78 °C, and one run was done in which ~ 10% trimethyl borate was added to the methanol. All the runs gave similar results.

The 2-trifluoromethylpropene (TMP) was obtained from Peninsular Chem-Research Inc., and was purified by distillation *in vacuo* from -95° to -160 °C. All gas pressures were measured either with a McLeod gage or a Hg manometer used in conjunction with a cathetometer.

Irradiation was from a Phillips Zn resonance lamp TYP 93106E. The effective radiation was at 2139 Å. After irradiation the gases non-condensable at -196 °C were collected with a Toepler pump and analyzed for N₂ by gas chromatography using a 10 ft. long by ¼ in. o.d. copper column packed with 5 Å molecular sieves. The condensables were then analyzed for CO₂ using a 24 ft. long by ¼ in. o.d. copper column packed with Porapak Q. These columns were run at room temperature. In runs with TMP, the non-condensable fraction at -95 °C was analyzed for 2-trifluoromethylpropionaldehyde and 2-trifluoromethylpropylene oxide on a ¼ in. o.d. by 8 ft. long copper column packed with 20% Kel-F oil No. 3 on Chromasorb P. The carrier gas in all cases was He.

At room temperature ~ 4 mTorr of CO₂ was obtained in runs in which the N₂O was omitted. Thus 4 mTorr were subtracted from the CO₂ measured in each run. In the worst cases this amounted to corrections of 20 to 25%, but in most cases the correction was less than 10%. In the higher temperature work it was found that in runs without N₂O, the CO₂ produced followed the expression:

$$1 \times 10^{-4} \leq \frac{[\text{CO}_2]_{\text{mTorr}}}{[\text{time}]_{\text{h}} [\text{CO}]_{\text{Torr}} [\text{CH}_3\text{OH}]_{\text{Torr}}} \leq 3 \times 10^{-4}$$

when the CH₃OH pressure exceeded 100 Torr. The corrections were thus calculated for each run with N₂O added by the following equation:

$$[\text{CO}_2]_{\text{mTorr}} = 2 \times 10^{-4} [\text{time}]_{\text{h}} [\text{CO}]_{\text{Torr}} [\text{CH}_3\text{OH}]_{\text{Torr}}$$

In the worst case ~ 40% of the CO₂ was thus attributed to the dark reactions or from reactions involving the photolysis of the methanol, but most corrections were between 10 and 20%. For the two runs at 72 °C with CH₃OH pressures < 100 Torr, the above formula was not obeyed and the corrections were 43 and 37%.

Results

Mixtures of N_2O , CH_3OH , and CO were photolyzed, and the N_2 and CO_2 produced were measured. The results at $25^\circ C$ are given in Table 1. The reactant pressures were varied as follows: $[CH_3OH]$ from 4.2 to 94.0 Torr, $[N_2O]$ from 7.4 to 173 Torr, and $[CO]$ from 5.15 to 83.2 Torr. The ratios $[N_2O]/[CH_3OH]$ and $[CH_3OH]/[CO]$ were varied by factors of 124 and 49, respectively. The total pressure was varied from 28.0 to 203 Torr. The results were unaffected by variations in total pressure as long as the reactant pressure ratios remained unchanged. The absorbed intensity is given approximately by $R\{N_2\}$, since one N_2 molecule is formed in the primary absorption act. Additional N_2 is produced in the $O(^1D)-N_2O$ reaction, but this can only raise the quantum yield to 1.41 [2] as an upper limiting value. $R\{N_2\}$ was varied by a factor of 24.2.

The ratio $R\{N_2\}/R\{CO_2\}$ varies from 3.8 to 20.2, and the variation is a complex function of the reactant pressures. However, there is no noticeable effect with variations in $R\{N_2\}$ (*i.e.* with the absorbed intensity).

Less extensive data were obtained at $67 - 77^\circ C$, and they are summarized in Table 2. The results are more or less the same as at $25^\circ C$.

In order to see if the $O(^1D)-CH_3OH$ interaction led to deactivation of $O(^1D)$ to produce $O(^3P)$, a test was made for $O(^3P)$ atoms. Mixtures of about 2.5 Torr trifluoromethylpropylene (TMP), 77 Torr of CH_3OH , and 30 Torr of N_2O were photolyzed. Under these conditions $> 90\%$ of the $O(^1D)$ reacts with CH_3OH , and any $O(^3P)$ produced would react with TMP to produce its epoxide and aldehyde [3]. These products were not found and it can be concluded that the $O(^1D)-CH_3OH$ interaction produces $O(^3P)$ less than 5% of the time.

Discussion

The reactions of pertinence are:



where R is most likely CH_2OH , but it may also include any CH_3O that is

TABLE 1

Photolysis of N₂O at 2139 Å and 25 °C in the presence of CH₃OH and CO

$\frac{[\text{N}_2\text{O}]}{[\text{CH}_3\text{OH}]}$	$\frac{[\text{CH}_3\text{OH}]}{[\text{CO}]}$	[CH ₃ OH] (Torr)	[N ₂ O] (Torr)	[CO] (Torr)	Irradiation time (h)	$R\{\text{N}_2\}$ (mTorr/h)	$\frac{R\{\text{N}_2\}}{R\{\text{CO}_2\}}$
0.162	1.97	86.4	14.0	43.8	18.08	15.3	3.8
0.188	3.14	86.1	16.2	27.4	3.67	55.0	6.31
0.201	2.99	76.3	15.3	25.5	12.00	55.7	5.43
0.215	4.38	57.8	12.4	13.2	17.50	157	5.06
0.328	1.52	79.5	26.1	52.1	7.00	329	3.53
0.336	1.48	80.1	26.9	54.3	7.92	31.9	4.87
0.344	3.92	94.0	32.3	32.2	17.5	35.8	8.25
0.355	1.06	87.8	31.2	83.2	5.83	41.2	4.0
0.372	4.94	84.5	31.4	17.1	18.92	43.0	11.0
0.390	5.72	85.2	33.2	14.9	17.08	37.3	14.2
0.393	12.1	85.2	33.5	7.05	20.42	46.5	20.2
0.397	3.16	86.1	34.2	27.2	1.75	82.9	9.06
0.400	1.94	87.5	35.0	45.1	7.42	42.3	7.11
0.412	1.20	77.3	31.8	64.3	3.50	49.7	5.27
0.477	3.03	15.5	7.4	5.11	4.50	98	5.66
0.523	2.48	30.0	15.7	12.1	2.00	196	6.11
0.717	8.74	74.3	53.2	8.50	6.08	132	17.0
0.717	10.8	74.3	53.2	6.89	7.58	116	19.5
1.05	3.08	80.0	84.4	26.0	2.00	182	7.0
1.06	3.08	80.0	85.1	26.0	3.58	256	6.95
1.49	0.822	20.3	30.3	24.7	4.17	46.0	6.0
2.08	0.915	7.5	15.6	8.2	12.00	51.1	6.45
5.13	0.425	5.4	27.7	12.7	4.50	56.9	5.02
6.40	0.499	20.0	128	40.1	2.00	370	4.97
7.77	0.248	4.2	32.6	16.9	2.33	43.8	4.87
10.2	0.42	10.3	105	24.6	1.25	312	8.66
10.3	1.75	9.4	96.6	5.37	2.75	112	15.4
11.9	0.374	10.2	121	27.3	2.75	193	6.39
15.6	0.415	8.6	134	20.7	1.75	341	11.9
20.1	0.404	8.6	173	21.3	1.75	308	16.9

produced. Reactions (3a) or (3b) may proceed through insertion of O(¹D) into a C-H bond followed by decomposition, and thus the extent to which they occur, as well as reaction (3d), could be dependent on the total pressure. However, our results indicate no total pressure dependence, and thus this complication is omitted. The results also indicate that reaction (3c) is negligible, and further consideration of it can be omitted.

The fates of R and H are unimportant, as long as they do not produce additional HO or CO₂. With H this is clearly the case. R should be mainly CH₂OH. If R is CH₃O, the possibility exists that additional CO₂ could be produced *via*

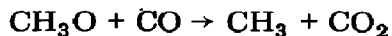


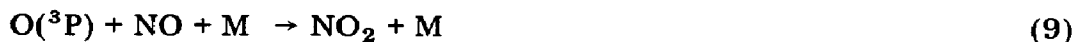
TABLE 2

Photolysis of N₂O at 2139 Å and 72 ± 5 °C in the presence of CH₃OH and CO

$\frac{[N_2O]}{[CH_3OH]}$	$\frac{[CH_3OH]}{[CO]}$	[CH ₃ OH] (Torr)	[N ₂ O] (Torr)	[CO] (Torr)	Irradiation time (h)	$R\{N_2\}$ (mTorr/h)	$\frac{R\{N_2\}}{R\{CO_2\}}$
0.429	5.94	394	169	66.2	9.17	244	15.4
0.441	5.89	388	171	65.9	4.92	288	18.7
0.457	8.98	359	164	40.0	8.85	201	35.6
0.463	5.77	378	175	65.5	7.58	191	15
0.470	2.49	364	171	146	1.25	276	9.33
0.489	8.06	354	173	43.9	5.50	182	15.9
0.489	8.43	354	173	42.0	3.25	179	29.2
0.500	10.1	346	173	34.2	4.75	173	17.1
0.503	4.12	352	177	85.5	2.08	293	13
1.04	1.1	166	173	151	1.33	310	5.68
1.22	1.17	188	230	160	5.42	240	5.28
3.60	0.531	18.9	68.0	35.6	2.83	223	5.58
6.11	0.532	19.0	116	35.7	2.00	186	6.00

However, the results of Wiebe and Heicklen [4] and Lissi *et al.* [5] show this reaction to be unimportant, especially when there are alternate molecules (CH₃OH, NO) present with which CH₃O can react. This reaction can also be ignored.

Under the conditions of our experiments, it will be seen that reaction (4) is less important than reaction (3), but not negligible. The O(³P) that is formed could react as follows:



At 25 °C the rate coefficients for these reactions are known to be 6.2×10^{-14} cm³/s for reaction (7) [6], 7.1×10^{-17} cm³/s for reaction (8) [7] (in the presence of 190 Torr N₂O, reaction (8) is in the pressure-dependent region), and 9.5×10^{-32} cm⁶/s with O₂ as a chaperone for reaction (9) [8]. Under our conditions, reaction (9) has an effective second order rate coefficient of $\sim 10^{-12}$ cm³/s. Consequently, the only reaction of importance is reaction (7).

Under the conditions where a large fraction of the O(¹D) atoms react with N₂O, reaction (2b) plays a significant role and NO accumulates. It very efficiently removes HO *via*



In our experiments reaction (10) is believed to be in the high-pressure region and is nearly second order [9].

The NO also plays another role which is not understood. If relatively

large amounts of NO accumulate, excess CO₂ is produced. This was confirmed by adding NO as a reactant, and excess CO₂ was produced. The amount of excess CO₂ increased as [CO]/[NO] decreased, but was unimportant for [CO]/[NO] > 60 at 25 °C. In our experiments with no added NO, we estimated the average pressure of NO produced, $\overline{[NO]}$, and used only those runs with [CO]/[NO] > 60 at 25 °C and [CO]/[NO] ≥ 375 at 72 °C. (The effect was more pronounced at 72 °C.) The mechanism leads to the two steady-state rate laws:

$$\frac{\alpha\beta R\{N_2\}}{R\{CO_2\}} = \frac{k_3}{k_{3a}} + \frac{(k_2 + k_{2a})\delta [N_2O]}{k_{3a}[CH_3OH]} \quad (I)$$

$$\frac{\gamma R\{N_2\}}{R\{CO_2\}} = 1 + \frac{k_5[CH_3OH]}{k_6[CO]} + \frac{k_{10}[NO]}{k_6[CO]} \quad (II)$$

where α , β , δ , and γ are:

$$\alpha \equiv 1/(1 + k_5[CH_3OH]/k_6[CO] + k_{10}[NO]/k_6[CO])$$

$$\beta \equiv 1 + k_4[CO]/k_{3a}[CH_3OH]$$

$$\delta \equiv 1 + k_4[CO]/(k_2 + k_{2a})[N_2O]$$

$$\gamma \equiv \beta / \{ (k_3/k_{3a}) + \delta(k_2 + k_{2a})[N_2O]/k_{3a}[CH_3OH] \}$$

In utilizing eqn. (II), which is useful when most of the O(¹D) atoms are removed by reaction with CH₃OH, the term $k_{10}[NO]/k_6[CO]$ was dropped since its contribution was negligible.

We first desire to plot $\alpha\beta R\{N_2\}/R\{CO_2\}$ vs. $\delta [N_2O]/[CH_3OH]$ to obtain a straight-line plot and evaluate k_3/k_{3a} and $(k_2 + k_{2a})/k_{3a}$. However, to compute α , β , and δ , we must know k_5/k_6 , k_{10}/k_6 , k_4/k_{3a} , and $k_4/(k_2 + k_{2a})$. The last ratio is known to be 0.23 [8], and k_{10}/k_6 was found to be 16.1 at a total pressure of 96 Torr and 22 at a total pressure of 408 - 768 Torr from work done recently in our laboratory [9]. The values used in this study were 16 at 25 °C and 22 at 72 °C because of the higher pressures used at the higher temperatures. The values for k_5/k_6 and k_4/k_{3a} are obtained from eqns. (I) and (II) by successive iteration. First, $R\{N_2\}/R\{CO_2\}$ was plotted vs. $[N_2O]/[CH_3OH]$ and $[CH_3OH]/[CO]$ to obtain first approximations for k_3/k_{3a} , $(k_2 + k_{2a})/k_{3a}$, and k_5/k_6 . Then a first value for k_4/k_{3a} could be calculated using the obtained value of $(k_2 + k_{2a})/k_{3a}$ and a value of 2.85 for k_2/k_4 [8]. Now α , β , δ , and γ can be computed and the iteration process is repeated until a consistent set of parameters is found. In computing these parameters, the following known rate coefficient ratios were used: $k_{10}/k_6 = 16$ at 25 °C and 22 at 72 °C [9], $k_2/k_4 = 2.85$ [8], $k_{2b}/k_{2a} = 1.44$ [2]. The correction terms β and δ are near unity. Therefore, they do not greatly influence the evaluated rate coefficient ratios.

Figure 1 shows our final plot based on eqn. (I). The data at both temperatures fit the same plot, and $k_3/k_{3a} = 2.2 \pm 0.4$ and $(k_2 + k_{2a})/k_{3a} = 0.56 \pm 0.10$. Since $k_{2a}/k_2 = 0.41$ and $k_{3a}/k_3 = 0.46$, then $k_3/k_2 = 5.5 \pm 2.0$. Figure 2 is based on eqn. (II). The data at 72 °C lie slightly higher than those at 25 °C. The plots at the two temperatures give $k_5/k_6 = 0.63 \pm 0.10$ at 25 °C and 0.98 ± 0.20 at 72 °C. The slight increase in the ratio with temperature indicates that reaction (5) has some activation energy.

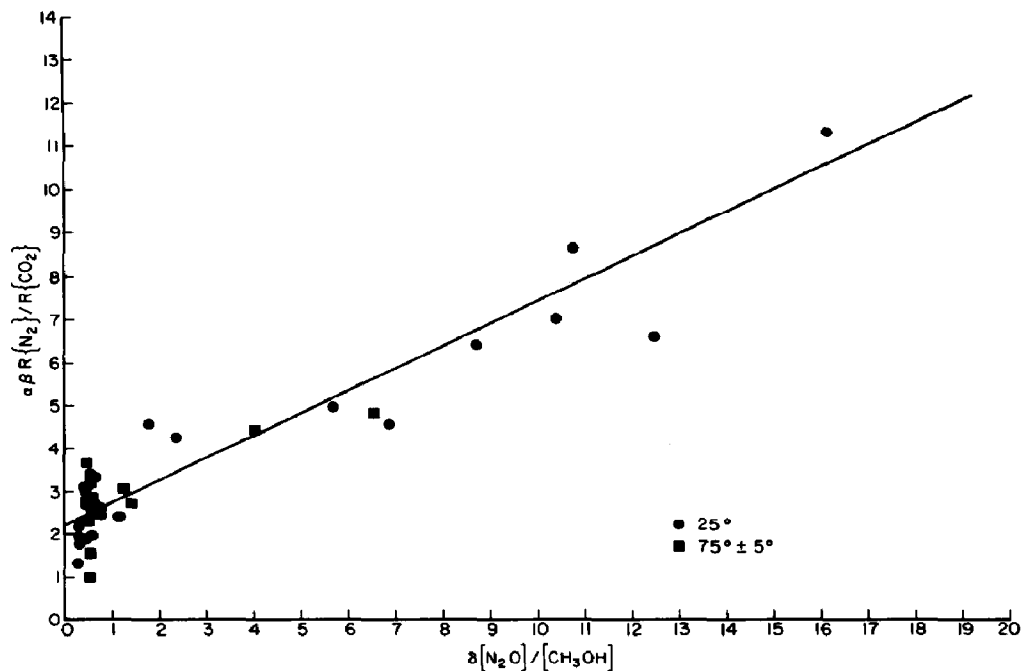


Fig. 1. Plot of $\alpha\beta R\{N_2\}/R\{CO_2\}$ vs. $\delta [N_2O]/[CH_3OH]$ in the photolysis of N_2O at 2139 Å in the presence of CH_3OH and CO at 25 and 72 °C.

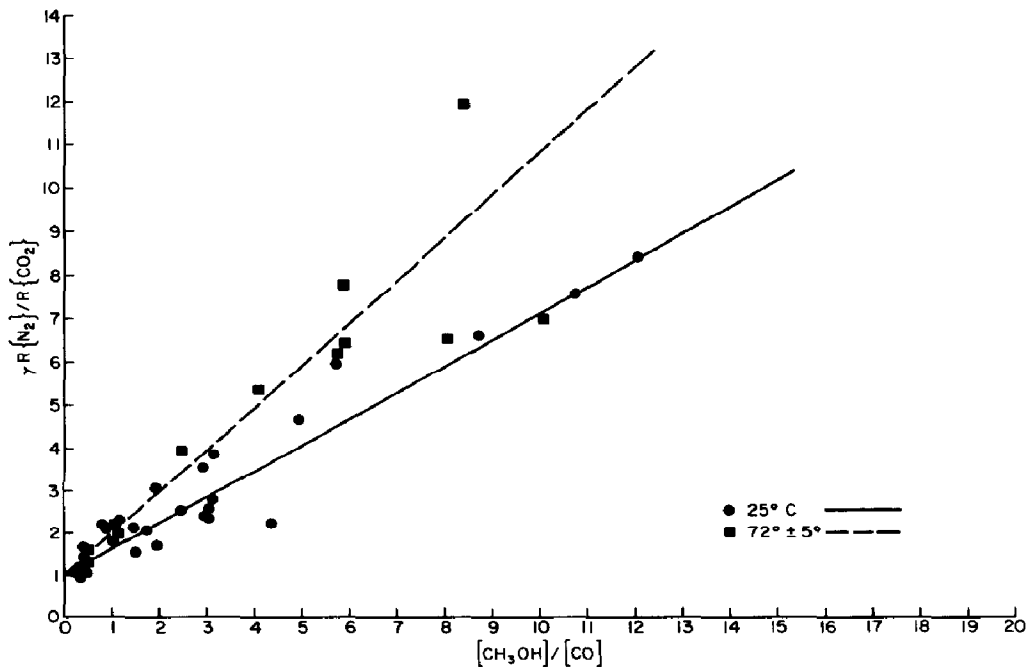


Fig. 2. Plots of $\gamma R\{N_2\}/R\{CO_2\}$ vs. $[CH_3OH]/[CO]$ in the photolysis of N_2O at 2139 Å in the presence of CH_3OH and CO at 25 and 72 °C.

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