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THE REACTIONS OF $O(^1D)$ AND OH WITH CH_3OH, OXIDATION OF THE HCO RADICAL, AND THE PHOTOCHEMICAL OXIDATION OF FORMALDEHYDE

by

Terry Lee Osif

July 14, 1976

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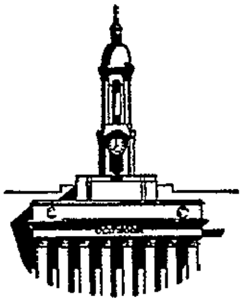

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N_2O was photolyzed at 2139 A in the presence of CH_3OH and CO. The $O(^1D)$ produced in the photolysis could react with CH_3OH to produce OH radicals, and thus the reactions of both $O(^1D)$ and OH could be studied. The reaction of $O(^1D)$ with CH_3OH was found to give OH 46 ± 10% of the time and $O(^3P) < 5\%$ of the time. Presumably the remainder of the reaction produced CH_3O_2H or H_2CO plus H_2O. The relative rate coefficient for $O(^1D)$ reaction with CH_3OH compared to N_2O was found to be 5.5 ± 2.0 at both 25 and 72°C.

The relative rate coefficient for OH reacting with CH_3OH compared to CO is 0.63 ± 0.10 at 25°C and 0.98 ± 0.20 at 72°C.

OXIDATION OF THE HCO RADICAL

Mixtures of Cl_2, O_2, H_2CO, and sometimes N_2 or He were irradiated at 3660 A at several temperatures to photodecompose the Cl_2. The Chlorine atoms abstract a hydrogen atom from H_2CO to produce HCO radicals which can react with O_2.

$$HCO + O_2 (+M) \rightarrow HCO_3 (+M) \qquad 33a$$
$$HCO + O_2 \rightarrow CO + HO_2 \qquad 33b$$
$$HCO + O_2 \rightarrow CO_2 + OH \qquad 33c$$

The HCO_3 radical ultimately becomes HCOOH, so that HCOOH, CO, and CO_2 become measures of the relative importance of the three reaction paths. It was found that $k_{33a}/k_{33b} = 5 \pm 1$ and $k_{33c}/k_{33b} \leq 0.19$ at ~ 23°C (total pressure = 62 to 704 Torr) and -7°C (total pressure = 344 to 688 Torr). Values could not be obtained at -37 or -50°C because of changes in the mechanism.

As the $[Cl_2]/[O_2]$ ratio increases, the HCO radical can also react with Cl_2.

$$HCO + Cl_2 \rightarrow HClCO + Cl \rightarrow HCl + CO + Cl \qquad 40a$$
$$HCO + Cl_2 \rightarrow HCOCl_2 \rightarrow \text{termination} \qquad 40b$$

At the upper two temperatures $k_{40a}/k_{40b} \sim 7.5$ and $k_{40b}/k_{33b} = 6\ (+7,\ -2)$.

THE PHOTOCHEMICAL OXIDATION OF FORMALDEHYDE

Formaldehyde in the presence of N_2 and/or O_2 (usually dry air) was photolyzed with a medium pressure Hg lamp used in conjunction with various filters which transmit different relative amounts of Hg lines from 2894 A to 3660 A. It was hoped to measure the following branching ratios as functions of total pressure, temperature, I_a, and wavelength,

$$H_2CO + h\nu \rightarrow HCO + H \qquad \text{Rate} = \alpha I_a \qquad 75$$
$$H_2CO + h\nu \rightarrow H_2 + CO \qquad \text{Rate} = \beta I_a \qquad 76$$

but lack of a complete understanding of the mechanism prohibits an unambiguous interpretation of the results.

The results suggest that reaction 75 and 76 might decrease with increasing total pressure. The application of very reasonable assumptions leads to a high pressure value of 5.9 for k_{33a}/k_{33b} and a half quenching pressure of 88 Torr for reaction 33a. This contradicts the results presented above that k_{33a} was pressure independent for total pressures down to 62 Torr. However, in that study only one run was done at 62 Torr. The half quenching pressure of 88 Torr obtained in this study is based on several experiments done over a total pressure range of 646 to 35 Torr. Thus, this result is believed to be more reliable.

The average values obtained for ϕ_{75} from eight separate studies were 1.27 (one study), ~ 0.55 (five studies), and ~ 0.30 (two studies). The value of ~ 0.55 is in very good agreement and the value of ~ 0.30 is in fair agreement with values found by others in the photolysis of formaldehyde in the absence of O_2.

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The HCO_3 radical ultimately becomes HCOOH, so that HCOOH, CO, and CO_2 become measures of the relative importance of the three reaction paths. It was found that $k_{33a}/k_{33b} = 5 \pm 1$ and $k_{33c}/k_{33b} \leq 0.19$ at ∿ 23°C

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[1] Reaction numbers are those used in main part of text.

(total pressure = 62 to 704 Torr) and -7°C (total pressure = 344 to 688 Torr). Values could not be obtained at -37 or -50°C because of changes in the mechanism.

As the $[Cl_2]/[O_2]$ ratio increases, the HCO radical can also react with Cl_2.

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The results suggest that reaction 75 and 76 might decrease with increasing total pressure. The application of very reasonable assumptions leads to a high pressure value of 5.9 for k_{33a}/k_{33b} and a half quenching pressure of 88 Torr for reaction 33a. This contradicts the results presented above that k_{33a} was pressure independent for total pressures down to 62 Torr. However, in that study only one run was done at 62 Torr. The half quenching pressure of 88 Torr obtained in this study is based on several experiments done over a total pressure range of 646 to 35 Torr. Thus, this result is believed to be more reliable.

The average values obtained for ϕ_{75} from eight separate studies were 1.27 (one study), ∿ 0.55 (five studies), and ∿ 0.30 (two studies). The value of ∿ 0.55 is in very good agreement and the value of ∿ 0.30 is in fair agreement with values found by others in the photolysis of formaldehyde in the absence of O_2.

CHAPTER I

THE REACTIONS OF $O(^1D)$ AND OH WITH CH_3OH.

INTRODUCTION

Crutzen (1974) has written a review of the photochemical processes which determine the distribution of important minor constituents in the stratosphere and mesosphere. He found that using the rate data which were available for most of the reactions he used in his model led to volume mixing ratios for molecular hydrogen less than those measured. The largest disagreement occurred at approximately 45 km., where the calculated value was approximately a factor of five less than the measured value. He suggested that this deviation can be explained by the H_2 produced in the photodecomposition of formaldehyde produced in the methane oxidation cycle. The detailed steps of this cycle are not fully understood, but presumably are

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad 1$$

$$CH_3 + O_2\ (+M) \rightarrow CH_3O_2\ (+M) \qquad 2$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad 3$$

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \qquad 4$$

$$CH_3O_2H + h\nu \rightarrow CH_3O + OH \qquad 5$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad 6$$

$$CH_2O + h\nu \rightarrow CO + H_2 \qquad 7$$

$$CH_2O + h\nu \rightarrow H + HCO \qquad 8$$

He also suggested that the deviation may be due, at least in part, to the H_2 produced in the photodecomposition of methanol produced in the cold, lower stratosphere by the reaction

$CH_3O + HO_2 \rightarrow CH_3OH + O_2$ 9

$CH_3OH + h\nu \rightarrow CH_2O + H_2$ 2000 A 10

The amount of hydrogen produced from methanol would depend on the amount of methanol present, which would in turn depend on the rates of other competing reactions in which methanol is involved. An examination of Tables 1 and 2 reveals that two such reactions which must be considered are

$OH + CH_3OH \rightarrow$ products 11

$O(^1D) + CH_3OH \rightarrow$ products 12

A search of the literature revealed no direct measurements of these reactions, so the following work was undertaken to measure them. The $O(^1D)$ reaction was studied in competition with N_2O and the OH reaction was studied in competition with CO. N_2O was chosen to measure the relative $O(^1D)$ reaction rates for the following reasons.

1. N_2O absorbs radiation at 2139 A and produces one N_2 molecule and one $O(^1D)$ atom.

   $N_2O + h\nu \rightarrow N_2 + O(^1D)$ 13

2. The only radiation from a Zn lamp that N_2O absorbs is the 2139 A line. Therefore no optical filters are needed.
3. The N_2 production is related in a known way to the absorbed light intensity, Ia. Therefore, from the measurement of the N_2 produced Ia can be calculated.
4. Since $O(^1D)$ atoms react with N_2O to produce N_2, N_2O can be

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

   used to measure relative reaction rates of $O(^1D)$ without necessitating the measurement of another product.

Table 1. Concentration of $O(^1D)$ for an overhead sun under equilibrium conditions.[a]

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

---

a) Nicolet, 1970.

Table 2. Production of OH and HO_2 by oxidation of H_2O, (P), total concentration of $[OH] + [HO_2]$ for an overhead sun, and the time to reach 50% of the equilibrium value.[a]

Altitude (km.)	P ($cm.^{-3}$ $sec.^{-1}$)	$[OH] + [HO_2]$ ($cm.^{-3}$)	Equilibrium Time (sec.)
15	7.2×10^2	3.3×10^7	1.06×10^4
20	2.6×10^3	5.8×10^7	6.2×10^3
25	5.1×10^3	7.4×10^7	4.0×10^3
30	9.3×10^3	9.2×10^7	2.7×10^3
35	1.5×10^4	1.0×10^8	1.8×10^3
40	2.1×10^4	1.1×10^8	1.3×10^3
45	2.0×10^4	9.6×10^7	1.3×10^3
50	1.1×10^4	7.1×10^7	1.8×10^3
55	4.2×10^4	4.4×10^7	2.9×10^3
60	1.4×10^3	3.1×10^7	5.9×10^3
65	4.6×10^2	2.1×10^7	1.3×10^4
70	2.8×10^2	1.6×10^7	2.8×10^4

a) Nicolet, 1970.

5. N_2O is condensable in liquid nitrogen.
   a. Noncondensable impurities can simply be pumped away when the N_2O is frozen. This is especially important for N_2.
   b. The N_2 produced in a run from the photolysis of N_2O can be separated easily from the N_2O before analysis.
6. N_2O is stable and easily stored.
7. A wide range of N_2O pressures can usually be used.

OH was produced by some of the $O(^1D) + CH_3OH$ interactions.

$$O(^1D) + CH_3OH \rightarrow OH + R \qquad 12a$$

CO was chosen to measure the relative OH reaction rates. One of the products of this reaction is CO_2, which is easily collected and measured.

$$OH + CO \rightarrow CO_2 + H \qquad 15$$

The reaction of $O(^1D)$ with N_2O has been studied in this laboratory (Greenberg and Heicklen, 1970; Simonaitis, Greenberg, and Heicklen, 1972). N_2O has previously been used to measure relative $O(^1D)$ rate constants (Greenberg and Heicklen, 1972; Goldman, Greenberg, and Heicklen, 1971), and CO has previously been used to measure relative OH rate constants (Sie, Simonaitis, and Heicklen, 1976a, 1976b). Thus, these techniques are known to work.

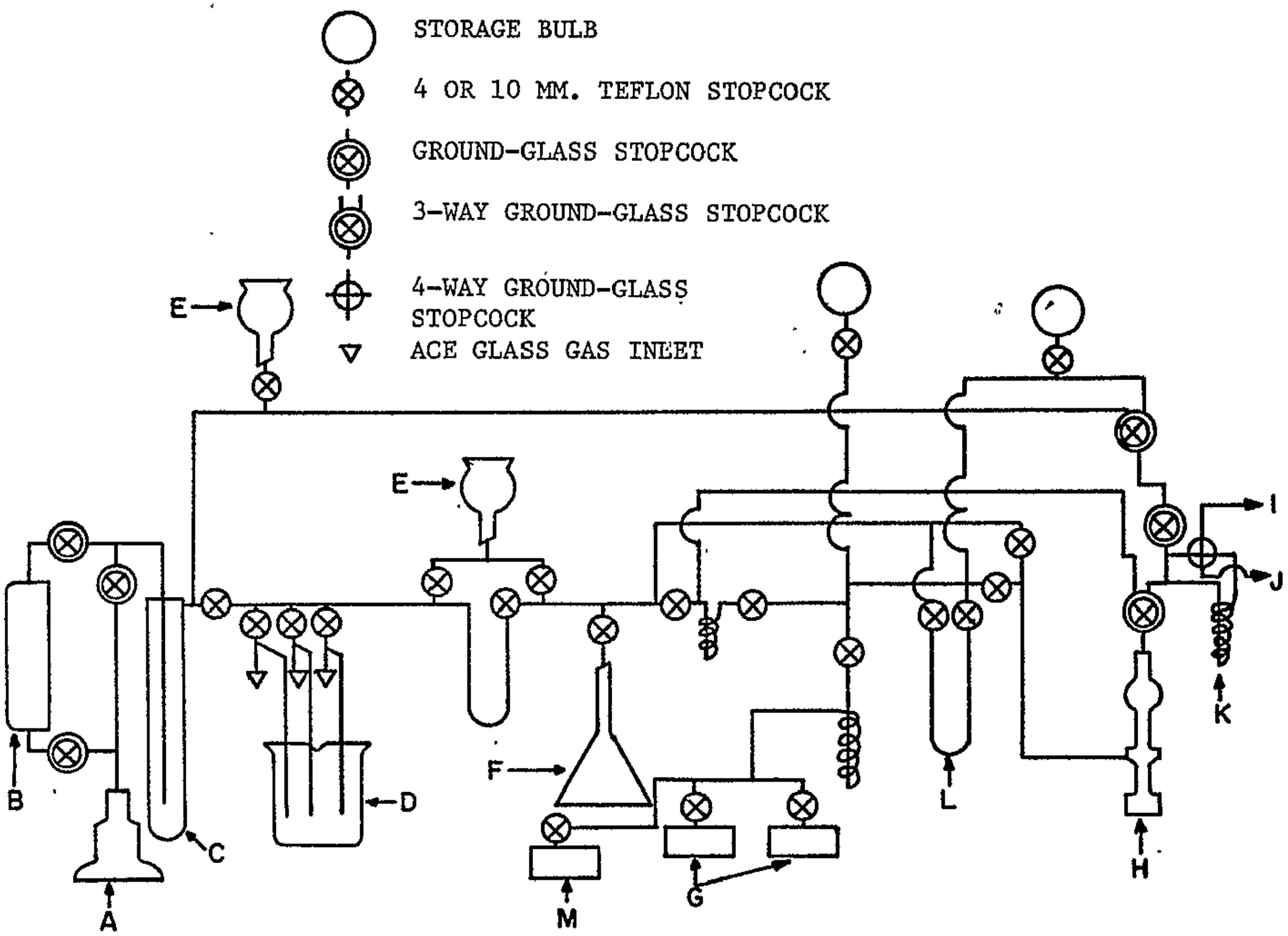
EXPERIMENTAL

Mixtures of N_2O, CH_3OH, and CO were irradiated at 25 ± 2°C and 72 ± 5°C at 2139 A, and the N_2 and CO_2 produced were measured.

A conventional high-vacuum line using ground-glass stopcocks greased with Apiezon N and Teflon stopcocks (West Glass Corporation) with Viton "O" rings was used. (See Figure 1.) Pressures were measured with a mercury manometer used in conjunction with a cathetometer, a McLeod gauge (Consolidated Vacuum Corporation) and a Veeco thermocouple gauge (Model TG-7 with a vacuum gauge tube Model DV-1M).

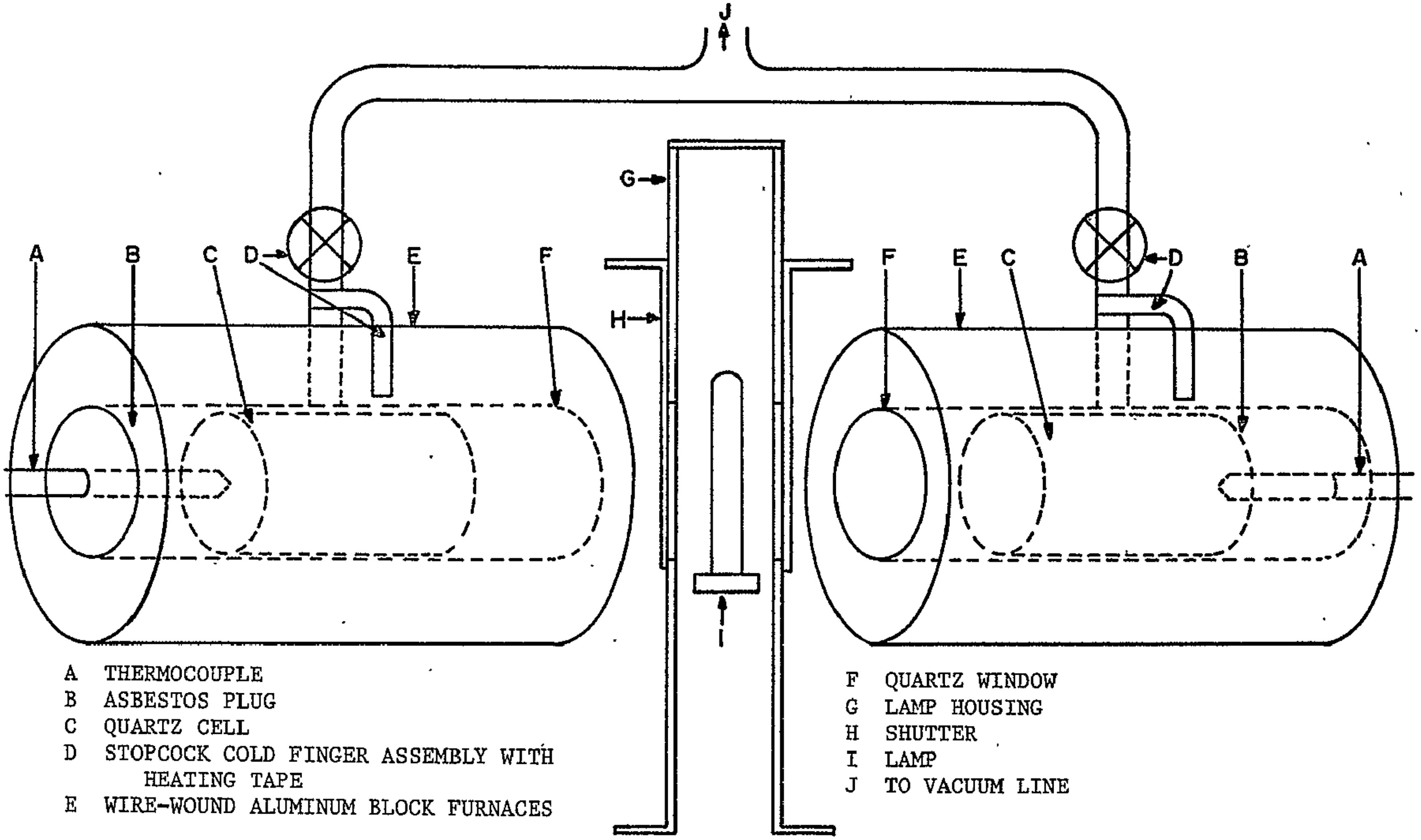
The reactions were carried out in two cylindrical quartz cells 10 cm. long and 5 cm. in diameter. Each cell was enclosed in a wire-wound aluminum block furnace. The temperature was measured with an iron vs. constantan thermocouple which was placed against the center of the end of the cell. (See Figure 2.) The thermocouple electromotive force was measured with a precision potentiometer made by the Rubicon Company of Philadelphia. The furnaces were each powered by a Powerstat variable autotransformer which was set at the voltage required to give the steady state temperature desired.

The cold finger and Teflon stopcock assembly which was located outside of the aluminum furnace was wrapped with heating tape. Since the heating tape had braided fibrous glass insulation, it could be immersed in liquid nitrogen or organic slushes without damage. The heating tapes were also powered by Powerstat variable autotransformers and the temperatures were measured by iron vs. constantan thermocouples. The temperature of the cold finger and stopcock assembly was kept at ∿ 100°C when the furnace was kept at ∿ 72°C.



A	FOREPUMP
B	MERCURY DIFFUSION PUMP
C	LIQUID NITROGEN TRAP
D	BEAKER OF MERCURY
E	VEECO THERMOCOUPLE GAUGE
F	McLEOD GAUGE
G	QUARTZ REACTION CELL IN WIRE-WOUND ALUMINUM BLOCK FURNACE
H	TOEPLER PUMP
I	LINE TO CARRIER GAS CYLINDER
J	LINE TO G. C. DETECTOR
K	G. C. LOOP
L	MERCURY MANOMETER
M	QUARTZ REACTION CELL

Figure 1. Mercury vacuum line.



A THERMOCOUPLE
B ASBESTOS PLUG
C QUARTZ CELL
D STOPCOCK COLD FINGER ASSEMBLY WITH HEATING TAPE
E WIRE-WOUND ALUMINUM BLOCK FURNACES

F QUARTZ WINDOW
G LAMP HOUSING
H SHUTTER
I LAMP
J TO VACUUM LINE

Figure 2. Wire-wound aluminum block furnaces.

A third 10 cm. long by 5 cm. diameter quartz cell without a furnace was used to test for intensity and pressure dependencies (lower pressures could be used with higher intensities) at room temperature. Two lamps were used, one at each end of the cell.

The N_2O or CH_3OH was usually placed in the cell first, and its pressure was measured directly. After the stopcock to the cell was closed, the cell cold finger was immersed in liquid nitrogen and the line was evacuated. A known pressure of the other condensable gas was then placed in a section of the line whose volume ratio to the cell was known. The cell stopcock was then opened and this gas was also allowed to condense in the cell cold finger. The CO was usually added last and its pressure was measured directly. The pressure of the second gas added was calculated by multiplying the pressure measured in the line by the appropriate volume and temperature ratios. After the liquid nitrogen was removed from the cold finger, it was heated with a heat gun in the room temperature runs. For the runs done at ∿ 72°C, the heating tape was turned on to vaporize the N_2O and CH_3OH. The photolysis was begun 10 to 30 minutes later. This time was to allow complete mixing of the reactants.

Sometimes the gases were added separately without being frozen, and the pressures of the second and third gases added were obtained by difference.

The N_2O and CO used were Matheson C. P. grade. The N_2O was purified by passage over ascarite and degassed at -196°C. The CO was purified by a modification of the procedure used by Millikan (1963). It was passed through 4 feet of 1/4 inch o. d. copper tubing packed with 8-14 mesh activated alumina which was immersed in a dry ice/ acetone bath, and through 10 feet of 1/2 inch o. d. copper tubing containing copper wool, which was immersed in liquid nitrogen. The CO thus purified was found to be free of CO_2 but contained 0.028% N_2. The experimental results were corrected for this N_2, and this was usually less than a 10% correction.

Certified A. C. S. spectro analyzed methanol was obtained from Fisher Scientific Company. Some runs were done in which the methanol was just degassed at -196°C, most runs were done with methanol that was distilled <u>in vacuo</u> from -46°C to -78°C, and one run was done in which ~ 10% trimethyl borate was added to the methanol. Porter (1957) reported that methanol vapor in contact with Pyrex glass for ten hours contained as much as 12 mole percent of trimethyl borate, so this experiment was done to see if this was a serious problem. All the runs gave similar results.

The 2-trifluoromethylpropene (TMP) was obtained from Peninsular Chem-Research Inc., and was purified by distillation <u>in vacuo</u> from -95°C to -160°C.

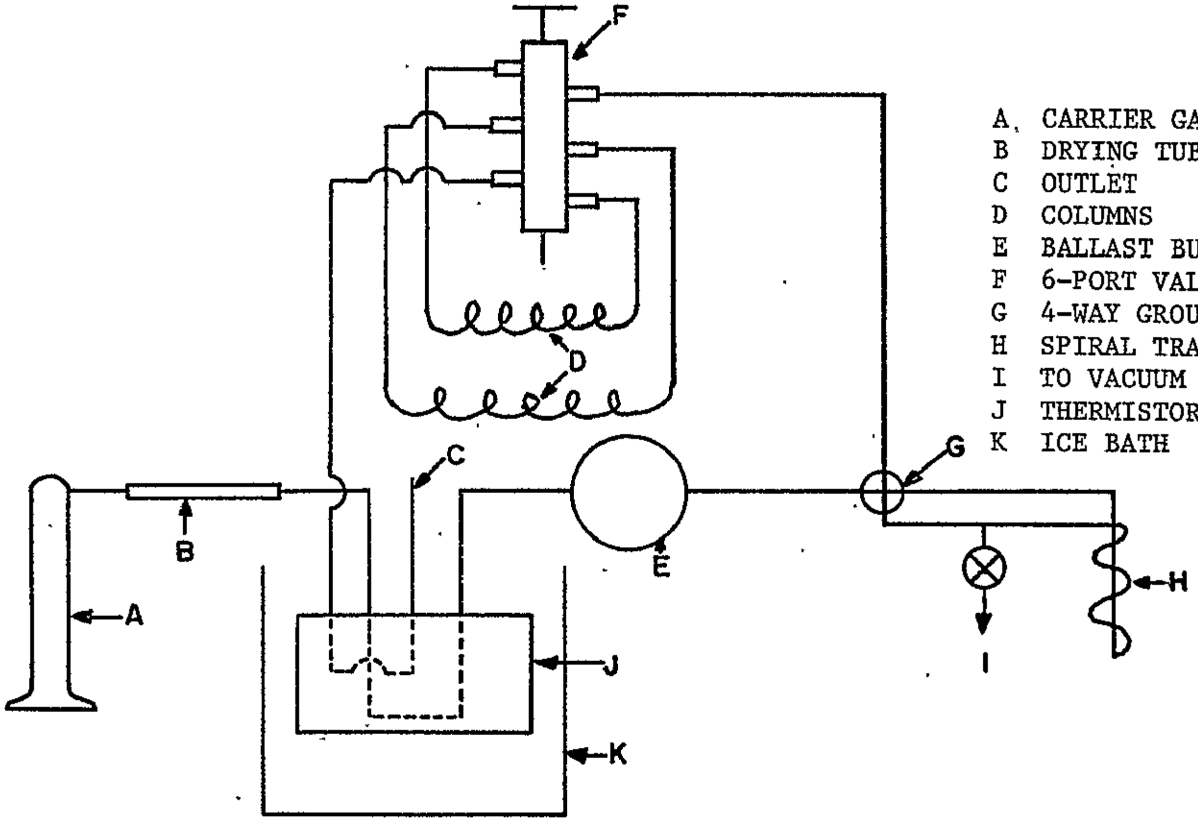
Irradiation was from a Phillips Zn resonance lamp TYP 93106E. The effective radiation was at 2139 A. After irradiation the gases noncondensable at -196°C were collected with a Toepler pump and analyzed for N_2 by gas chromatography using a 10 foot long by 1/4 inch o. d. copper column packed with 5A molecular sieves. The condensables were analyzed for CO_2 using a 24 foot long by 1/4 inch o. d. copper colum packed with Porapak Q. This column would not separate the CO_2 from the higher N_2O pressures used at 72°C. Therefore the condensable gases were analyzed in two segments, and the CO_2 in each segment was summed to obtain the total CO_2 produced.

These columns were run at room temperature. Helium, which was used as the carrier gas, was passed through drierite and ascarite to remove any water vapor or CO_2. The flow rate through the molecular sieve column was 1.0 cm.^{3}/sec. and 0.92 cm.^{3}/sec. through the Porapak Q column. The retention times for N_2 and CO_2 were approximately 9 and 17 minutes respectively. A Gow-Mac stainless steel block thermistor detector Model 10-777 was used and was operated at 15.0 milliamps and 0°C. (See Figure 3.)

In runs with TMP, the noncondensable fraction at -95°C was analyzed for 2-trifluoromethylpropionaldehyde and 2-trifluoromethylpropylene oxide on a 1/4 inch o. d. by 8 foot long copper column packed with 20% Kel-F oil No. 3 on Chromasorb P. The column temperature was ∿ 36°C and the flow rate was 0.45 cm.^{3}/sec..

The above aldehyde and oxide were produced for calibrating the gas chromatograph by reacting the $O(^3P)$ produced in the mercury photosensitized decomposition of N_2O at 2537 A with TMP. Under the conditions used, $O(^3P)$ and N_2 are produced at the same rate. The N_2 produced is a measure of Ia, and since the aldehyde is produced with a quantum yield of 0.38 and the oxide with a quantum yield of 0.58, an absolute calibration for each can be obtained (Moss and Jennings, 1968).

At room temperature ∿ 4 mTorr of CO_2 was obtained in runs in which the N_2O was omitted. This was independent of experimental conditons. Thus 4 mTorr were substracted from the CO_2 measured in each run. In the worst cases this amounted to corrections of 20 to 25%, but in most



A. CARRIER GAS CYLINDER
B DRYING TUBE
C OUTLET
D COLUMNS
E BALLAST BULB
F 6-PORT VALVE
G 4-WAY GROUND-GLASS STOPCOCK
H SPIRAL TRAP
I TO VACUUM LINE
J THERMISTOR DETECTOR
K ICE BATH

Figure 3. Gas chromatograph.

cases the correction was less than 10%. In the higher temperature work, it was found that CO_2 was produced in runs without N_2O, and the CO_2 produced followed equation I

$$1 \times 10^{-4} \leq \frac{[CO_2]_{mTorr}}{[time]_h [CO]_{Torr} [CH_3OH]_{Torr}} \leq 3 \times 10^{-4} \qquad \text{I}$$

when the CH_3OH pressure exceeded 100 Torr. The corrections were thus calculated for each run with N_2O added by using equation II.

$$CO_2 \ mTorr = 2 \times 10^{-4} [time]_h [CO]_{Torr} [CH_3OH]_{Torr} \qquad \text{II}$$

This CO_2 was produced either by dark reactions or from reactions involving photolysis of the methanol. In the worst case, this amounted to a correction of ∿ 40%, but most corrections were between 10 and 20%. For the two runs at ∿ 72°C with CH_3OH pressures less than 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 at 2139 A, and the N_2 and CO_2 produced were measured. Most of the results at 25 ± 2°C are given in Table 3. 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 5.37 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 the total pressure as long as the reactant pressure ratios remained unchanged. The absorbed light intensity, I_a, 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 (Simonaitis, Greenberg, and Heicklen, 1972) as an upper limiting value. $R\{N_2\}$ was varied by a factor of 24.2.

I_a was changed by varying the N_2O pressure and the lamps. Five or six different lamps were used in this study, and in some experiments, two lamps were used at once. Sometimes N_2O was photolyzed alone in one cell while a N_2O, CH_3OH, and CO mixture was photolyzed in the other. The agreement between these two rates of nitrogen production was always very good when the $O(^1D)$-N_2O and $O(^1D)$-CH_3OH reactions (See DISCUSSION) were taken into account, along with a geometrical factor to correct for the fact that both cells were not illuminated equally. This geometrical factor was obtained by placing the same pressure of N_2O in both cells and photolyzing both at the same time with the same lamp. The ratio of the rates of nitrogen production was taken as being equal to the ratio of the light intensities through the two cells. This agree-

Table 3. Photolysis of N_2O at 2139 A and 25 ± 2°C in the presence of CH_3OH and CO.

$\frac{[N_2O]}{[CH_3OH]}$	$\frac{[CH_3OH]}{[CO]}$	$[CH_3OH]$, Torr	$[N_2O]$, Torr	[CO], Torr	Irradiation time, hr.	$R\{N_2\}$, mTorr/hr.	$\frac{R\{N_2\}}{R\{CO_2\}}$
0.162	1.97	86.4	14.0	43.8	18.08	15.3	3.80
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	2.92	94.0	32.3	32.2	17.50	35.8	8.25
0.355	1.06	87.8	31.2	83.2	5.83	41.2	4.00
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	98.0	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	7.00
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	6.00

Table 3. (Concluded)

$\frac{[N_2O]}{[CH_3OH]}$	$\frac{[CH_3OH]}{[CO]}$	$[CH_3OH]$, Torr	$[N_2O]$, Torr	$[CO]$, Torr	Irradiation time, hr.	$R\{N_2\}$ mTorr/hr.	$\frac{R\{N_2\}}{R\{CO_2\}}$
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	0.420	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

ment between the internal and external actinometries means that there were no significant unaccounted for sources of N_2.

The ratio $R\{N_2\}/R\{CO_2\}$ varies from 3.53 to 27.4, 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°C, and some are summarized in Table 4. The results are more or less the same as at 25°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 2-trifluoromethylpropylene (TMP), 77 Torr of CH_3OH, and 30 Torr of N_2O were photolyzed at 2139 A. Under these conditions, more than 90% of the $O(^1D)$ reacts with CH_3OH, and any $O(^3P)$ produced would react with TMP to produce its epoxide and aldehyde (Moss and Jennings, 1968). 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.

NO is a reaction product in this system. The amount of CO_2 produced was found to depend also on the [CO]/[NO] ratio.

Table 4. Photolysis of N_2O at 2139 A and 72 ± 5°C in the presence of CH_3OH and CO.

$\frac{[N_2O]}{[CH_3OH]}$	$\frac{[CH_3OH]}{[CO]}$,	$[CH_3OH]$, Torr	$[N_2O]$, Torr	[CO], Torr	Irridation time, hr.	$R\{N_2\}$, mTorr/hr.	$\frac{R\{N_2\}}{R\{CO_2\}}$
0.429	5.94	394	169	66.3	9.17	244	15.4
0.441	5.89	388	171	65.9	4.92	227	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
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	13.0
1.04	1.10	166	173	151	1.33	310	5.68
1.22	1.17	188	230	160	5.42	294	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

DISCUSSION

The reactions of pertinence are:

$N_2O + h\nu \rightarrow N_2 + O(^1D)$ 2139 Å 13

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

$\rightarrow 2NO$ 14b

$O(^1D) + CH_3OH \rightarrow OH + R$ 12a

$\rightarrow H_2O + CH_2O$ 12b

$\rightarrow O(^3P) + CH_3OH$ 12c

$\rightarrow CH_3O_2H$ 12d

$O(^1D) + CO \rightarrow O(^3P) + CO$ 16

$OH + CH_3OH \rightarrow H_2O + R$ 11

$OH + CO \rightarrow CO_2 + H$ 15

where R is most likely CH_2OH, but it may also include any CH_3O that is produced. Reactions 12a or 12b 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 12d, could be dependent on the total pressure. However, the results indicate no total pressure dependence, and thus this complication is omitted. The results also indicate that reaction 12c 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 OH or CO_2. With H this is clearly the case. R should be mainly CH_2OH. If R is CH_3O, the possibility exists that additional CO_2 could be produced via reaction 17.

$CH_3O + CO \rightarrow CH_3 + CO_2$ 17

However, the results of Wiebe and Heicklen (1973) and Lissi, Massif, and Villa (1973) show this reaction to be unimportant, especially when there are alternate molecules (CH_3OH, NO) present with which CH_3O can react. Lissi et al. report a value of approximately 10^{-19} cm.^{3}/sec. for k_{17}. Since reaction 17 is so slow, it seems likely that if any CH_3O is formed, it would react via

$$CH_3O + CH_3OH \rightarrow CH_3OH + CH_2OH \qquad 18$$

and the CH_2OH would dimerize to form ethylene glycol (Hagege, Roberge, and Vermeil, 1968).

$$2CH_2OH \rightarrow HOCH_2CH_2OH \qquad 19$$

Therefore reaction 17 can be ignored.

Under the conditions of these experiments, reaction 16 is less important than reaction 12, but not negligible. The $O(^3P)$ that is formed could react as follows:

$$O(^3P) + CH_3OH \rightarrow OH + R \qquad 20$$

$$O(^3P) + CO \rightarrow CO_2 \qquad 21$$

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad 22$$

At 25°C the rate coefficients for these reactions are known to be 6.2×10^{-14} cm.^{3}/sec. for reaction 20 (Lefevre, Meagher, and Timmons, 1972), 7.1×10^{-17} cm.^{3}/sec. for reaction 21 (in the presence of 190 Torr N_2O, reaction 21 is in the pressure dependent region) (Simonaitis and Heicklen, 1972), and 6.9×10^{-32} cm.^{6}/sec. with O_2 as a chaperone for reaction 22 (Garvin and Hampson, 1974). Under these conditions, reaction 22 has an effective second order rate coefficient of $\sim 10^{-12}$ cm.^{3}/sec. A consideration of these rate coefficients and the CH_3OH, CO, and NO pressures reveals that the only reaction of importance is reaction 20.

Under the conditions where a large fraction of the O(^{1}D) atoms react with N_2O, reaction 14b plays a significant role and NO accumulates. It very efficiently removes OH via reaction 23.

$$OH + NO \rightarrow HONO \qquad 23$$

In these experiments reaction 23 is believed to be in the high pressure region and is nearly second order (Sie, Simonaitis, and Heicklen, 1976b).

The NO also plays another role which is not understood. If relatively large amounts of NO accumulate, excess CO_2 is produced. This was confirmed by adding NO as a reactant, and observing that excess CO_2 was produced. This is shown in Table 5.

In the experiments with no added NO, the average pressure of the NO produced from reaction 14b, $\overline{[NO]}$, was calculated via equation III. This equation was derived from the mechanism and the appropriate steady state approximations.

$$\overline{[NO]} = \frac{[N_2]_{produced}}{\frac{k_{14} + k_{14a}}{k_{14b}} + \frac{k_{12}[CH_3OH]}{k_{14b}[N_2O]} + \frac{k_{16}[CO]}{k_{14b}[N_2O]}} \qquad III$$

All the data were treated as described below. In the first plots of equations IV and V (See below), the higher points were given more weight in drawing the lines. The lower points were suspected of being low because excess CO_2 might have been produced during the run. Upon examining these early plots, it was noticed that the distance of a point from the line was dependent on the $[CO]/\overline{[NO]}$ ratio. The rate constants obtained from the final plots of equations IV and V were used with equation IV to calculate a theoretical $R\{N_2\}/R\{CO_2\}$ ratio (i.e. the $R\{N_2\}/R\{CO_2\}$ ratio that would put the data point on the line) for several runs. This calculated value of $R\{N_2\}/R\{CO_2\}$ divided by the

Table 5. Effect of added NO on the R{N_2}/R{CO_2} ratio.

[CH_3OH], Torr	[N_2O], Torr	[CO], Torr	R{N_2}/R{CO_2}	[NO], Torr	[CO]/[NO]
			25° ± 2°C		
77.3	31.8	64.3	5.26	--	
77.5	32.4	63.8	5.83	.205	311
			5.26/5.83=.902		
80.1	26.9	54.3	4.91	--	-
78.6	26.3	54.6	4.90	.280	195
			4.91/4.90=1.00		
74.3	53.2	8.50	17.0	--	-
73.9	53.5	7.50	13.2	.287	26.1
			17.0/13.2=1.30		
14.3	53.2	6.89	19.5	--	-
67.0	51.0	5.91	13.8	.287	20.6
			19.5/13.8=1.40		
			72 ± 5°C		
352	177	85.5	13.0	--	-
346	177	84.0	2.47	.420	200
			13.0/2.47=5.26		

experimentally measured value of $R\{N_2\}/R\{CO_2\}$ gives a measure of the excess CO_2 produced. Tables 6 and 7 show this ratio with increasing $[CO]/\overline{[NO]}$ ratio, and the CH_3OH, N_2O, and CO pressures at 25 ± 2°C and 75 ± 5°C respectively. Figures 4 and 5 show plots of ($R\{N_2\}/R\{CO_2\}$ calculated)/($R\{N_2\}/R\{CO_2\}$ measured) vs. the $[CO]/\overline{[NO]}$ ratio at 25 ± 2°C and 72 ± 5°C respectively. From these it can be seen that the excess CO_2 production is not important for $[CO]/\overline{[NO]} > 58$ at 25 ± 2°C and for $[CO]/\overline{[NO]} \geq 300$ at 72 ± 5°C. Runs not meeting these criteria were removed from the plots of equations IV and V.

An investigation was undertaken to try to deduce the source of the extra CO_2. It was thought that the NO might react in some way in the dark to produce CO_2. A mixture of 376 Torr CH_3OH, 0.340 Torr NO, 161 Torr N_2O, and 82.4 Torr CO was kept in the dark for approximately 2 hours. There was no significant difference in the CO_2 produced in this run and similar dark runs with no added NO. Thus it can be concluded that the excess CO_2 is not produced in the dark.

It is known that CH_3O reacts with NO to produce CH_3ONO via reaction 24 (Wiebe, Villa, Hellman, and Heicklen, 1973).

$$CH_3O + NO \rightarrow CH_3ONO \qquad 24$$

Mixtures of CH_3OH and NO and mixtures of CH_3OH, NO, and N_2O were irradiated. A 10 foot x 1/4 inch o. d. stainless steel column packed with 60-80 mesh propylene carbonate on Chromosorb W was used to measure any CH_3ONO which may have been produced. The CH_3ONO yield was always less than 3 mTorr. It was reasoned that this might be a steady state concentration of CH_3ONO. To test this, a mixture of 30.6 mTorr CH_3ONO, 225 mTorr NO, and 316 Torr of CH_3OH, as well as a mixture of 30.8 mTorr

Table 6. Comparison of $R\{N_2\}/R\{CO_2\}_{\text{calculated}}$ to $R\{N_2\}/R\{CO_2\}_{\text{measured}}$ at 25 ± 2°C.

$[CO]/[\overline{NO}]^a$	$\dfrac{R\{N_2\}/R\{CO_2\}^b}{R\{N_2\}/R\{CO_2\}^c}$	$[CH_3OH]$, Torr	$[N_2O]$, Torr	$[CO]$, Torr
3.2	5.60	11.2	133	4.6
7.7	3.33	10.9	209	8.3
9.2	2.45	10.2	105	5.3
13.1	1.46	9.0	80.2	5.2
13.2	1.32	9.1	156	5.1
14.1	1.70	10.9	139	4.8
46.1	1.99	12.1	208	8.4
58.3	1.13	9.4	96.6	5.4
94.9	0.782	7.5	15.6	8.2
103	0.948	8.6	134	20.3
113	0.793	8.6	173	21.3
123	1.05	74.3	53.2	6.9
166	0.996	74.3	53.2	8.5
171	1.30	10.2	121	27.3
194	1.00	85.2	33.5	7.1
206	1.02	5.4	27.7	12.7
210	0.894	10.3	105	24.6
219	1.25	20.0	128	40.1
225	1.71	57.8	12.4	13.2
260	1.25	15.5	7.4	5.1
317	1.15	80.0	85.1	26.0
587	0.885	84.5	31.4	17.1
616	0.959	4.2	32.6	16.9
620	0.766	85.2	33.2	14.9
643	1.01	30.0	15.7	12.1
728	1.24	79.5	26.1	52.1
771	1.13	80.0	84.4	26.0

---

a) $[\overline{NO}]$ was calculated using equation III.
b) $R\{N_2\}/R\{CO_2\}$ was calculated using equation IV.
c) $R\{N_2\}/R\{CO_2\}$ was experimentally measured.

Table 7. Comparison of $R\{N_2\}/R\{CO_2\}_{calculated}$ to $R\{N_2\}/R\{CO_2\}_{measured}$ at 72 ± 5°C.

$[CO]/[\overline{NO}]^a$	$\frac{R\{N_2\}/R\{CO_2\}^b}{R\{N_2\}/R\{CO_2\}^c}$	$[CH_3OH]$, Torr	$[N_2O]$, Torr	[CO], Torr
6.5	7.10	10.1	183	7.9
7.7	6.19	11.5	123	6.8
12.5	4.87	12.6	201	7.9
20.6	3.12	11.0	157	7.4
27.7	2.71	13.7	155	8.0
32.5	2.70	12.8	130	7.35
41.4	2.46	11.5	182	8.1
300	0.956	18.9	68.0	35.6
394	1.16	19.0	116	35.7
513	0.662	359	164	40.0
726	1.06	394	169	66.3
886	1.56	346	173	34.2
3110	0.972	352	177	85.5
4560	0.950	166	172	151

a) $[\overline{NO}]$ was calculated using equation III.
b) $R\{N_2\}/R\{CO_2\}$ was calculated using equation IV.
c) $R\{N_2\}/R\{CO_2\}$ was experimentally measured.

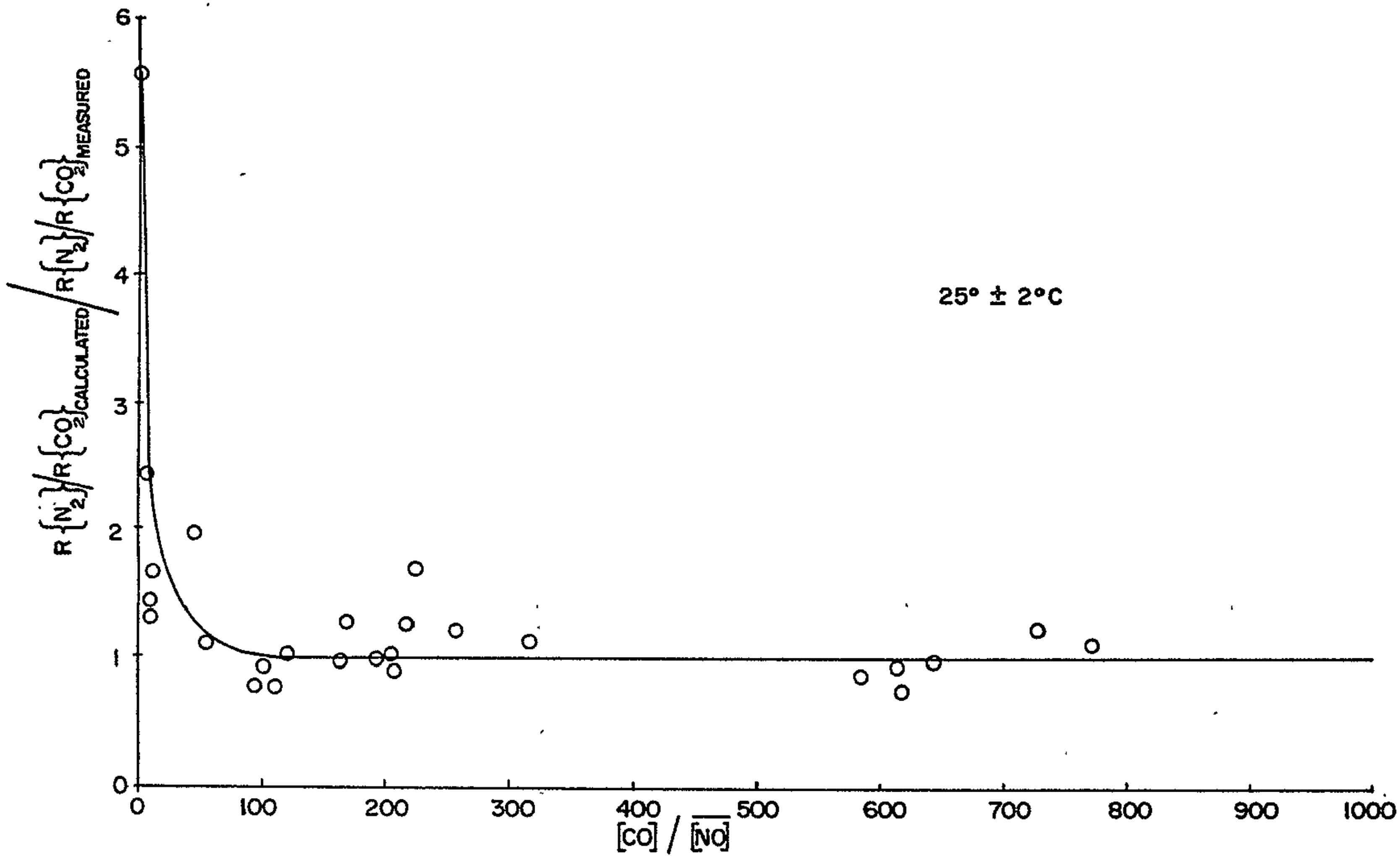


Figure 4. Plot of $(R\{N_2\}/R\{CO_2\})_{calc.}/(R\{N_2\}/R\{CO_2\})_{meas.}$ vs. $[CO]/[\overline{NO}]$ at 25 ± 2°C.

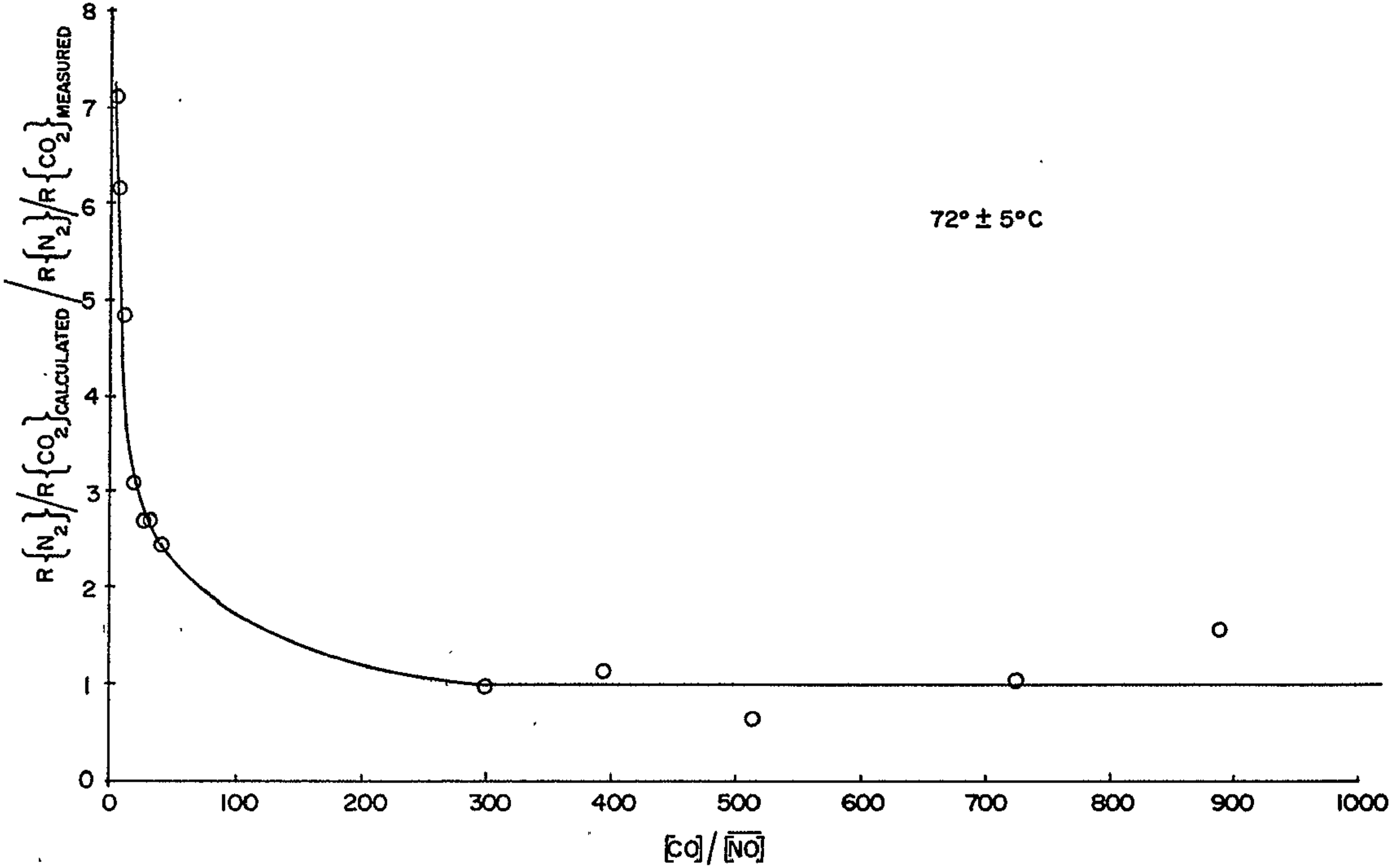


Figure 5. Plot of $(R\{N_2\}/R\{CO_2\})_{calc.}/(R\{N_2\}/R\{CO_2\})_{meas.}$ <u>vs</u>. $[CO]/[\overline{NO}]$ at 72 ± 5°C.

CH_3ONO, 220 mTorr NO, 300 Torr CH_3OH, and 70.1 Torr N_2O were each irradiated for 5.1 hours at ∿ 72°C. Less than 3 mTorr of CH_3ONO were recovered from each run. This supports the supposition that the CH_3ONO is in a steady state of a few mTorr.

It was then thought that excited methoxy radicals, CH_3O^*, might oxidize CO.

$CH_3ONO + h\nu \rightarrow CH_3O^* + NO$ 25

$CH_3O^* + CO \rightarrow CO_2 + CH_3$ 26

Various amounts of CH_3ONO, CO, and CH_3OH were irradiated and the amount of CO_2 produced was measured. The quantum yield of CO_2 production was less than 0.05. A CO_2 quantum yield greater than 2 is needed to account for the excess CO_2 if a steady state CH_3ONO pressure of 5 mTorr is assumed. Thus this possibility was also disproven.

The nitrous acid produced <u>via</u> reaction 23 was also considered. This reaction would cause the CO_2 produced in a run with NO added to decrease relative to an identical run with no added NO because OH's that would produce CO_2 are lost when they react with NO. However if the HONO decomposes to species that produce more CO_2 than was lost as a result of reaction 23, a net excess of CO_2 would be produced.

Three possible ways that HONO may photolytically or thermally decompose are shown in reactions 27 to 29 (Johnston and Graham, 1974).

$HONO \rightarrow OH + NO$ 27

$\rightarrow HNO + O$ 28

$\rightarrow H + NO_2$ 29

Reaction 27 produces only one species, OH, which can produce CO_2, and thus no net increase of CO_2 can be produced. The oxygen atom produced in reaction 28 would at least sometimes abstract a hydrogen atom from methanol to replace the original OH. Again this cannot lead to excess CO_2. The HNO's would probably recombine *via* reaction 30 (Johnston and Graham, 1974).

$$2HNO \rightarrow H_2O + N_2O \qquad 30$$

The reaction

$$HNO + CO \rightarrow HCO + NO \qquad 31$$

is very unlikely because of its high endothermicity. The H-NO bond energy (calculated from National Bureau of Standards JANAF Tables, 1971) is 50 kcal/mole and the H-CO bond energy is only 29 kcal/mole. Thus this set of reactions would not increase the CO_2 yield.

The H atom produced in reaction 29 cannot lead to CO_2 as was discussed earlier. The NO_2 would be photolyzed.

$$NO_2 + h\nu \rightarrow NO + O(^1D) \qquad 32$$

However, neither would this lead to an increase in the CO_2 yield. Thus it seems that the nitrous acid is not involved in the increased CO_2 yield.

Excited nitric oxide, NO*, formed when NO is irradiated, was also considered. A calculation showed that NO* would have to produce CO_2 with a quantum yield of ∿ 1 to account for the excess CO_2.

A mixture of 13.4 Torr NO, 18.2 Torr CH_3OH, and 12.5 Torr CO was irradiated at 2139 A for 0.53 hours. The quantum yield of CO_2 production was less than 0.05. Thus NO* is also not the source of the excess CO_2.

Since the search for the source of the excess CO_2 was not the primary purpose of this investigation and because it is believed that the runs in which excess CO_2 was produced were identified and removed from Figures 6 and 7, the search was dropped.

There was no evidence of any other secondary reactions.

The mechanism leads to the following two steady state rate laws:

$$\frac{\alpha\beta R\{N_2\}}{R\{CO_2\}} = \frac{k_{12}}{k_{12a}} + \frac{(k_{14} + k_{14a})\delta[N_2O]}{k_{12a}[CH_3OH]} \qquad \text{IV}$$

$$\frac{\gamma R\{N_2\}}{R\{CO_2\}} = 1 + \frac{k_{11}[CH_3OH]}{k_{15}[CO]} + \frac{k_{23}[\overline{NO}]}{k_{15}[CO]} \qquad \text{V}$$

where α, β, δ, and γ are:

$$\alpha \equiv 1/(1 + k_{11}[CH_3OH]/k_{15}[CO] + k_{23}[NO]/k_{15}[CO]) \qquad \text{VI}$$

$$\beta \equiv 1 + k_{16}[CO]/k_{12a}[CH_3OH] \qquad \text{VII}$$

$$\delta \equiv 1 + k_{16}[CO]/(k_{14} + k_{14a})[N_2O] \qquad \text{VIII}$$

$$\gamma \equiv \beta/\{(k_{12}/k_{12a}) + \delta(k_{14} + k_{14a})[N_2O]/k_{12a}[CH_3OH]\} \qquad \text{IX}$$

In utilizing equation V, which is useful when most of the $O(^1D)$ atoms are removed by reaction with CH_3OH, the term $k_{23}[\overline{NO}]/k_{15}[CO]$ was dropped since its contribution was negligible.

It was desired to plot $R\{N_2\}/R\{CO_2\}$ vs. $\delta[N_2O]/[CH_3OH]$, to obtain a straight line plot, and thus evaluate k_{12}/k_{12a} and $(k_{14} + k_{14a})/k_{12a}$. However, to compute α, β, and δ, k_{11}/k_{15}, k_{23}/k_{15}, k_{16}/k_{12a}, and $k_{16}/(k_{14} + k_{14a})$ must be known. The last ratio is known to be 0.23 (Garvin and Hampson, 1974), and k_{23}/k_{15} 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 by colleagues in this laboratory (Sie, Simonaitis, and Heicklen, 1976b). 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 temperature. The values for k_{11}/k_{15} and k_{16}/k_{12a} are obtained from equation IV and V by successive iteration. First, $R\{N_2\}/R\{CO_2\}$ was plotted vs. $\delta[N_2O]/[CH_3OH]$ and

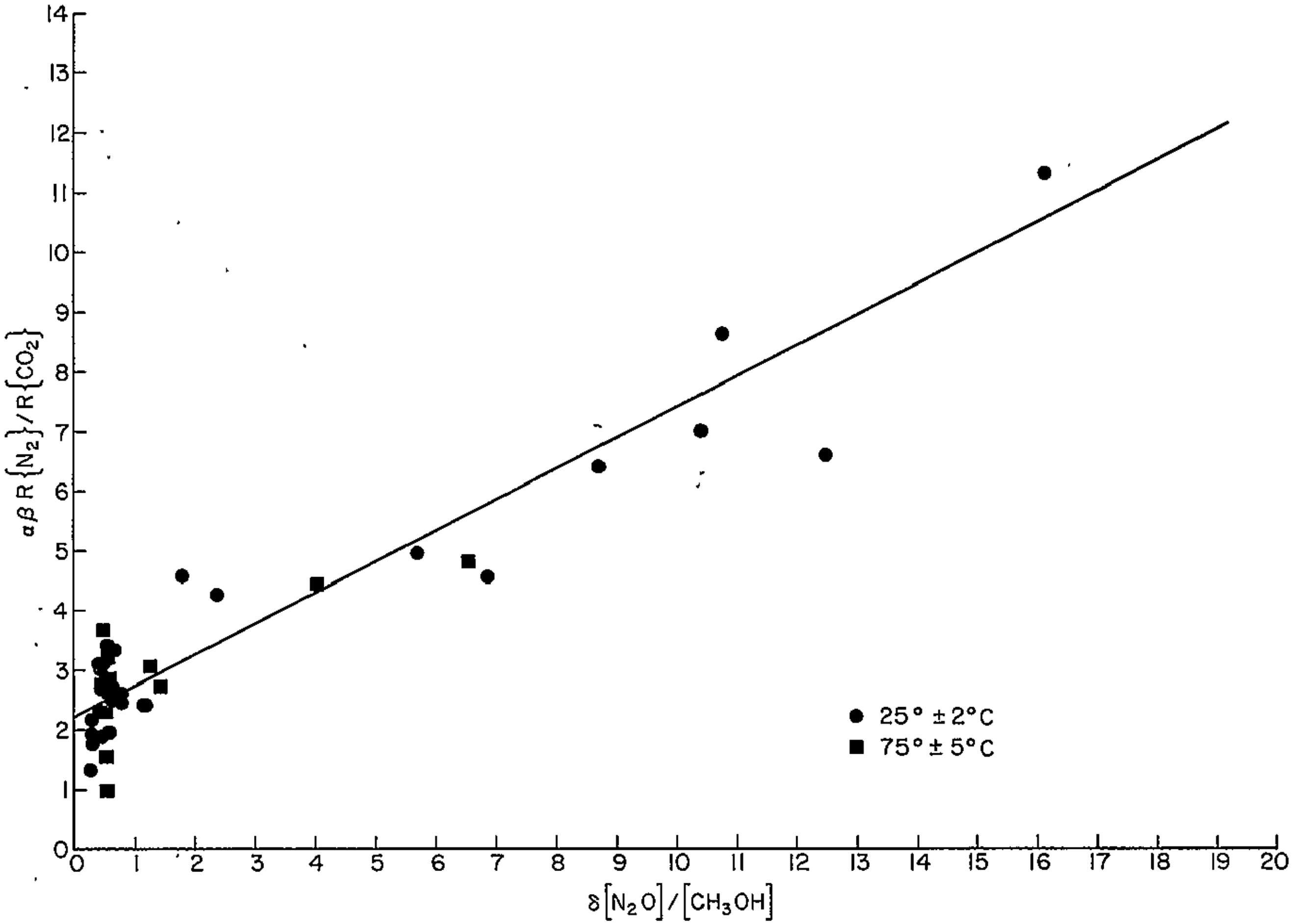


Figure 6. Plot of $\alpha\beta R\{N_2\}/R\{CO_2\}$ vs. $\delta[N_2O]/[CH_3OH]$ at 25 ± 2°C and 72 ± 5°C.

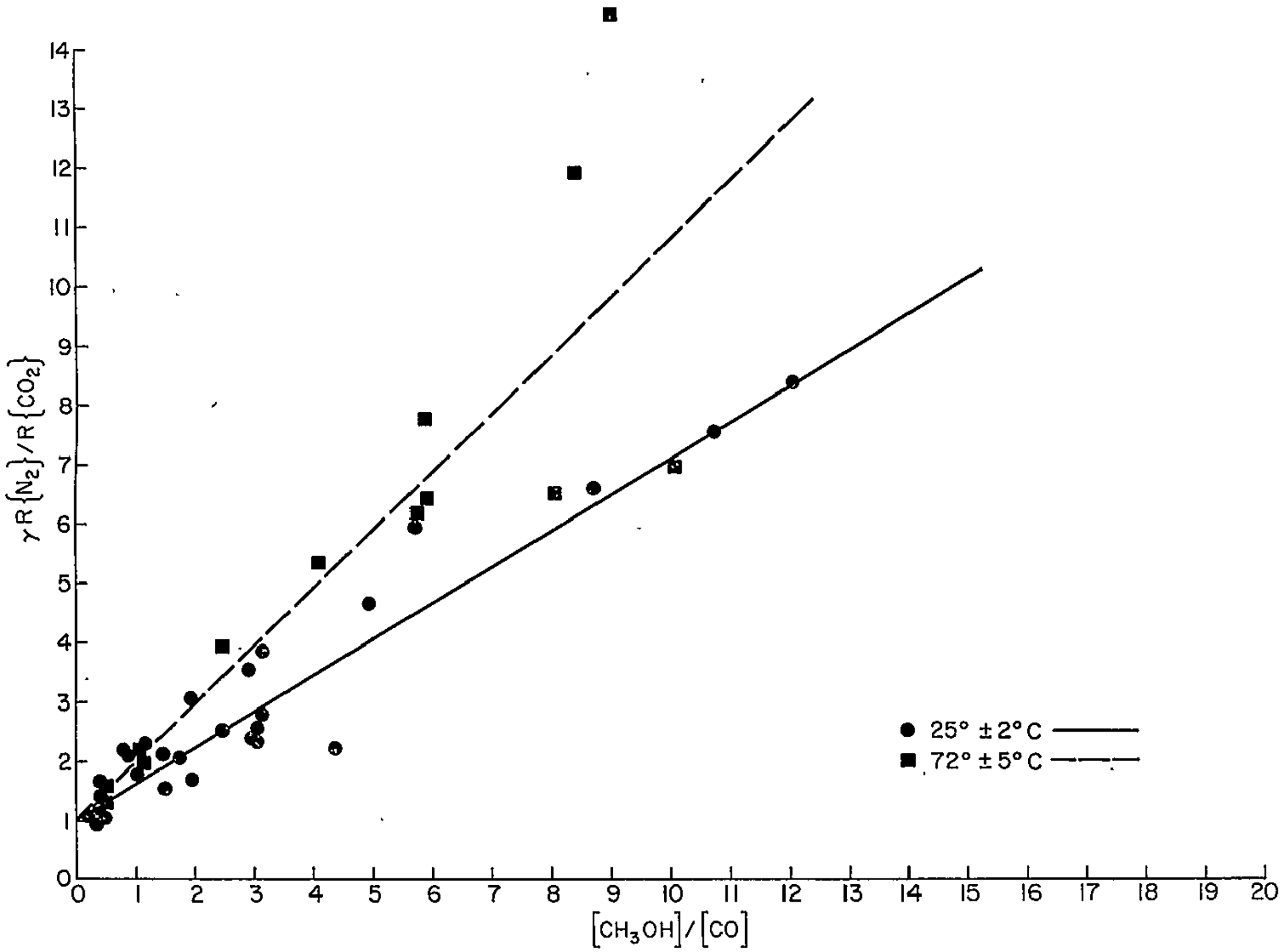


Figure 7. Plot of $\gamma R\{N_2\}/R\{CO_2\}$ vs. $[CH_3OH]/[CO]$ at 25 ± 2°C and 72 ± 5°C.

$[CH_3OH]/[CO]$ to obtain first approximations for k_{12}/k_{12a}, $(k_{14} + k_{14a})/k_{12a}$, and k_{11}/k_{15}. Then a first value for k_{16}/k_{12a} could be calculated using the obtained value of $(k_{14} + k_{14a})/k_{12a}$ and a value of 2.85 for k_{14}/k_{16} (Garvin and Hampson, 1974), and a value of 0.41 for k_{14a}/k_{14} (Simonaitis, Greenberg, and Heicklen, 1972). 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: $k_{23}/k_{15} = 16$ at 25°C and 22 at 72°C (Sie, Simonaitis, and Heicklen, 1976b), $k_{14}/k_{16} = 2.85$ (Garvin and Hampson, 1974), $k_{14b}/k_{14a} = 1.44$ (Simonaitis, Greenberg, and Heicklen, 1972). The correction terms β and δ are near unity. Therefore, they do not greatly influence the evaluated rate coefficient ratios.

Figure 6 shows the final plot based on equation IV. The data at both temperatures fit the same plot, and the value obtained for k_{12}/k_{12a} from the intercept is 2.2 ± 0.4 and the value obtained for $(k_{14} + k_{14a})/k_{12a}$ from the slope is 0.56 ± 0.10. Since $k_{14a}/k_{14} = 0.41$ (Simonaitis, Greenberg, and Heicklen, 1972) and $k_{12a}/k_{12} = 0.46 \pm 0.10$, then $k_{12}/k_{14} = 5.5 \pm 2.0$. Figure 7 is based on equation V. The data at 72°C lie slightly higher than those at 25°C. The slopes of the lines at the two temperatures give $k_{11}/k_{15} = 0.63 \pm 0.10$ at 25°C and 0.98 ± 0.20 at 72°C. The slight increase in the ratio with temperature indicates that reaction 11 has some activation energy.

The lines shown in Figures 6 and 7 were obtained by least squares and the error limits placed on the slopes and intercept were obtained from lines (not shown) that represent outside reasonable limits drawn through the points in the figures.

Table 8. Summary of rate constant ratios used and measured in this study.

$k_{23}/k_{15} = 16$ at 25°C and 22 at 72°C[a]

$k_{14}/k_{16} = 2.85$[b]

$k_{14b}/k_{14a} = 1.44$[c]

$k_{14a}/k_{14} = 0.41$[c]

$k_{12}/k_{12a} = 2.2 \pm 0.4$[d]

$(k_{14} + k_{14a})/k_{12a} = 0.56 \pm 0.10$[d]

$k_{11}/k_{15} = 0.63 \pm 0.10$ at 25°C and

0.98 ± 0.20 at 72°C[d]

$k_{16}/k_{12a} = 0.14 \pm 0.3$[e]

$k_{12}/k_{14} = 5.5 \pm 2.0$[e]

$k_{16}/(k_{14} + k_{14a}) = 0.23$[f]

$k_{12}/k_{14b} = 9.3 \pm 3.3$[e]

$(k_{14} + k_{14a})/k_{14b} = 2.4$[f]

a) Sie, Simonaitis, and Heicklen, 1976b.
b) Garvin and Hampson, 1974.
c) Simonaitis, Greenberg, and Heicklen, 1972.
d) Calculated from this study.
e) Calculated from values found in this study and other ratios reported in this table.
f) Calculated from other ratios reported in this table.

Note: After this study was completed a report was published by Campbell, McLaughlin, and Handy (1976) on the reactions of OH radicals with alcohol vapors at 292°K. The chain mechanism occurring in the dark in the $H_2O_2/NO_2/CO$ system (Campbell, Handy, and Kirby, 1975), involves OH radicals and was used as the source of OH radicals in their system. They measured k_{11} relative to the OH + n-butane reaction ($k = 2.3 \times 10^{-12}$ cm.^{3}/sec.) and reported $k_{11} = (9.4 \pm 0.9) \times 10^{-13}$ cm.^{3}/sec. The value of k_{11} obtained from $k_{11}/k_{15} = 0.63 \pm 0.10$ (present study), $k_{OH + H_2}/k_{15} = 0.0235$ (Sie, Simonaitis, and Heicklen, 1976a), and $k_{OH + H_2} = 7.1 \times 10^{-15}$ cm.^{3}/sec. (Garvin and Hampson, 1974), is $(1.9 \pm 0.3) \times 10^{-13}$ cm.^{3}/sec. These two values of k_{11} are different by at least a factor of four. These are the only two known measurements of k_{11} and more work must be done to alleviate this discrepancy.

CHAPTER II

OXIDATION OF THE HCO RADICAL.

INTRODUCTION

Formyl radical reactions with oxygen occur in flames and combustion (Lewis and von Elbe, 1961, p. 557; Peeters and Mahnen, 1973), in explosions (McKellar and Norrish, 1960), in the chemistry of the upper (Whitten, Sims, and Turco, 1973; Nicolet, 1974, 1975) and lower (Levy, 1973a, 1973b) atmosphere, and in photochemical smog (McQuigg and Calvert, 1969; Calvert, Kerr, Demerjian, and McQuigg, 1972; Calvert, Demerjian, and Kerr, 1973). A complete characterization of HCO + O_2 chemistry is important for understanding these processes.

The rather small amount of work devoted to understanding HCO radical oxidation is surprising when its importance is considered. Much of the information obtained here is inferred from studies whose main objective was other than the study of HCO chemistry.

Three possible HCO + O_2 reactions are considered.

$$HCO + O_2\ (+M) \rightarrow HCO_3\ (+M) \qquad 33a$$

$$HCO + O_2 \rightarrow CO + HO_2 \qquad 33b$$

$$HCO + O_2 \rightarrow CO_2 + OH \qquad 33c$$

Faltings, Groth, and Harteck (1938) photolized mixtures of CO and H_2 at 1295 and 1470 A, and found that H_2O and H_2O_2 were products. Reaction 33b was proposed to explain these results. They believed the H_2O and H_2O_2 were formed from the HO_2 radicals produced in reaction 33b. Mercury sensitized experiments on H_2CO mixtures containing traces of O_2 confirmed this conclusion. Since the reaction occurred even when the O_2 pressure was low, they reported that the reaction was fast.

The low yield of CO_2 in the thermal (Fort and Hinshelwood (1939); Bone and Gardner, 1936; Axford and Norrish, 1948) and photochemical (Carruthers and Norrish, 1936a; Style and Summers, 1946; Horner, Style, and Summers, 1954) oxidation of H_2CO, which almost certainly involves the oxidation of HCO radicals, suggests that reaction 33c is relatively unimportant. This was also confirmed by Baldwin, Fuller, Longthorn, and Walker (1972). They found that less than 0.5% of the H_2CO oxidized when it was added to slowly reacting mixtures of H_2 and O_2 appeared as CO_2.

McKellar and Norrish (1960) studied the explosive combustion of H_2CO initiated by flash photolysis. They found that the HCO bands, which were observed during the flash photolysis of H_2CO, were not seen when mixtures of H_2CO and O_2 were flashed unless the $[H_2CO]/[O_2]$ ratio was greater than 3. They reasoned that this was due to a rapid reaction between HCO and O_2.

Lewis and von Elbe (1961, p. 101), after reviewing the thermal H_2CO oxidation results of others (Axford and Norrish, 1948; Bone and Gardner, 1936; Spence, 1936; Snowden and Styles, 1939), concluded that reaction 33b has such an activation energy that in the temperature range of the experiments ($\sim$ 300-370°C) it is negligible compared to the ternary reaction 33a.

McMillan and Calvert (1965), after reviewing the work of Pearson (1963) on the photolysis of mixtures of acetone and $^{18}O_2$, suggested a value for k_{33b} of approximately 4×10^{-18} cm.^{3}/sec. at 36°C. They compared this value to a typical radical-oxygen combination rate value of about 1.7×10^{-13} cm.^{3}/sec., and conclude that reaction 33a may account for most of the HCO disappearance at low temperature and high pressure.

Demerjian, Kerr, and Calvert (1974) selected $k_{33b} \sim 1.7 \times 10^{-13}$ cm.^{3}/sec. and $k_{33a} \sim 6.8 \times 10^{-14}$ cm.^{3}/sec. ($k_{33a}/k_{33b} = 0.4$) such that simulated data for the aldehyde/NO/NO_2 systems was optimized to fit experimental data.

Becker, Fink, Langen, and Schurath (1973) report that according to preliminary results (not described) $k_{33a} < 10^{-15}$ cm.^{3}/sec. No later report could be found.

Peeters and Mahnen (1973) measured the concentration of all species, unstable as well as stable, throughout the reaction zone of a few low-pressure methane/oxygen flames. They report $k_{33b} \sim 5 \times 10^{-11}$ cm.^{3}/sec. for 1400°K < T < 1800°K.

Washida, Martinez, and Bayes (1974) were probably the only investigators to measure HCO oxidation with this measurement being their main objective. They used a cylindrical fast-flow reactor which was coupled to a photoionization mass spectrometer. Formyl radicals were formed in the following way. A microwave discharge was passed through He which contained a trace of N_2. This produced N atoms.

$N_2 \rightarrow 2N$ microwave discharge 34

The N atoms reacted with NO, which was added downstream, to produce O atoms.

$N + NO \rightarrow N_2 + O$ 35

The O atoms react with ethylene to produce formyl radicals.

$O + C_2H_4 \rightarrow HCO + CH_3$ 36

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By monitoring the HCO concentration's approach to its steady state value in a series of runs with different O atom concentrations, an absolute rate constant, $k_{37} = (2.1 \pm 0.4) \times 10^{-10}$ cm.^{3}/sec., was obtained for reaction 37.

$$\begin{aligned} HCO + O &\rightarrow CO_2 + H && 37a \\ &\rightarrow CO + OH && 37b \end{aligned}$$

Molecular oxygen was then added to the system so that the competition between reaction 33 and reaction 37 could be studied. This was done by measuring the change in the HCO steady state concentration as a function of the $[O_2]/[O]$ ratio. The value obtained for $k_{33}/k_{37} = (2.74 \pm 0.21) \times 10^{-2}$. Using the absolute value for k_{37} mentioned above, the value of k_{33} was calculated to be $(5.7 \pm 1.2) \times 10^{-12}$ cm.^{3}/sec.

Because no products were measured, the value obtained for k_{33} cannot be separated unambiguously into its component parts from reactions 33a, 33b, and 33c. However, because Washida _et al_. saw no variation in k_{33}/k_{37} over the pressure range 1.5 to 5 Torr, they concluded that the pressure dependent reaction 33a was unimportant under their conditions. They also regarded reaction 33c as unimportant, using some of the indirect evidence presented above. Thus it was concluded that the measured value of k_{33} refers primarily to reaction 33b.

Because of the large value of k_{33b}, it was suggested that it will compete with the three-body recombination, even at atmospheric pressure. At lower pressures, such as in the upper atmosphere, the two-body reaction would dominate.

Thus, it is seen that there is general agreement that reaction 33c is relatively unimportant. However, the estimates of the relative importance of reactions 33a and 33b differ.

In this study HCO radicals were produced by Cl atoms abstracting H atoms from H_2CO as in reaction 38.

$$Cl + H_2CO \rightarrow HCl + HCO \qquad 38$$

The HCO radicals react with O_2 according to reaction 33.

$$HCO + O_2 \ (+M) \rightarrow HCO_3 \ (+M) \qquad 33a$$

$$HCO + O_2 \rightarrow CO + HO_2 \qquad 33b$$

$$\rightarrow CO_2 + OH \qquad 33c$$

It is believed that HCO_3 ultimately gives HCOOH in this system. Thus by measuring the amounts of HCOOH, CO, and CO_2 produced, the relative efficiencies of reactions 33a, 33b, and 33c can be determined.

As was stated earlier, HCO + O_2 reactions occur in flames and combustion, in explosions, in the upper and lower atmosphere, and in photochemical smog. However, the main purpose of this investigation was to gain an understanding of HCO + O_2 chemistry so that the results of a photooxidation of formaldehyde study (presented in Chpater III) could be interpreted.

EXPERIMENTAL

Mixtures of Cl_2, H_2CO, O_2, and in some cases an inert gas, N_2 or He, were irradiated at 3660 A and at several temperatures. The products CO, CO_2, and HCOOH were measured. The reactions were carried out in a cylindrical quartz cell 5 cm. in diameter and 10 cm. long. Irradiation was from a Hanovia utility ultraviolet quartz lamp which passed through a Corning 7-37 filter. Since this filter passes light from ∿ 3800 A to ∿ 3300 A, the effective radiation was at 3660 A.

A conventional mercury free high-vacuum line utilizing Teflon stopcocks with Viton "O" rings and glass stopcocks greased with Apiezon N was used to handle the gases. (See Figure 8.) Pressures were measured with a silicone oil manometer in conjunction with a cathetometer, a 0 - 800 Torr Wallace and Tiernan absolute pressure indicator, and a Veeco thermocouple gauge.

For the studies done below room temperature, the reaction cell was housed in a box constructed by Dyfoam (made by Zonolite). Two evacuated cylindrical Pyrex cells with quartz windows were placed through the box wall, one through each of two opposite sides. In this way light entered the box from one side *via* one Pyrex cell, passed through the photolysis cell, and passed out of the other side of the box through the second Pyrex cell to impinge on a RCA 935 phototube. This is shown in Figure 9.

The temperature inside the box was lowered by passing nitrogen gas through a copper coil immersed in liquid nitrogen and flushing this cold nitrogen through the box. The temperature was measured with an

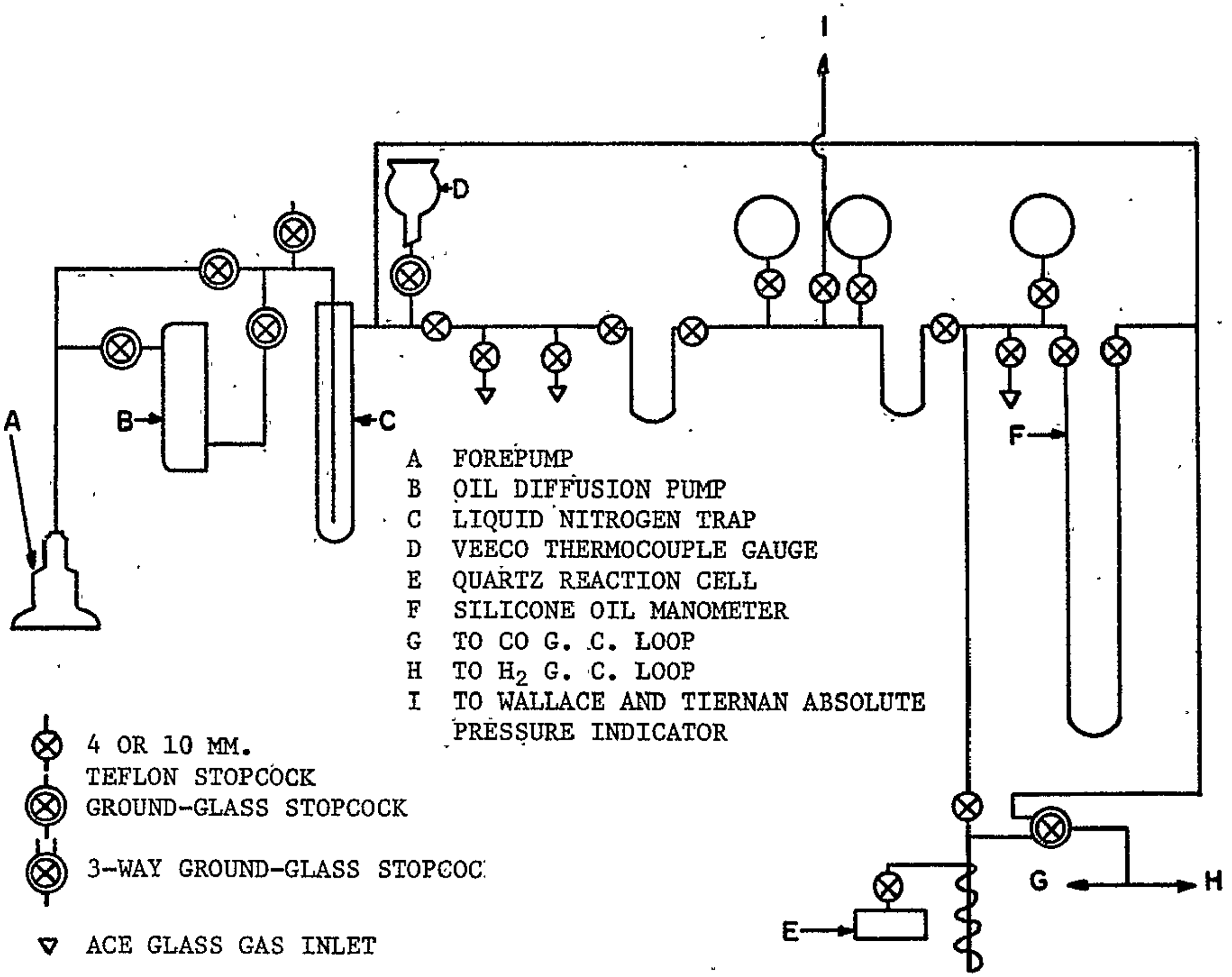
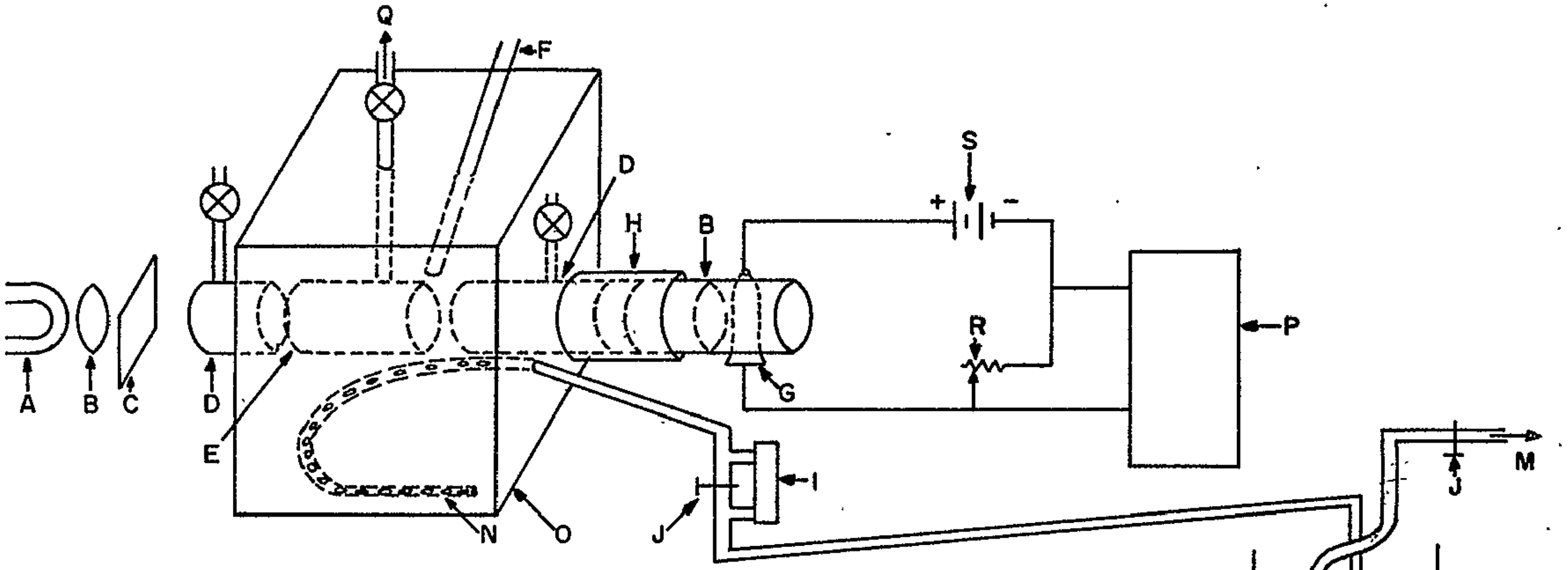


Figure 8. Mercury free vacuum line.



A HANOVIA UTILITY ULTRAVIOLET QUARTZ LAMP
B QUARTZ LENS
C CORNING GLASS FILTER
D EVACUATED CELL WITH QUARTZ WINDOWS
E QUARTZ REACTION CELL
F THERMOCOUPLE
G RCA 935 PHOTOTUBE
H LIGHT TIGHT CYLINDRICAL HOUSING
I FLOW METER
J NEEDLE VALVE
K COPPER COIL
L LIQUID NITROGEN DEWAR
M TO NITROGEN COMPRESSED GAS CYLINDER
N COPPER LOOP WITH EXIT HOLES
O DYFOAM BOX
P TEXAS 1 MILLIVOLT CHART RECORDER
Q TO VACUUM LINE
R 50,000 OHM VARIABLE RESISTOR
S 45 VOLT "B" BATTERY

Figure 9. The cold box, cooling and optical systems, and the phototube circuit.

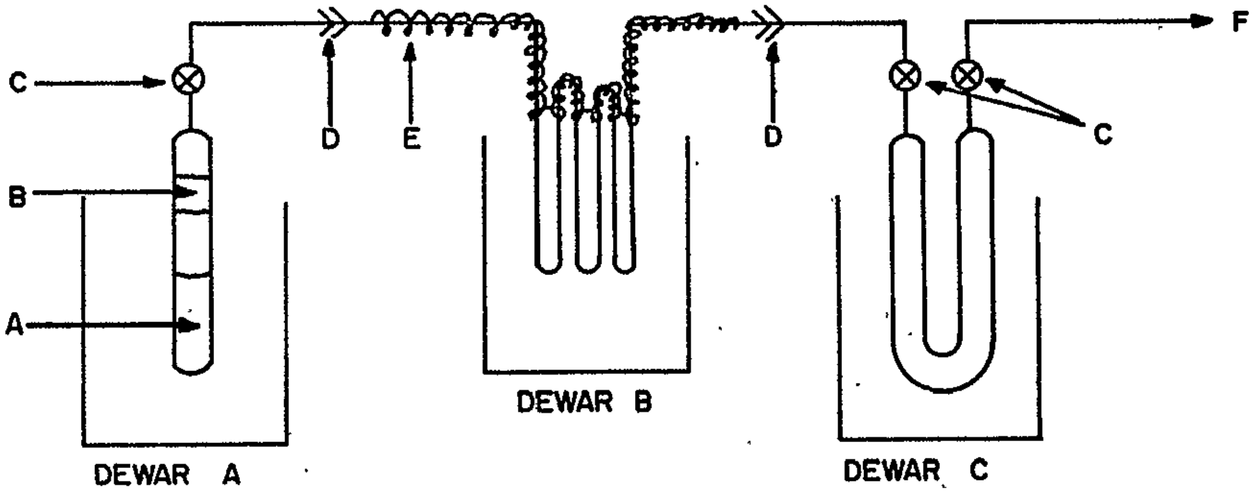
iron vs. constantan thermocouple and was manually controlled by changing the flow rate.

Actinometry was done by photolyzing $CH_3N_2CH_3$ for which $\Phi\{N_2\} = 1.0$ (Calvert and Pitts, 1966, p. 463). The light intensity after passing through the cell, I, was always monitored with the RCA phototube. From the N_2 produced, measured by gas chromatography, the measured extinction coefficient of azomethane (see Table 9), the light intensity, I_o (mTorr/min.), was calculated using Beer's Law. Since I_o is proportional to the phototube signal when the cell is empty, the now calibrated phototube signal gave a measure of I_o before each run with chlorine. Thus the absorbed light intensity, I_a, for the runs with chlorine was calculated from Beer's Law, knowing I_o, the measured extinction coefficient of Cl_2, and the average Cl_2 pressure (computed as the initial chlorine pressure minus 1/4 the CO produced, since each Cl atom consumed produces one CO molecule). This was done instead of matching absorbances because I_a/I_o was always less than 16% and was usually 4 to 5%.

The formaldehyde was prepared from Fisher Scientific paraformaldehyde by a procedure patterned after that of Spence and Wild (1935). The apparatus shown in Figure 10 was attached to the vacuum line and evacuated. Water was placed in Dewar A and heated electrically to 90-100°C. Dry ice/acetone was placed in Dewar B and current was passed through the heating wire to warm the wrapped tubing to 90-120°C. The system was being pumped on continuously. Liquid nitrogen was then placed in Dewar C. When enough formaldehyde was obtained in the trap in Dewar C all heating was stopped, all the stopcocks were closed, and

Table 9. Extinction coefficients at 3660 A to base 10, Torr^{-1} cm.$^{-1}$.

Temp., °C	$CH_3N_2CH_3$	Cl_2
25	1.87×10^{-4}	1.39×10^{-3}
-7	1.85×10^{-4}	1.53×10^{-3}
-37	1.91×10^{-4}	1.56×10^{-3}
-50	2.02×10^{-4}	1.75×10^{-3}



A	PARAFORMALDEHYDE
B	GLASS WOOL
C	TEFLON STOPCOCK
D	ACE GLASS CONNECTOR
E	HEATING WIRE
F	TO VACUUM LINE

Figure 10. Formaldehyde purification apparatus.

the apparatus was disassembled at the Ace Glass connections. The liquid nitrogen in Dewar C was replaced with dry ice/acetone, and the formaldehyde was distilled from this to a glass tube immersed in liquid nitrogen. This purified formaldehyde was stored at -196°C. The liquid nitrogen was removed only long enough to obtain the formaldehyde pressure needed for a run.

The chlorine was obtained from the Matheson Co. It was degassed at -160°C and distilled from -130°C (n-C_5H_{12} slush) to -160°C (i-C_5H_{12} slush). After purification it was stored at room temperature in a darkened storage bulb. The azomethane was prepared as described by Renaud and Leitch (1954).

The oxygen and nitrogen were also obtained from the Matheson Co. The nitrogen was always passed through a trap containing glass wool immersed in liquid nitrogen. The oxygen was treated the same, except the liquid nitrogen was replaced with liquid argon when the total pressure was greater than about 130 Torr. The oxygen and nitrogen were then analyzed by gas chromatography and found to be free of CO_2. The oxygen was also free of CO, but the nitrogen contained 0.035% CO. The CO yields were appropriately corrected in the runs with nitrogen. Runs were also done with helium instead of nitrogen to avoid this problem. This helium was taken from the carrier gas stream of the gas chromatograph and was used without purification.

After photolysis, the noncondensables at -196°C (or -186°C, depending on the oxygen pressure) were analyzed for CO by gas chromatography using a 12 foot long by 1/4 inch o.d. copper column packed with 13X molecular sieves, operated at 0°C. The condensables were distilled from -130°C to -196°C. The gases condensed by liquid nitrogen were analyzed for CO_2 by gas chromatography using a 10 foot long by 1/4 inch o. d. copper column packed with 50-80 mesh Porapak Q. The condensables at -130°C were then transferred to an ir cell and analyzed for HCOOH. A Beckman IR 10 spectrometer was used for the room temperature runs and a Beckman Microspec spectrometer was used for the others. Most of, if not all, the formaldehyde was removed from the formic acid, either by pumping for ∿ 30 minutes a -130°C or by the polymerization that occurred when the chlorine and formaldehyde were condensed prior to analysis. (In later experiments at -95°C bath (acetone slush) was used instead of the -130°C bath, and the formaldehyde could be pumped away in ∿ 2 minutes.) If small amounts of formaldehyde did remain, it would not interfere greatly with most of the HCOOH analysis because the HCOOH spectrum is much stronger than that of formaldehyde.

Since formic acid exists as a mixture of dimer and monomer, the ir was calibrated for HCOOH by placing known "total" pressures of formic acid (measured on a monometer) in the ir cell and measuring the absorbance at 2940, 1740, and 1213 $cm.^{-1}$. These were plotted in the usual manner. The equilibrium constant, K = 2.85 Torr at 300°C (Coolidge, 1928), was used to convert the "total" formic acid pressure in a run to the pressure it would be if it were all monomer. All formic acid pressures reported here have been thus corrected.

RESULTS AT ROOM TEMPERATURE AND -7 ± 1°C

When Cl_2 was photolyzed at 3660 A in the presence of H_2CO and O_2 the products measured were CO, CO_2, and HCOOH. The HCOOH exists as a mixture of the dimer and monomer. However from the known equilibrium constant, K = 2.85 Torr at 300°C (Coolidge, 1928), the total HCOOH yield (assuming all monomer) could be obtained and these values are listed in Tables 10 and 11, along with quantum yields of CO and CO_2.

The parameters were varied as follows:

Room temperature: $[O_2]$ from 696 to 1.88 Torr, $[Cl_2]$ from 5.41 to 1.04 Torr, $[H_2CO]$ from 11.2 to 2.32 Torr, $[Cl_2]/[O_2]$ from 0.807 to 0.0020, I_a from 75.4 to 8.4 mTorr/min., the irradiation time from 17.5 to 0.25 min., and total pressure from 704 to 62 Torr.

-7 ± 1°C: $[O_2]$ from 645 to 1.53 Torr, $[Cl_2]$ from 4.59 to 1.13 Torr, $[H_2CO]$ from 10.1 to 2.84 Torr, $[Cl_2]/[O_2]$ from 0.91 to 0.0022, I_a from 30.0 to 7.18 mTorr/min., the irradiation time from 60 to 1.5 min., and total pressure from 688 to 344 Torr.

The product yields were independent of the variation in all parameters except the ratio $[Cl_2]/[O_2]$. As this ratio increased $\Phi\{CO\}$ increased from a lower limiting value of 2.0 to an upper limiting value of 15 at both temperatures. $\Phi\{HCOOH\}$ however was measured only at low $[Cl_2]/[O_2]$. At high $[Cl_2]/[O_2]$ ratios, it would have been difficult to obtain enough HCOOH to measure accurately, without decomposing an excessive amount of H_2CO. At low $[Cl_2]/[O_2]$ ratios, scatter is not surprising, considering the difficulties in measuring HCOOH. One problem is that some of the acid may be lost to the walls. This is believed to have been the major problem. Another problem is that the measured ir

Table 10. Product quantum yields in the photolysis of chlorine at 3660 A in the presence of O_2 and H_2CO, at room temperature (∿ 23°C).

$\frac{[Cl_2]}{[O_2]}$	$[Cl_2]$, Torr[a]	$[O_2]$, Torr	$[H_2CO]$, Torr	$[N_2]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	Φ{CO}	Φ{HCOOH}	$Φ\{CO_2\}$
0.0020	1.29	659	3.71	0	0	20.8	2.0	-	10.8	-
0.0021	1.37	655	3.50	0	0	22.2	2.4	1.63	-	-
0.0021	1.39	655	3.47	0	0	22.0	6.5	1.87	9.00	-
0.0021	1.38	649	10.0	0	0	21.0	3.0	1.58	10.3	-
0.0024	1.47	609	3.83	0	0	24.2	9.45	1.86	8.50	-
0.0024	1.38	570	6.44	0	0	21.8	5.0	1.91	11.1	-
0.0031	2.15	696	6.27	0	0	18.7	17.5	-	-	0.16
0.0039	1.36	345	3.30	0	0	20.2	5.0	2.15	-	-
0.0040	1.34	339	4.22	0	0	20.4	4.0	2.10	8.67	-
0.0040	1.36	346	3.77	0	0	21.2	4.0	2.20	-	-
0.0040	1.38	349	4.18	0	0	20.8	4.0	2.08	8.92	-
0.0042	1.40	332	8.93	0	0	23.2	3.5	2.10	10.3	-
0.0044	1.49	337	3.18	0	0	22.4	11.0	2.08	-	-
0.0045	1.50	334	4.82	0	0	23.3	6.25	2.24	8.50	-

Table 10. (Continued)

$\frac{[Cl_2]}{[O_2]}$	$[Cl_2]$, Torr[a]	$[O_2]$, Torr	$[H_2CO]$, Torr	$[N_2]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	Φ{CO}	Φ{HCOOH}	$Φ\{CO_2\}$
0.0046	1.46	319	9.90	316	0	23.6	3.5	1.34	9.67	-
0.014	1.30	90	9.06	0	0	19.7	4.0	2.98	11.8	-
0.015	1.53	105	5.65	0	0	21.6	2.0	3.27	11.8	-
0.016	1.54	95	6.90	0	0	23.2	4.0	2.87	-	-
0.016	5.41	331	8.90	0	0	75.4	1.0	2.20	9.42	-
0.017	1.57	95.0	3.28	0	0	24.4	2.0	2.51	11.2	-
0.021	1.04	48.8	5.66	0	590	17.4	10.0	3.17	-	-
0.023	1.20	52.8	5.94	0	590	20.1	10.0	3.04	-	-
0.024	2.35	100	5.96	524	0	22.8	17.5	3.33	-	0.27
0.028	1.47	52.5	7.90	0	0	60.4	2.75	3.18	10.3	-
0.035	1.08	30.6	5.11	0	608	18.0	4.0	4.50	-	-
0.037	2.04	55.4	4.51	0	588	33.0	1.5	3.83	-	-
0.050	2.44	48.8	10.8	584	0	26.0	8.0	5.40	-	0.17
0.070	1.13	16.1	5.35	0	631	19.2	2.0	5.53	-	-
0.081	1.07	13.2	5.19	625	0	8.4	4.0	9.92	-	0.13
0.083	2.23	27.0	11.0	613	0	20.5	7.0	8.75	-	0.13

Table 10. (Concluded)

$\frac{[Cl_2]}{[O_2]}$	$[Cl_2]$, Torr[a]	$[O_2]$, Torr	$[H_2CO]$, Torr	$[N_2]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	Φ{CO}	Φ{HCOOH}	$Φ\{CO_2\}$
0.100	2.63	26.2	11.2	615	0	21.8	2.0	9.92	-	0.36
0.167	2.15	12.9	7.30	627	0	22.2	12.5	7.96	-	0.15
0.172	2.23	13.0	7.11	627	0	22.3	4.0	10.1	-	0.15
0.222	1.25	5.62	3.86	0	641	20.6	2.0	8.92	-	-
0.226	2.62	11.6	7.41	638	0	25.8	2.0	11.8	-	0.14
0.234	2.78	11.9	7.41	618	0	27.5	0.75	11.8	-	0.33
0.382	3.90	10.2	7.42	0	597	51.4	0.25	12.9	-	-
0.396	2.02	5.10	4.66	0	638	34.0	2.0	12.0	-	-
0.697	1.31	1.88	6.20	0	610	17.9	1.75	12.9	-	-
0.714	1.47	2.06	9.74	0	605	20.2	0.75	16.4	-	-
0.725	1.50	2.07	2.32	0	606	20.5	0.75	14.6	-	-
0.740	2.47	3.34	11.0	639	0	26.9	5.0	14.8	-	-
0.807	4.63	5.74	2.49	0	605	62.9	0.25	11.4	-	-

a) $[Cl_2] = [Cl_2]_{initial} - [CO]/4$.

Table 11. Product quantum yields in the photolysis of chlorine at 3660 A in the presence of O_2 and H_2CO at -7 ± 1°C. Pressures reported are at room temperature.

$[Cl_2]/[O_2]$	$[Cl_2]$, Torr^a	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	Φ{CO}	Φ{HCOOH}	$Φ\{CO_2\}$
0.0022	1.43	645	3.37	0	8.85	8.0	2.30	-	0.21
0.0022	1.33	609	9.80	0	8.33	8.0	3.27	11.5	-
0.0023	1.42	558	3.46	0	8.24	12.0	2.22	-	-
0.0023	1.45	628	2.94	0	9.28	8.0	2.84	9.33	0.11
0.0023	1.46	625	3.07	0	8.66	8.0	2.37	8.25	0.13
0.0023	1.41	603	9.80	0	9.37	8.0	3.46	8.66	0.03
0.0024	1.48	622	3.18	0	9.64	8.0	2.82	9.71	0.08
0.0034	1.16	338	7.65	0	7.19	16.0	3.48	11.8	0.04
0.013	4.24	330	10.1	0	26.5	3.0	-	11.2	0.03
0.017	1.13	65.2	6.94	275	7.18	60.0	3.17	6.77	0.15
0.020	1.32	65.4	6.17	276	8.35	17.1	3.75	10.8	0.08
0.020	1.37	67.6	9.50	350	9.37	5.0	4.12	13.7	0.06
0.021	1.47	68.9	6.34	269	13.3	10.0	3.40	9.46	0.09
0.023	1.51	66.2	9.72	262	9.69	16.0	3.94	11.2	0.07

Table 11 (Concluded)

$\frac{[Cl_2]}{[O_2]}$,	$[Cl_2]$, Torr[a]	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	Ia, mTorr/min.	Irradiation time, min.	$\Phi\{CO\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$
0.050	1.46	29.3	4.90	309	8.86	8.0	4.18	9.90	–
0.093	1.51	16.2	9.18	314	9.90	3.0	6.30	–	0.17
0.093	1.32	14.2	5.46	314	7.90	11.25	6.22	8.95	–
0.094	4.59	49.1	9.30	288	30.0	3.0	–	13.4	–
0.096	1.40	14.6	4.54	321	8.95	7.0	6.20	11.8	0.02
0.099	1.44	14.6	4.00	240	8.75	3.0	6.46	–	–
0.202	1.50	7.44	9.96	326	9.50	3.0	9.37	–	0.14
0.208	1.45	6.99	7.72	324	9.50	3.0	9.46	9.12	0.27
0.70	1.49	2.13	2.84	329	9.40	2.0	8.83	–	0.16
0.73	1.34	1.84	8.87	324	9.04	1.5	13.4	–	0.37
0.91	1.39	1.53	8.70	323	9.06	2.0	15.1	–	0.11

a) $[Cl_2] = [Cl_2]_{initial} - [CO]/4$.

spectrum may not be due only to HCOOH. In the room temperature runs, the HCOOH pressure could usually be measured at 2940, 1740, and 1213 $cm.^{-1}$. The three values obtained usually differed by only a few percent. At -7°C, when the Microspec was used instead of the IR 10, the 2940 $cm.^{-1}$ peak was usually impossible to measure accurately, and the 1213 $cm.^{-1}$ peak was sometimes obscurred by an "unknown" peak. Nevertheless, when the 1213 $cm.^{-1}$ peak could be used the pressure calculated from it was usually less than 10% different from the pressure calculated from the 1740 $cm.^{-1}$ peak. This suggests that there was no serious problem of spectral interference by some other compound.

The values of $\Phi\{CO_2\}$ are widely scattered, probably because of the low CO_2 yields in general, and the fact that there may be other sources of CO_2. $\Phi\{CO_2\}$ varies from 0.36 to 0.13 at room temperature and from 0.37 to 0.02 at -7°C.

It was observed that the H_2CO tended to polymerize on the walls of the reaction vessel. Thus irradiation done in the absence of added H_2CO also gave some products. In one run $\Phi\{CO_2\} = 0.49$ and $\Phi\{CO\} = 1.55$. However in the presence of gaseous H_2CO, all the chlorine atoms produced in the photolysis should react with gaseous H_2CO and the wall reaction is ignored (k for $Cl + CH_4 = (1.5 \pm 0.1) \times 10^{-13}$ $cm.^3/sec.$ (Garvin and Hampson, 1974) and the reaction of Cl with H_2CO should be faster.)

Some products were also found in dark runs. The yields presented in Tables 10 and 11 have been corrected accordingly. Usually the time necessary to add the gases to the cell and analyze the products was comparable to or greater than the irradiation time. Therefore no attempt was made to measure the dark yield per unit time.

At room temperature the dark correction for CO was 40 mTorr when the O_2 pressure was ∿ 600 Torr, 20 mTorr when the O pressure was ∿ 300 Torr, and no correction when the O_2 pressure was $\leq$ 100 Torr. The maximum correction was 30%, but the vast majority of the corrections were less than 10%.

The dark production of CO_2 at room temperature was ∿ 2 mTorr. The CO_2 measured after irradiation was usually between 10 and 20 mTorr, but the values ranged from 6.7 to 103 mTorr.

No products from the dark could be seen by ir at room temperature.

At -7°C, the dark production of CO when the Cl_2 pressure was ∿ 1.5 Torr, and the O_2 pressure was ∿ 600 Torr was ∿ 20 mTorr. The maximum correction was 11% and most were ∿ 5%. However, when the Cl_2 was ∿ 4.5 Torr, ∿ 50% to 70% of the CO found in the light runs was found in the dark runs. These CO yields were disregarded and are not reported here.

The CO_2 dark production at -7°C was ∿ 2 mTorr. The CO_2 measured after irradiation was usually less than 10 mTorr, but ranged from 3 to 63 mTorr.

No HCOOH was ever produced in the dark. However, there was another product which was sometimes seen in both light and dark runs at -7°C. Its largest absorption was at 1185 and 1175 cm.$^{-1}$, and it also absorbs at 2865, 2855, 2800, 2790, 2780, 980, 970, 965, 960, and 950 cm.$^{-1}$. (There may be more than one compound). No correlation could be found between this "unknown" and the experimental parameters or product quantum yields, nor was it seen at any other temperature. See Appendix II for more details.

RESULTS AT -37 ± 1°C AND -50 ± 1°C

The parameters were varied as follows:

-37 ± 1°C: $[O_2]$ from 548 to 1.74 Torr, $[Cl_2]$ from 1.50 to 1.29 Torr, $[H_2CO]$ from 10.5 to 1.86 Torr, $[Cl_2]/[O_2]$ from 0.753 to 0.0025, I_a from 11.5 to 9.20 mTorr/min., irradiation time from 10.0 to 3.0 min., and the total pressure from 556 to 330 Torr.

-50 ± 1°C, long irradiations: $[O_2]$ from 629 to 111 Torr, $[Cl_2]$ from 1.30 to 1.00 Torr, $[H_2CO]$ from 11.0 to 2.12 Torr, $[Cl_2]/[O_2]$ from 0.0090 to 0.0016, I_a from 11.4 to 4.70 mTorr/min., irradiation time constant at 60.0 min., and the total pressure from 673 to 123 Torr.

-50 ± 1°C, short irradiations: $[O_2]$ from 566 to 1.25 Torr, $[Cl_2]$ from 1.56 to 1.18 Torr, $[H_2CO]$ from 9.70 to 6.21 Torr, $[Cl_2]/[O_2]$ from 1.01 to 0.0023, I_a from 15.7 to 7.92 mTorr/min., irradiation time from 13.0 to 3.0 min., and the total pressure from 615 to 339 Torr.

At -37°C, the dark production of CO was less than 5 mTorr when the Cl_2 pressure was $\sim$ 1.5 Torr and the O_2 pressure was less than 80 Torr.

The following trends can be observed in the product quantum yields at -50 ± 1°C listed in Table 12.

1) $\Phi\{CO\}$ decreases with increasing irradiation time.

2) $\Phi\{HCOOH\}$ decreases with increasing irradiation time.

3) $\Phi\{CO_2\}$ increases with increasing irradiation time.

4) $\Phi\{CO\} \sim 4$ for all $[Cl_2]/[O_2]$ at short irradiation times.

5) $\Phi\{HCOOH\}$ is less than at room temperature.

(The values listed for $\Phi\{HCOOH\}$ are uncertain because of the inaccuracy in measuring such small amounts of HCOOH. However, there is little doubt of observation 5.)

Table 12. Product quantum yields in the photolysis of chlorine at 3660 A in the presence of O_2 and H_2CO at −37 ± 1°C and −50 ± 1°C. Pressures reported are at room temperature.

$[Cl_2]$, / $[O_2]$	$[Cl_2]$, Torr	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	$\Phi\{CO\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$
				−37 ± 1°C, Short Irradiations					
0.0025	1.39	548	6.23	0	10.3	10.0	3.15	5.6	0.30
0.019	1.47	76.6	6.52	262	11.5	3.0	3.29	9.0	0.17
0.020	1.46	74.6	1.86	256	9.60	5.0	3.37	10.0	0.06
0.055	1.40	25.6	10.5	309	9.95	5.0	4.78	11.0	0.20
0.058	1.44	25.0	6.36	306	10.6	5.0	4.87	11.1	0.08
0.062	1.50	24.1	6.59	303	11.0	5.0	4.13	10.3	0.13
0.093	1.42	15.3	6.80	313	10.4	5.0	4.58	9.6	0.05
0.191	1.42	7.45	6.65	317	10.4	5.0	6.83	11.1	0.04
0.209	1.43	6.84	2.03	320	9.87	4.0	3.93	7.7	0.05
0.246	1.47	5.98	2.06	329	10.6	4.0	4.31	8.6	0.04
0.276	1.48	5.36	7.21	362	10.7	5.0	7.29	10.9	0.09
0.390	1.35	3.46	6.62	328	9.72	3.0	7.16	8.8	0.24
0.724	1.29	1.78	6.76	334	9.20	4.0	10.7	8.3	0.04
0.753	1.31	1.74	7.29	339	9.99	3.0	9.61	7.1	0.40
				−50 ± 1°C, Irradiation Time = 60 min.					
0.0016	1.03	629	3.87	0	5.64	60.0	<0.019	0.62	1.38
0.0018	1.07	604	9.72	0	5.43	60.0	0.305	1.91	1.68

Table 12. (Continued)

$[Cl_2]/[O_2]$	$[Cl_2]$, Torr	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	Φ{CO}	Φ{HCOOH}	$Φ\{CO_2\}$
0.0020	1.02	513	9.88	0	6.12	60.0	0.264	1.71	1.43
0.0020	1.14	560	6.16	0	4.70	60.0	0.431	1.53	-
0.0030	1.08	362	4.53	0	9.74	60.0	0.156	0.65	1.28
0.0035	1.30	369	2.12	0	11.4	60.0	<0.023	0.24	0.811
0.0037	1.23	337	6.62	0	10.6	60.0	<0.27	0.93	0.86
0.0077	1.00	129	10.2	533	5.31	60.0	0.354	1.63	1.71
0.0081	1.05	130	3.52	520	5.63	60.0	<0.09	0.83	-
0.0088	1.09	124	4.5	0	6.30	60.0	0.76	1.04	1.03
0.0090	1.00	111	11.0	0	5.55	60.0	1.16	1.36	1.18
					-50 ± 1°C, Short Irradiations				
0.0023	1.28	566	6.36	0	10.9	3.0	4.66	4.75	0.05
0.0024	1.30	554	9.10	0	7.92	13.0	3.66	3.51	-
0.0035	1.18	337	6.50	0	10.2	10.0	2.94	3.64	0.09
0.0036	1.24	337	6.44	0	9.0	3.0	4.70	4.55	0.07
0.0040	1.40	348	6.25	0	12.1	5.0	4.52	6.44	0.21
0.0041	1.38	335	9.70	0	10.9	3.0	5.44	3.36	0.04
0.0046	1.52	328	9.60	0	13.3	3.25	2.68	2.26	0.12
0.018	1.33	73.5	6.55	271	15.1	3.0	2.02	1.82	-
0.019	1.40	73.7	6.27	264	11.4	3.0	3.78	2.87	0.10
0.057	1.43	25.3	6.64	308	12.7	3.0	3.17	1.89	0.04

Table 12. (Concluded)

$\frac{[Cl_2]}{[O_2]}$,	$[Cl_2]$, Torr	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	$\Phi\{CO\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$
0.073	1.43	19.5	6.44	317	13.2	3.0	3.24	3.52	0.03
0.095	1.39	14.6	6.52	323	12.3	3.0	3.26	3.00	0.03
0.192	1.36	7.1	6.66	327	13.4	3.0	3.27	5.80	0.03
0.419	1.56	3.72	6.21	328	15.7	3.0	3.94	2.80	0.03
0.660	1.30	1.98	7.78	604	8.05	4.5	5.53	-	-
0.690	1.40	2.03	6.56	330	13.9	3.0	4.45	2.34	0.04
0.763	1.48	1.94	6.91	330	12.3	3.0	5.06	1.95	0.14
1.01	1.27	1.25	6.96	333	13.4	3.0	5.95	2.44	0.02

The results at -37 ± 1°C, listed in Table 12, are somewhat intermediate between those at -50 ± 1°C and room temperature. $\Phi\{HCOOH\}$ is independent of $[Cl_2]/[O_2]$, but the value is the same as the low $[Cl_2]/[O_2]$ values at -7°C and toom temperature. $\Phi\{CO\}$ increases slightly with increasing $[Cl_2]/[O_2]$, but not as rapidly as at room temperature, and its value at low $[Cl_2]/[O_2]$ is between those at room temperature and -50°C. $\Phi\{CO_2\}$ is more or less comparable to those at the higher temperatures.

DISCUSSION OF RESULTS AT ROOM TEMPERATURE AND $-7 \pm 1°C$

At 3660 A only the Cl_2 absorbs and it photodecomposes to give chlorine atoms which can then react with H_2CO.

$Cl_2 + h\nu \rightarrow 2Cl$ 3660 A   Rate = I_a 39

$Cl + H_2CO \rightarrow HCl + HCO$ 38

The HCO can react with O_2 or Cl_2.

$HCO + O_2\ (+M) \rightarrow HCO_3\ (+M)$ 33a

$HCO + O_2 \rightarrow CO + HO_2$ 33b

$HCO + O_2 \rightarrow CO_2 + OH$ 33c

$HCO + Cl_2 \rightarrow HClCO + Cl \rightarrow HCl + CO + Cl$ 40a

Reaction 33a should be pressure dependent at sufficiently low pressures, but at the pressures used in these studies, there is no indication of a total pressure effect so reaction 33a can be considered to be in the second order region.

The fates of the species produced from the HCO reactions are as follows: HCO_3 ultimately gives HCOOH. The favored route is

$HCO_3 + H_2CO \rightarrow HCO_3H + HCO$ 41

$HCO_3H \rightarrow HCOOH + (1/2)O_2$ on the wall   42

There is no direct evidence for reaction 41. Performic acid was never seen in this study. However it was always at least 45 minutes after the run that the ir spectrum was taken. It was assumed that all the HCO_3H decomposed in that time.

It has been shown that for the analogous oxidation of CH_3CHO, the sole initial acid is peracetic acid and it decomposes quantitatively to CH_3COOH (Weaver, Meagher, Shortridge, and Heicklen, 1975). The same behavior for HCO oxidation is expected with the conversion of HCO_3H to

HCOOH being even faster. Performic acid has been observed to be much less stable than peracetic acid, its decomposition being appreciable even at 0°C (Giguère and Olmos, 1952). Bone and Gardner (1936) however, in the thermal oxidation of H_2CO reported seeing peroxides, "one which behaved as though it were the performic acid," and formic acid. Formic acid has also been seen by many other workers in the photooxidation of H_2CO (Carruthers and Norrish, 1936a; Horner, Style, and Summers, 1954; Horner and Style, 1954; Style and Summers, 1946; Hanst and Calvert, 1959).

The HO_2 radical is removed by

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad 43$$

which proceeds with a rate coefficient of $k_{43} = 3.3 \times 10^{-12}$ cm.^{3}/sec. (Garvin and Hampson, 1974). The possible competing reaction

$$HO_2 + H_2CO \rightarrow H_2O_2 + HCO \qquad 44$$

is so slow ($k_{44} = 1.7 \times 10^{-12} \exp\{-8000/RT\}$ cm.^{3}/sec. (Garvin and Hampson, 1974) that it never makes more than an 8% contribution to $\Phi\{CO\}$ and usually much less. Since this is within the experimental uncertainty of the CO measurements, this reaction can be ignored.

The OH radical reacts rapidly with H_2CO.

$$OH + H_2CO \rightarrow H_2O + HCO \qquad 45$$

The rate coefficient for the reaction of Cl with CH_4 is $k = (1.5 \pm 0.1) \times 10^{-13}$ cm.^{3}/sec. (Garvin and Hampson, 1974). The rate coefficient k_{38} is probably larger. The rate coefficient $k_{45} = 1.4 \times 10^{-11}$ cm.^{3}/sec. (Garvin and Hampson, 1974). These rate coefficients are so large that competing reactions can be ignored. Even the reaction of Cl with O_2 plays no role since it is highly reversible (Watson, 1974).

$Cl + O_2 \rightleftarrows ClO_2$ 46

Finally the HClCO species is known to decompose readily to HCl and CO (Sanhueza, Hisatsune, and Heicklen, 1975). To check that all the HClCO was decomposing before analysis at room temperature, the gases of two runs were allowed to remain in the photolysis cell for an hour after photolysis before the analysis was started. Normally, the time between the end of photolysis and the start of the analysis was less than one minute. If all the HClCO were not decomposing, these two runs should contain an excess of CO relative to the others. They did not. At -7°C and -37°C, the gases were permitted to warm for ∿ 25 minutes after photolysis before the analysis was started. At -50°C, this time varied from 40 to 80 minutes, but most were ∿ 60 minutes.

The above mechanism predicts that $\Phi\{CO\}$ should continually increase with increasing $[Cl_2]/[O_2]$. Figures 11 and 12 show plots of $\Phi\{CO\}/2$ vs. $[Cl_2]/[O_2]$ at room temperature and -7 ± 1°C, respectively, and it appears that an upper limiting value is reached at each temperature. Consequently an additional terminating step is needed which is important at high $[Cl_2]/[O_2]$ ratios but which is independent of I_a or any of the individual reactant pressures. The indicated step is the analogous one to reaction 33a.

$HCO + Cl_2\ (+M) \rightarrow HCOCl_2\ (+M) \rightarrow$ termination 40b

The production of formyl chloride from the photolysis of Cl_2 in the presence of formaldehyde was shown by Krauskopf and Rollefson (1934). They reported quantum yields of ∿ 10^4 at total pressures of 30 to 60 Torr at 80°C. Presumably, the product of the $HCO + Cl_2$ termination reaction postulated here is unstable under these conditions

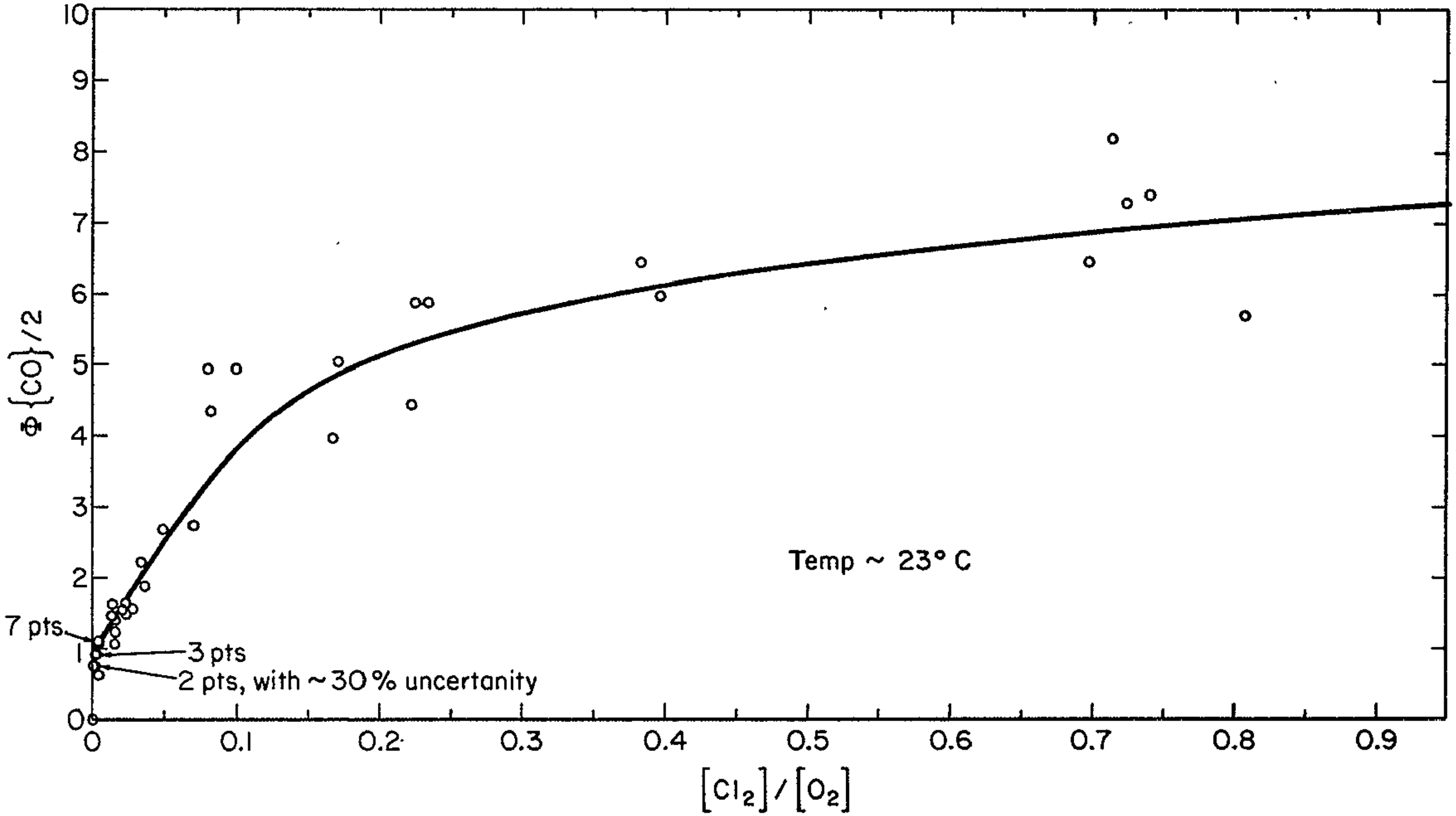


Figure 11. Plot of $\Phi\{CO\}/2$ vs. $[Cl_2]/[O_2]$ in the photolysis of Cl_2 in the presence of O_2 and H_2CO at room temperature (∿ 23°C).

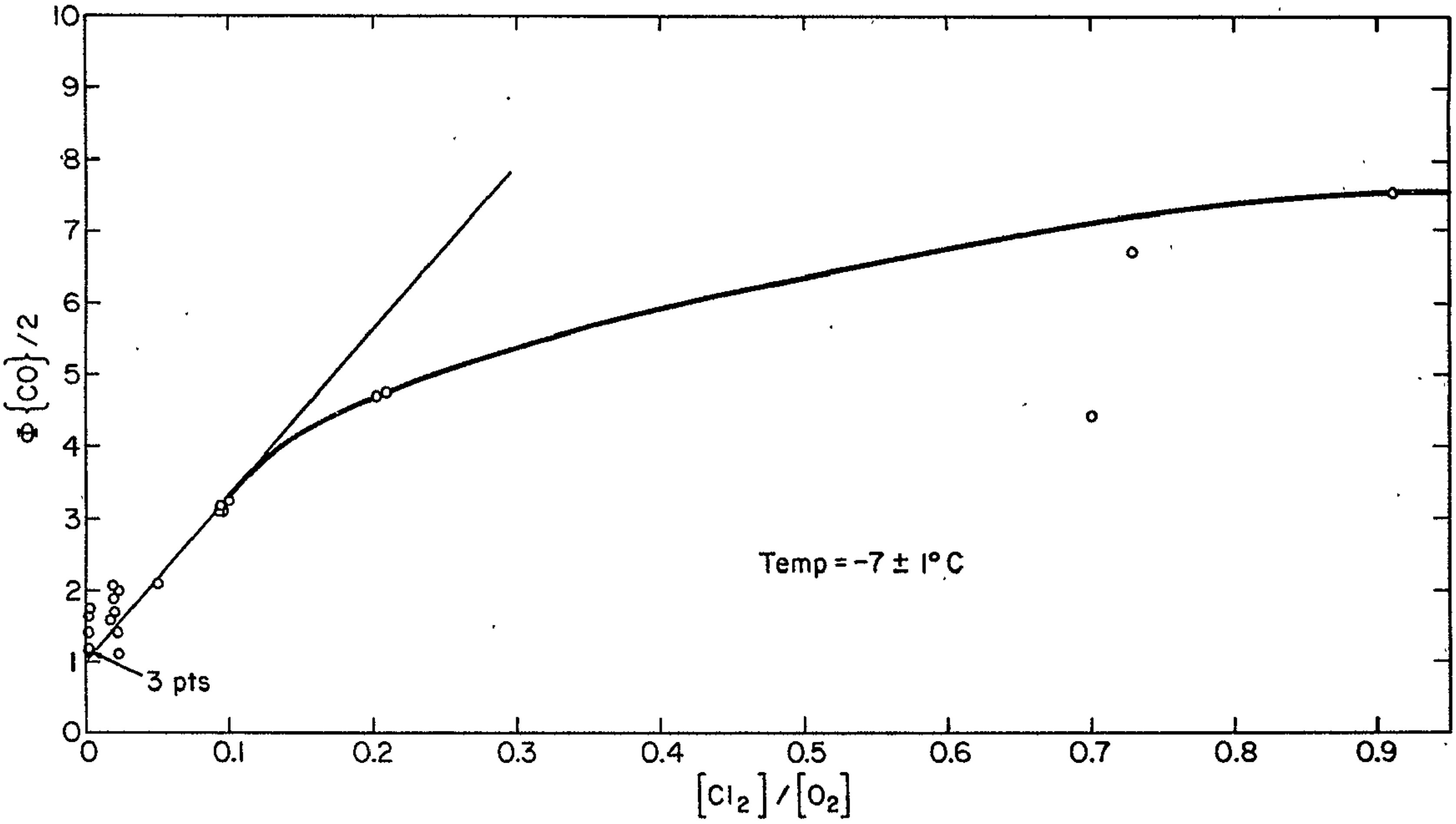


Figure 12. Plot of $\Phi\{CO\}/2$ vs. $[Cl_2]/[O_2]$ in the photolysis of Cl_2 in the presence of O_2 and H_2CO at −7 ± 1°C.

and thus would not be an effective termination reaction, allowing larger quantum yields to be obtained in their system.

The mechanism now predicts that at high values of $[Cl_2]/[O_2]$, the upper limiting value of $\Phi\{CO\}/2$ should be equal to k_{40a}/k_{40b}. The data points in Figure 11 indicate an upper limiting value of ∿ 7.5 for $\Phi\{CO\}/2$ at high values of $[Cl_2]/[O_2]$. In Figure 12, the data are much more limited, but the same upper limiting value for $\Phi\{CO\}/2$ is not unreasonable, and this is assumed to be the case. Application of the steady-state hypothesis to the mechanism gives

$$[HCO] = 2I_a/(k_{33b}[O_2] + k_{40b}[Cl_2]) \qquad \text{X}$$

and the quantum yields of each of the measured products should follow the rate laws:

$$\frac{\Phi\{CO\} - 2}{2k_{40a}/k_{40b} - \Phi\{CO\}} = \frac{k_{40b}[Cl_2]}{k_{33b}[O_2]} \qquad \text{XI}$$

$$\Phi\{HCOOH\}^{-1} = \frac{k_{33b}}{2k_{33a}} + \frac{k_{40b}[Cl_2]}{2k_{33a}[O_2]} \qquad \text{XII}$$

$$\Phi\{CO_2\}^{-1} = \frac{k_{33b}}{2k_{33c}} + \frac{k_{40b}[Cl_2]}{2k_{33c}[O_2]} \qquad \text{XIII}$$

Figure 13 shows log-log plots of the left-hand-side of equation XI vs. $[Cl_2]/[O_2]$ at room temperature and −7 ± 1°C where the value of k_{40a}/k_{40b} ∿ 7.5 is used to evaluate the ordinate. In Figure 13 the points at low and high values of $[Cl_2]/[O_2]$ are inaccurate because they are computed from small differences of similar numbers. Since the slope of the log-log plot is forced to unity, the dashed lines represent outside reasonable limits for the points at $[Cl_2]/[O_2]$ between 0.02 and 0.6. From these lines outside limits to k_{40b}/k_{33b} are found to be 4 and 13. The solid line represents the best fit to the data and gives $k_{40b}/k_{33b} = 6$. Thus $k_{40b}/k_{33b} = 6$ (+7, −2).

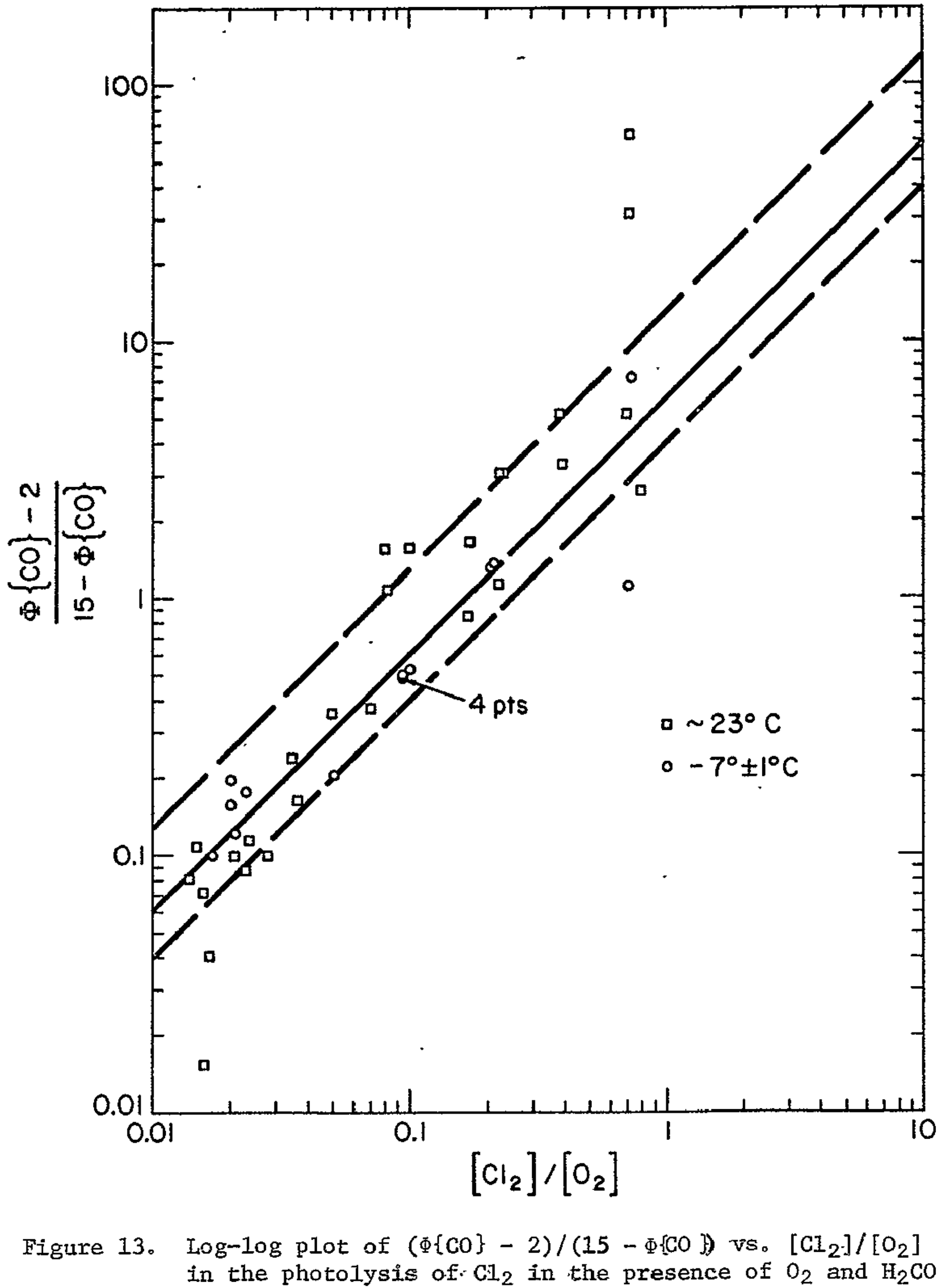


Figure 13. Log-log plot of $(\Phi\{CO\} - 2)/(15 - \Phi\{CO\})$ vs. $[Cl_2]/[O_2]$ in the photolysis of Cl_2 in the presence of O_2 and H_2CO at room temperature (∿ 23°C) and −7 ± 1°C.

All of the data obtained for $\Phi\{HCOOH\}$ were at low values of $[Cl_2]/[O_2]$, where the last term in equation XII is negligible. The values for $\Phi\{HCOOH\}$ generally lie between 8 and 12 at -7°C and room temperature, so that $k_{33a}/k_{33b} = 5 \pm 1$. The pressure ranged from 704 to 62 Torr at room temperature and from 688 to 344 Torr at -7°C.

The data for CO_2 were badly scattered but at both temperatures they never exceeded 0.38, so that the upper limiting value for k_{33c}/k_{33b} is 0.19 at both temperatures. This is an extreme upper limit and the true value is probably much closer to 0.0 than 0.19. The low yield of CO_2 is in agreement with work done by Carruthers and Norrish (1963a), Hroner, Style, and Summers (1954), and Style and Summers (1946), who found low yields of CO_2 in the photochemical oxidation of formaldehyde.

The rate coefficient ratios obtained in this study are summarized in Table 13.

The lack of pressure dependence on the ratio k_{33a}/k_{33b} is noteworthy. Reaction 33a can be written in the following elementary steps.

$HCO + O_2 \rightarrow HCO_3^*$ k_{33a1}

$HCO_3^* \rightarrow HCO + O_2$ k_{33a2}

$HCO_3^* + M \rightarrow HCO_3 + M$ k_{33a3}

The rate of HCO_3 production under steady state conditions is expressed in equation XIV.

$$\frac{d[HCO_3]}{dt} = \frac{k_{33a1}\, k_{33a3}\, [HCO][O_2][M]}{k_{33a2} + k_{33a3}[M]} \qquad \text{XIV}$$

At sufficiently high pressures, $k_{33a3}[M] >> k_{33a2}$, equation XIV reduces to equation XV, and the reaction proceeds as a second order process with a rate constant of k_{33a1}.

Table 13. Summary of rate coefficient ratios at room temperature and -7 ± 1°C, and for total pressures of 704 to 62 Torr and 688 to 344 Torr, respectivley.

k_{40b}/k_{33b}	6(+7, -2)
k_{33a}/k_{33b}	5 ± 1
k_{33c}/k_{33b}	$\leq$ 0.19
k_{40a}/k_{40b}	$\sim$ 7.5

$$\frac{d[HCO_3]}{dt} = k_{33a1}[HCO][O_2] \qquad \text{XV}$$

At sufficiently low pressures, $k_{33a3}[M] << k_{33a2}$, equation XIV reduces to equation XVI, and the reaction proceeds as a third order process with a rate constant of $k_{33a1}k_{33a3}/k_{33a2}$.

$$\frac{d[HCO_3]}{dt} = \frac{k_{33a1}\ k_{33a3}[HCO][O_2][M]}{k_{33a.}} \qquad \text{XVI}$$

In this study $d[HCO_3]/dt$(= $d[HCOOH]/dt$)was measured if the assumption that all HCO_3 produce HCOOH is valid. Since there was no pressure dependence seen on the ratio k_{33a}/k_{33b}, the implication is that $k_{33a}/k_{33b} = k_{33a1}/k_{33b}$ in the pressure range studied (704 to 62 Torr at room temperature).

Washida, Martinez, and Bayes (1974) also studied reaction 33 at room temperature. They monitored the HCO concentration using a cylindrical fast-flow reactor which was coupled to a photoionization mass spectrometer. Since they only monitored the HCO concentration and no products, the value they obtained for k_{33} cannot be separated unambigously into its component parts from reactions 33a, 33b, and 33c. As was seen above, reaction 33a should become pressure dependent at low pressures. Because they saw no pressure dependence over the pressure range of 1.5 to 5 Torr, they concluded that reaction 33a was unimportant under their conditions. (They also regarded reaction 33c as unimportant, based on the low yield of CO_2 found by others in the photooxidation of formaldehyde.)

Thus, there seems to be a contradiction here. The present work suggesting that reaction 33a is important because formic acid is formed, and the work of Washida _et al_. suggesting that reaction 33a isn't important because of the lack of pressure dependence. (The possibility of reaction 33a remaining second order down to a pressure of 1.5 Torr seems very unlikely.)

Using the findings of the present work, it is possible to make reasonable predictions of the pressure dependency of reaction 33 under the conditions of Washida et al.

Suppose reaction 33a has a half quenching pressure of ∿ 40 Torr and this was not seen in the present work because of the scatter. (Only one run was done at 62 Torr.) That is, at ∿ 40 Torr, reaction 33a is half as important as it is at infinite pressure. If the value of 5 (from the range of 4 to 6) is chosen for the ratio of k_{33a}/k_{33b} at infinite pressure, the pseudo-second order rate constant for equation 33a, k_{33a}', can be written as shown in equation XVII.

$$k_{33a}' = \frac{2.5}{40}[M]k_{33b} \qquad \text{XVII}$$

This expression should be good up to at least 40 Torr. The value of $k_{33} = k_{33a}' + k_{33b}$ measured by Washida et al. at 1.5 Torr would be $(2.5/40)(1.5)k_{33b} + k_{33b} = k_{33b}(.09 + 1.0)$, and at 5 Torr would be $(2.5/40)(5)k_{33b} + k_{33b} = k_{33b}(.31 + 1.0)$. Therefore, the measured rate constant would only change by 20% in going from 1.5 to 5 Torr. If the half quenching pressure were 25 Torr (in which case the observation of pressure independence at 62 Torr could be correct), the value would change by 30%, and a half quenching pressure of 15 Torr would result in a 46% change. These changes are small compared to the change of 333% which would be expected if reaction 33b did not occur. Thus, it may be that Washida et al. overlooked a change of 20 or 30%. (There are some results presented in Chapter III that suggest that the change is even less than 10%). If this is so, there is no contradiction between their results and these.

DISCUSSION OF RESULTS AT -37 ± 1°C AND -50 ± 1°C

As was stated in RESULTS of this chapter, the following trends were observed in the product quantum yields at -50 ± 1°C listed in Table 12.

1) $\Phi\{CO\}$ decreases with increasing irradiation time.
2) $\Phi\{HCOOH\}$ decreases with increasing irradiation time.
3) $\Phi\{CO_2\}$ increases with increasing irradiation times.
4) $\Phi\{CO\} \sim 4$ for all $[Cl_2]/[O_2]$ at short irradiation times.
5) $\Phi\{HCOOH\}$ is less than at room temperature.

At -50°C there seems to be a correlation between the CO and HCOOH quantum yields and the initial H_2CO pressure. That is, the runs with lower initial H_2CO pressure usually have lower CO and HCOOH quantum yields. This suggests that the H_2CO is polymerizing in 60 minutes. No CO or HCOOH is produced after the H_2CO is polymerized, but the quantum yield was calculated on the assumption that HCOOH and CO were being produced the entire time. Thus the calculated CO and HCOOH quantum yields are too small. The calculated quantum yields of CO_2 are too large. When the H_2CO is gone, the Cl atoms react with the polymer to produce CO_2. Thus the CO_2 which was assumed to have come from reaction 33c actually came from the polymer. This explains the first three observations.

The mechanism used for the room temperature and -7°C work was modified to fit the experimentally observed trends at -50°C and short irradiation times.

Reactions 39, 38, 33a, and 33b were kept.

$$Cl_2 + h\nu \rightarrow 2Cl \quad 3660\ A \qquad 39$$

$$Cl + H_2CO \rightarrow HCl + HCO \qquad 38$$

$HCO + O_2$ (+M) → HCO_3 (+M) 33a

$HCO + O_2 \rightarrow CO + HO_2$ 33b

Reaction 33c was dropped because of the low CO_2 quantum yields.

$HCO + O_2 \rightarrow CO_2 + OH$ 33c

Reactions 40a and 40b were dropped because the CO and HCOOH quantum yields show no dependence on the $[Cl_2]/[O_2]$ ratio (observation 4), which these reactions would require.

$HCO + Cl_2 \rightarrow HClCO + Cl \rightarrow HCl + CO + Cl$ 40a

$HCO + Cl_2$ (+M) → $HCOCl_2$ (+M) → termination 40b

Reaction 41 is also included. It is believed to be slow enough for reaction 47 to compete.

$HCO_3 + H_2CO \rightarrow HCO_3H + HCO$ 41

$HCO_3 + HCO_3 \rightarrow 2OH + 2CO + O_2$ 47

A reaction like 47 is required for the quantum yield of CO to rise above 2 (observation 4). Reaction 47 may not be elementary. Reaction 43 is known to have a small activation energy, ∿ 0.5 kcal./mole, so it will still be important at -50°C. Reaction 44 however, has an activation energy of 8 kcal./mole (Garvin and Hampson, 1974). This reaction was unimportant at room temperature, and will thus be even less important here.

$2HO_2 \rightarrow H_2O_2 + O_2$ 43

$HO_2 + H_2CO \rightarrow H_2O_2 + HCO$ 44

If reaction 47 is important, reaction 45 will be important also.

$OH + H_2CO \rightarrow H_2O_2 + HCO$ 45

Reaction 46 is again ignored because the product quantum yields seem to be independent of the $[O_2]/[H_2CO]$ ratio.

$$\mathrm{Cl} + \mathrm{O_2} \rightleftarrows \mathrm{ClO_2} \qquad 46$$

Reaction 42 is kept. It may occur on warming the cell before analysis.

$$\mathrm{HCO_3H} \rightarrow \mathrm{HCOOH} + (1/2)\mathrm{O_2} \text{ on the wall} \qquad 42$$

The following expressions were obtained from the above mechanism for the CO and HCOOH quantum yields.

$$\Phi\{\mathrm{CO}\} = 2 + \frac{4k_{33a}}{k_{33b}(2+\varepsilon)} \qquad \mathrm{XVIII}$$

$$\Phi\{\mathrm{HCOOH}\} = \frac{2k_{33a}}{k_{33b}(1+2/\varepsilon)} \qquad \mathrm{XIX}$$

$$\varepsilon = \frac{k_{41}[\mathrm{H_2CO}]}{k_{48}[\mathrm{HCO_3}]} \qquad \mathrm{XX}$$

The above expressions were solved simultaneously for k_{33a}/k_{33b} for the runs done at -50°C and short irradiation times. Values obtained for 17 runs ranged from 0.9 to 4.5, with 8 of the runs yielding values between 2.1 and 2.6. The average of the 17 runs was 2.6. This is lower than the value of 5 ± 1 obtained at the warmer temperatures. The same or a larger value was expected because the activation energy of reaction 33a, a simple radical addition reaction, should be less than the activation energy of reaction 33b which requires the breaking of a bond. However, no reaction was added to the mechanism to account for observation 5, and the lower calculated value is a consequence of less HCOOH being produced at -50°C. The inclusion of reaction 48 would explain observation 5 without requiring a reduction in the value of k_{33a}/k_{33b} ratio. This reaction would be dependent

$$\mathrm{HCO_3} + \mathrm{HO_2} \rightarrow \mathrm{HCO_3H} + \mathrm{O_2} \qquad 48$$

on various reactant pressures, which might account for the rather wide range of values obtained for the k_{33a}/k_{33b} ratio just presented. Unfortunately, the rate relations obtained from the above mechanism (with reaction 48) is too complex and contains too many unknowns to solve for k_{33a}/k_{33b}, but the observations at -50°C have been qualatatively explained.

The results at -37°C can be explained by appropriate changes in the importance of some of the reactions between room temperature and -50°C. The fact that $\Phi\{HCOOH\}$ is the same at -37°C as at -7°C and room temperature at low $[Cl_2]/[O_2]$ means that k_{48} is unimportant relative to k_{41} at these temperatures. The independence of $\Phi\{HCOOH\}$ to the $[Cl_2]/[O_2]$ ratio suggests that k_{40b} is unimportant (see equation XII).

Figure 14 shows a plot of $\Phi\{CO\}/2$ vs. $[Cl_2]/[O_2]$ at -37 ± 1°C. The straight line was obtained by the method of least squares, and its correlation coefficient is 0.92. There is no definite fall off in the data points at high $[Cl_2]/[O_2]$, as there was in Figures 11 and 12. This, as well as the fact that no evidence of reaction 40b was found at -50°C farther supports the above conclusion that k_{40b} is unimportant.

The intercept in Figure 14 is significantly greater than 1.0. This extra CO is due to reaction 47 increasing in importance relative to reaction 41 as the temperature goes down.

The dependence of $\Phi\{CO\}/2$ on the $[Cl_2]/[O_2]$ ratio is due to reaction 40a. The slope of the line in Figure 14 is 4.45. The initial slope of the line in Figure 11 is $\sim$ 38. This lower value at -37°C reflects the lower importance of reaction 40a relative to reaction 33b at the lower temperature. This is also supported by the fact that no evidence of reaction 40a was found at -50°C.

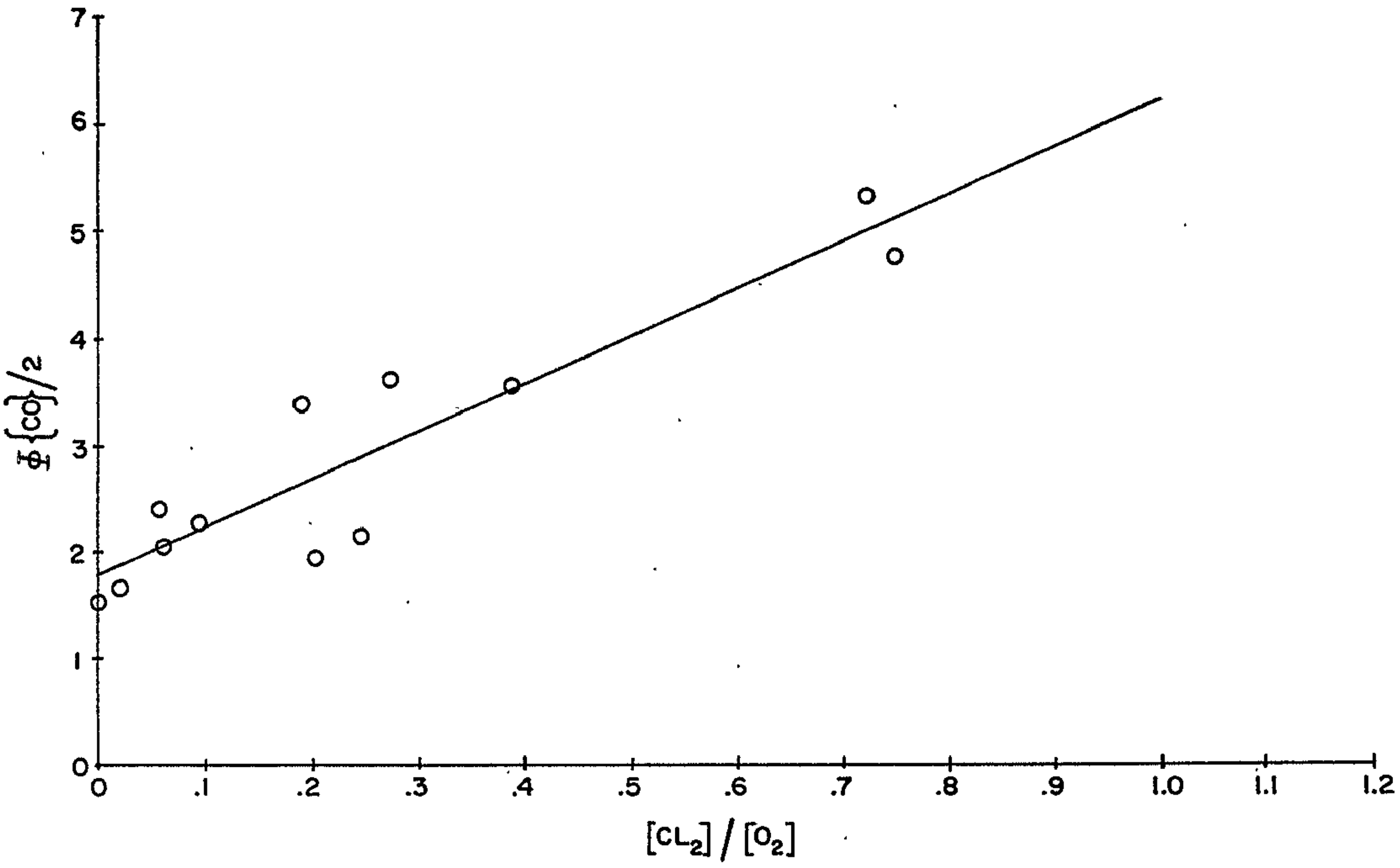


Figure 14. Plot of Φ{CO}/2 vs. $[Cl_2]/[O_2]$ in the photolysis of Cl_2 in the presence of O_2 and H_2CO at -37 ± 1°C.

The low quantum yields of CO_2 are due to the unimportance of reaction 33c compared to reactions 33a and 33b at all these temperatures.

CHAPTER III

THE PHOTOCHEMICAL OXIDATION OF FORMALDEHYDE.

INTRODUCTION

Photochemical smog formation has been a serious problem for many years. Although it is not limited to Los Angeles, it has been most thoroughly studied and documented there. Common complaints are objectionable odor, decreased visibility, eye irritation, and crop damage. It is also believed to be detrimental to human health.

Photochemical smog is formed when nitric oxide and unburned hydrocarbons which are emitted into the air from the exhaust of automobiles are exposed to sunlight. The nitric oxide and unburned hydrocarbons are themselves relatively innocuous. It is their photochemically produced reaction products which are harmful. Important among these is ozone, which is observed both in Los Angeles and in laboratory "smog chambers", not to accumulate until most of the NO present has been oxidized to NO_2. Thus, it is seen that the conversion of NO to NO_2 plays a very important role in photochemical smog formation and that a complete understanding of its mechanism is very desirable.

The termolecular reaction

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

has been recognized as being too slow to account for the conversion of NO to NO_2 in polluted atmospheres (Heicklen and Cohen, 1968). Heicklen, Westberg, and Cohen (1969) suggested a free radical mechanism to explain the conversion of NO to NO_2. Their mechanism consists of the three interrelated chains shown below with OH as the chain carrier.

The first chain develops from the OH radical attack on carbon monoxide.

$OH + CO \rightarrow CO_2 + H$ 15

$H + O_2 + M \rightarrow HO_2 + M$ 50

$HO_2 + NO \rightarrow NO_2 + OH$ 51

The overall reaction is:

$CO + NO + O_2 \rightarrow CO_2 + NO_2$ 52.

The second chain develops from the OH attack on alkenes. For isobutene the reactions are:

$C_4H_8 + OH \rightarrow C_4H_8OH$ 53

$C_4H_8OH + O_2 \rightarrow C_4H_8(OH)O_2$ 54

$C_4H_8(OH)O_2 + NO \rightarrow C_4H_8(OH)O + NO_2$ 55

$C_4H_8(OH)O \rightarrow C_3H_6O + CH_2OH$ 56

$CH_2OH + O_2 \rightarrow CH_2(OH)O_2$ 57

$CH_2(OH)O_2 + NO \rightarrow CH_2(OH)O + NO_2$ 58

$CH_2(OH)O \rightarrow CH_2O + OH$ 59

The overall reaction is

$C_4H_8 + 2NO + 2O_2 \rightarrow C_3H_6O + CH_2O + 2NO_2$ 60

The third chain develops from the OH attack on alkanes. For butane the reactions are:

$C_4H_{10} + OH \rightarrow C_4H_9 + H_2O$ 61

$C_4H_9 + O_2 \rightarrow C_4H_9O_2$ 62

$C_4H_9O_2 + NO \rightarrow C_4H_9O + NO_2$ 63

$C_4H_9O + O_2 \rightarrow C_4H_8O + HO_2$ 64

$HO_2 + NO \rightarrow NO_2 + OH$ 51

The overall reaction is:

$C_4H_{10} + 2NO + 2O_2 \rightarrow C_4H_8O + H_2O + 2NO_2$ 65

Thus, it is seen that many NO molecules can be oxidized to NO_2 by one OH radical.

There are a variety of ways in which these chains can be started. Heicklen, Westberg, and Cohen (1969) believed the hydrocarbons were the source of the initially produced OH.

Levy (1972) reviews several possible sources of OH.

$H_2O_2 + NO_2 \rightarrow HNO_3 + OH$ 66

$HNO_3 + h\nu \rightarrow OH + NO_2$ 67

$HNO_3 + O \rightarrow OH + NO_3$ 68

$H_2O_2 + NO \rightarrow HNO_2 + OH$ 69

$HNO_2 + h\nu \rightarrow NO + OH$ 70

$HNO_2 + O \rightarrow OH + NO_2$ 71

$O(^1D) + H_2O \rightarrow 2OH$ 72

$H_2O_2 + h\nu \rightarrow 2OH$ 73

$CH_3OOH + h\nu \rightarrow CH_3O + OH$ 74

Hydroxyl radicals are also produced by reaction 51. Thus, HO_2 radicals may be an important source of OH radicals. Calvert, Kerr, Demerjian, and McQuigg (1972) have pointed out that the photolysis of formaldehyde may be a significant source of HO_2 radicals in most urban atmospheres which are high in auto-exhaust pollution.

$CH_2O + h\nu \rightarrow HCO + H \quad \text{Rate} = \alpha I_a$ 75

$CH_2O + h\nu \rightarrow H_2 + CO \quad \text{Rate} = \beta I_a$ 76

$H + O_2 + M \rightarrow HO_2 + M$ 77

$HCO + O_2 \rightarrow CO + HO_2$ 33b

$HCO + O_2 \ (+M) \rightarrow HCO_3 \ (+M)$ 33a

Thus, it is seen that the H atoms and some of the HCO radicals produced in the photolysis of formaldehyde are converted to HO_2.

This study was undertaken to measure the relative importance of reactions 75 and 76 as a function of wavelength, temperature, I_a, and air pressure, so that a better estimate of the importance of formaldehyde photolysis in photochemical smog formation could be made. It was also hoped that the results would be beneficial in determining if formaldehyde photolysis could account for the disagreement between the measured and calculated volume mixing ratios for molecular hydrogen in the stratosphere and mesosphere (see the INTRODUCTION of Chapter I).

Some studies were made by other investigators of the photochemical oxidation of formaldehyde. However, no values were given for the quantum yields of reactions 75 and 76. The most applicable study was one done by Bufalini and Brubaker (1971). They photolyzed H_2CO and sometimes NO_2 in the ppm range in air at 23 ± 1°C. They suggested that the increase in hydrogen peroxide formed when formaldehyde was irradiated with sunlamps (λ = 3100 A) rather than blacklamps (λ = 3600 A) was indicative of reaction 75 being less important at the longer wavelengths.

Norrish and Kirkbride (1932) photolyzed formaldehyde at 110°C, and found ϕ_{76} to be 0.7, 1.1, and 0.9 in the spectral regions 3650-3340, 3130-3030, 2650-2540 A respectively. Thus, they concluded that reaction 75 was unimportant in each of these regions.

Gorin (1939) studied the photolysis of formaldehyde by iodine inhibition at 100°C and found $\phi_{75}/\phi_{76} > 10$ at 3130 A and 2537 A, and equal to 2.3 at 3650 A.

Calvert and Steacie (1951) photolyzed formaldehyde at 3130 A from 100 to 300°C and found reaction 75 to be unimportant.

Klein and Schoen (1956) photolyzed mixtures of H_2CO and D_2CO at 140°C and reported $\phi_{75}/\phi_{76} = 5$ at 3130 A and 0.5 to 5 at 3650 A.

DeGraff and Calvert (1967) photolyzed H_2CO and D_2CO in the presence of added olefin from 91 to 129°C. They found $\phi_{75}/\phi_{76} = 1.4$ at 3340 A, 1.1 at 3130 A, 0.23 at 2654 A, and 0.18 at 2537 A.

McQuigg and Calvert (1969) flashed H_2CO, D_2CO, HDCO, and mixtures of H_2CO and D_2CO with a xenon lamp employing various filters from 60 to 100°C. They found $\phi_{75}/\phi_{76} = 1$ at 3130 A and that the value of ϕ_{75}/ϕ_{76} decreases with increasing wavelength. The value of ϕ_{75}/ϕ_{76} at 3130 A is in good agreement with that of DeGraff and Calvert (1967), but the effect of wavelength on ϕ_{75}/ϕ_{76} was found to be opposite in the two studies.

Sperling and Toby (1973) photolyzed formaldehyde from 80 to 120°C and found $\phi_{75}/\phi_{76} = 4$ at 3130 A, 2 at 3340 A, and 0.4 at 3660 A.

Thus, not only are the values of ϕ_{75}/ϕ_{76} at 3130 A widely different, but there is also disagreement on the dependence of ϕ_{75}/ϕ_{76} on wavelength.

C·2

EXPERIMENTAL

Mixtures of H_2CO, N_2 and O_2 (usually dry air) were photolized with a Hanovia utility ultraviolet quartz lamp used in conjunction with the filters listed in Tables 14 and 15. Studies were done at 0°C, room temperature (∿ 22°C) and ∿ 40°C. Both of the vacuum lines described in the first two chapters were used. A silicone oil manometer, a second gas chromatograph (used to measure H_2), a 12 liter bulb (used for storing air), and another Ace glass gas inlet (used to admit formaldehyde, located close to the cell) were added to the mercury line mentioned in Chapter I.

The reactions were carried out in a single quartz cell 5 cm. in diameter and 10 cm. long which was wrapped in black paper. A 3130 A interference filter (Baird-Atomic) was used at room temperature, but the light intensity was not monitored. The products measured were CO, H_2, and CO_2.

The mercury free vacuum line described in Chapter II was used without modification. However, the cold box used previously was replaced by a water tight box which was used for controlling the temperature. Ice water was used at 0°C, and a thermostated heating bath was used at 40°C. The light intensity was monitored by an RCA 935 phototube. This is shown schematically in Figure 15.

Actinometry was done as described in Chapter II, except that formaldehyde was being photolized instead of chlorine. The extinction coefficients are listed in Table 16.

The formaldehyde was prepared and handled and the products were measured as described in Chapter II. The noncondensables were also

Table 14. Filters used in this study.

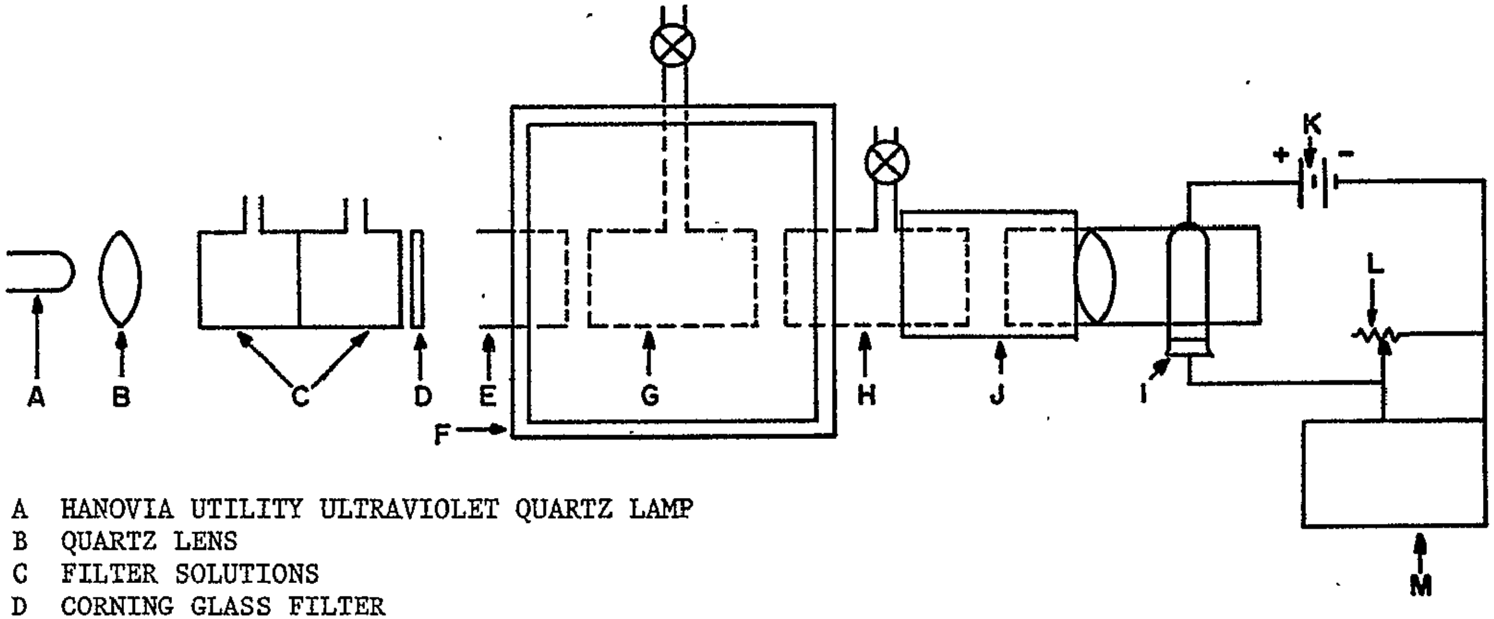
Filter No.	Filter
1	10 cm. 5×10^{-6} M K_2CrO_4, one Corning 0-53 and one Corning 7-54 glass filters
2	Filter No. 1 and three Corning 0-54 glass filters
3	Filter No. 1 plus one Corning 0-54 glass filter and one Kimwipe
4	5 cm. 5×10^{-4} M K_2CrO_4, 5 cm. 1.86×10^{-1} M $NiSO_4$, 2.6 cm. 9.42×10^{-3} M potassium biphthalate, and one Corning 7-54 glass filter[a]
5	10 cm. 6.25×10^{-5} M K_2CrO_4, 5 cm. 1.86×10^{-1} M $NiSO_4$, and one Corning 7-54 glass filter
6	10 cm. 4.5×10^{-4} M K_2CrO_4, 5 cm. 1.86×10^{-1} M $NiSO_4$, and one Corning 7-54 glass filter
7	3130 A interference filter (Baird-Atomic)

a) Calvert and Pitts, 1966, p. 732.

Table 15. Relative intensities of spectral lines transmitted by the filters used in this study. The intensities are assumed proportional to the response of an RCA 935 phototube used in conjunction with a Jarrell Ash monochromator, model number 82-410.

Wavelength	Filter No.[a]						
	1	2	3	4	5	6	7
2894 A	0.4	∿0	∿0	∿0	0.9	∿0	∿0
2967 A	4.8	∿0	∿0	∿0	9.4	∿0	∿0
3030 A	23.4	∿0	0.6	∿0	37.7	2.2	5.3
3130 A	100	100	100	100	100	100	100
3340 A	13.7	186	33.0	0.2	7.1	∿0	2.6
3660 A	16.1	290	42.4	∿0	0.1	∿0	∿0

a) See Table 14.



A	HANOVIA UTILITY ULTRAVIOLET QUARTZ LAMP
B	QUARTZ LENS
C	FILTER SOLUTIONS
D	CORNING GLASS FILTER
E	52 MM. TUBING WITH A QUARTZ WINDOW
F	POLYSTYRENE BOX WITH AN INNER COATING OF SILICONE RUBBER
G	QUARTZ REACTION CELL
H	EVACUATED CELL WITH QUARTZ WINDOWS
I	RCA 935 PHOTOTUBE
J	LIGHT TIGHT CYLINDRICAL HOUSING
K	45 VOLT "B" BATTERY
L	50,000 OHM VARIABLE RESISTOR
M	TEXAS 1 MILLIVOLT CHART RECORDER

Figure 15. The constant temperature box, optical system, and the phototube circuit.

Table 16. Extinction coefficients (to base 10, Torr^{-1} cm.$^{-1}$) measured with the filters used in this study.

Filter No.[a]	Extinction Coefficient	
	H_2CO	$CH_3N_2CH_3$
1	8.69×10^{-5}	1.50×10^{-4}
2	2.54×10^{-5}	1.64×10^{-4}
3	6.64×10^{-5}[b]	1.54×10^{-4}[b]
4	1.24×10^{-4}	1.60×10^{-4}
5	1.16×10^{-4}	1.38×10^{-4}
6	1.20×10^{-4}[c]	1.57×10^{-4}[c]
7	1.17×10^{-4}	1.53×10^{-4}

a) See Table 14.

b) Assumed to be a third of the way between the values for filters 1 and 2.

c) Assumed about equal to the values for filters 4 and 7 because of the similarity in their transmittance (See Table 15.).

analyzed for H_2 using a 12 foot long by 1/4 inch o. d. copper column packed with 60-80 mesh 5 A molecular sieves operated at room temperature. Argon was used as the carrier gas and the thermal conductivity detector was operated at 10.0 milliamps and at 0°C.

Air was taken from the lab and slowly passed over glass wool at -186°C and stored in a 12 liter bulb. Oxygen, nitrogen, and azomethane were prepared as described in Chapter II.

RESULTS FROM THE PHOTOLYSIS OF FORMALDEHYDE IN THE MERCURY VACUUM LINE.

Formaldehyde, in the presence of O_2 and N_2, (usually dry air) was photolized at room temperature with a medium pressure mercury lamp used in conjunction with a 3130 Å interference filter. The products measured were CO, CO_2, and H_2.

The parameters were varied as follows:

[M] from 4.9 to 751 Torr, [O_2] from 0.8 to 750 Torr, [N_2] from 3.0 to 529 Torr, [H_2CO] from 1.00 to 9.76 Torr, the irradiation time from 145 to 740 minutes, and I_a from 0.19 to 2.75 mTorr/minute.

The quantum yield of CO ranged from 0.75 to 1.63 and averaged 1.17 (quantum yields were measured for only about half of the runs). The [CO_2]/[CO] ratio varied from 0.07 to 0.27 and averaged 0.15. The ([CO] - [H_2])/[CO] ratio ranged from 0.71 to 0.84 and averaged 0.76 for O_2 pressures above 20 Torr and total pressures above 99 Torr. However, the value of this ratio dropped with lower O_2 and total pressures. These results are shown in Tables 17, 18, and 19.

In a few runs CO was used instead of N_2. For these runs there was about 3 to 4 times as much CO_2 produced as in similar runs with N_2. This is shown in Table 20.

Table 17. Product yields in the photolysis of formaldehyde at 3130 A in the presence of O_2 and N_2 at room temperature, utilizing a mercury line.

[M], Torr	$[O_2]$, Torr	$[N_2]$, Torr	$[H_2CO]^a$, Torr	Time, min.	[CO], mTorr	$[H_2]$, mTorr	$[CO_2]$, mTorr	$\frac{[CO]-[H_2]}{[CO]}$	$\frac{[CO_2]}{[CO]}$
99	20.4	76.6	2.28	410	321	76	72	0.76	0.22
99	20.4	75.0	3.86	360	447	110	88	0.75	0.20
104	20.0	75.0	8.55	215	699	182	84	0.74	0.12
292	60.5	228	4.44	366	449	97	60	0.78	0.13
309	64.5	243	1.95	360	235	59	44	0.75	0.19
312	60.5	243	8.85	205	684	147	68	0.79	0.10
624	130	490	4.11	360	415	101	54	0.76	0.13
627	131	492	4.30	300	351	89	48	0.75	0.14
629	131	494	4.06	300	342	87	48	0.75	0.14
644	135	507	2.03	360	221	61	35	0.72	0.16
654	135	510	9.20	340	694	178	69	0.74	0.10
678	141	529	8.39	740	1080	231	-	0.79	-

a) Initial pressure.

Table 18. Product quantum yields in the photolysis of formaldehyde at 3130 A in the presence of O_2 and N_2 at room temperature, utilizing a mercury line. All pressures are in Torr.

$[M]$	$[O_2]$	$[N_2]$	$[H_2CO]^a$	Time, min.	I_a mTorr/min.	$\Phi\{CO\}$	$\Phi\{H_2\}$	$\Phi\{CO_2\}$	$\Phi'\{CO\}^b$	$\frac{[CO']-[H_2]}{[CO']}^b$
106	21.4	80.6	4.31	301	1.46	1.02	0.23	0.15	0.82	0.72
106	21.8	82.2	2.24	513	0.45	1.07	0.31	0.29	0.89	0.65
294	56.5	234	3.78	385	1.02	0.86	0.21	0.14	0.65	0.67
300	60.9	229	9.76	220	2.66	0.97	0.24	0.09	0.64	0.62
301	61.5	231	8.21	145	2.25	1.33	0.32	0.12	1.03	0.69
302	61.5	231	8.99	155	2.75	0.75	0.17	0.14	0.45	0.62
302	61.7	232	8.83	150	2.13	1.48	0.33	0.13	1.15	0.71
304	61.7	232	10.30	160	2.74	1.47	0.29	0.11	1.13	0.74
305	62.0	233	9.50	280	2.57	1.09	0.20	0.08	0.76	0.74
307	62.6	235	9.04	255	2.40	0.95	0.24	0.12	0.63	0.62
581	122	458	1.00	395	0.19	1.40	0.40	0.31	1.27	0.69
751	750	0	1.46	455	0.26	1.63	0.26	0.36	1.47	0.82

a) Initial pressure.
b) Corrected for CO which was produced as a result of reaction 44.

Table 19. Effect of low O_2 and total pressure on the ([CO] - [H_2])/[CO] ratio in the photolysis of formaldehyde at 3130 A in the presence of N_2 at room temperature, utilizing a mercury vacuum line.

[M], Torr	[O_2], Torr	[N_2], Torr	[H_2CO][a], Torr	$\frac{[CO] - [H_2]}{[CO]}$[b],	$\frac{[CO] - [H_2]}{[CO]}$[c]
27.9	20.5	0	7.72	0.69	0.61
				$\frac{0.69}{0.61} = 1.13$	
18.2	3.40	12.7	2.09	0.46	0.54
				$\frac{0.46}{0.54} = 0.85$	
10.9	2.00	7.6	1.32	0.35	0.44
				$\frac{0.35}{0.44} = 0.80$	
4.9	0.80	3.0	1.06	0.46	0.45
				$\frac{0.46}{0.45} = 1.02$	

---

a) Initial pressure.
b) Measured.
c) Calculated.

Table 20. Effect of substituting CO for N_2 on the product yields in the photolysis of formaldehyde at 3130 A in the presence of O_2 at room temperature, utilizing a mercury vacuum line.

[M], Torr	[O_2], Torr	[N_2], Torr	[CO], Torr	[H_2CO]^a, Torr	[H_2], mTorr	[CO_2], mTorr	Irradiation time, min.
633	126	0	503	4.06	93	180	300
629	131	494	0	4.06	87	48	300
					$\frac{180}{48} = 3.8$		
633	127	0	503	3.74	81	156	305
627	131	492	0	4.30	89	48	300
					$\frac{156}{48} = 3.3$		
579	116	0	462	1.05	37	65	390
581	122	458	0	1.00	38	23	395
					$\frac{65}{23} = 2.8$		

a) Initial pressure.

RESULTS FROM THE PHOTOLYSIS OF FORMALDEHYDE IN THE MERCURY FREE VACUUM LINE.

Formaldehyde, in the presence of O_2 and N_2, (usually dry air) was photolized at 0°C, ∿ 22°C, and ∿ 40°C with a medium pressure mercury lamp used in conjunction with the filters listed in Tables 14 and 15. The products measured were CO, CO_2, H_2, and HCOOH.

The parameters were varied as follows:

Filter No. 1, 0°C: [M] from 244 to 310 Torr, $[O_2]$ from 62 to 234 Torr, $[N_2]$ from 0 to 239 Torr, initial $[H_2CO]$ from 4.91 to 10.2 Torr, average $[H_2CO]$ from 3.53 to 9.22 Torr, irradiation time from 5.4 to 84 minutes, and I_a from 2.05 to 4.19 mTorr/minute.

$\Phi\{CO\}$ ranged from 1.75 to 4.20 and averaged 3.11, $\Phi\{H_2\}$ ranged from 0.33 to 0.81 and averaged 0.54. $\Phi\{HCOOH\}$ ranged from 8.22 to 13.6 and averaged 10.8. $\Phi\{CO_2\} \sim 0.05$, and $[HCOOH]/([CO] - [H_2])$ ranged from 2.28 to 7.17 and averaged 4.78. See Table 21.

Filter No. 2, ∿ 22°C: [M] from 35 to 646 Torr, $[O_2]$ from 11 to 641 Torr, $[N_2]$ from 0 to 483 Torr, initial $[H_2CO]$ from 5.06 to 10.3 Torr, average $[H_2CO]$ from 3.77 to 9.39 Torr, irradiation time from 80 to 393 minutes, and I_a from 0.125 to 0.352 mTorr/minutes.

$\Phi\{CO\}$ ranged from 3.19 to 6.68 and averaged 4.59. $\Phi\{H_2\}$ ranged from 0.68 to 1.75 and averaged 1.27. $\Phi\{HCOOH\}$ ranged from 3.30 to 17.4 and averaged 9.53. $\Phi\{CO_2\}$ ranged from 0.02 to 0.32 and averaged 0.13. $[HCOOH]/([CO] - [H_2])$ ranged from 0.97 to 5.84 and averaged 3.39. There may be a total pressure dependence on this last ratio as well as on $\Phi\{CO\}$ and $\Phi\{H_2\}$. See Table 22.

Table 21. Product quantum yields in the photolysis of formaldehyde in the presence of O_2 and N_2 at 0°C using filter no. 1 (See Tables 14 and 15). All pressures are in Torr.

[M]	$[O_2]$	$[N_2]$	$[H_2CO]$ initial	$[H_2CO]$ average	Time, min.	I_a, mTorr/min.	$\Phi\{CO\}$	$\Phi\{H_2\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$	$\frac{[CO]-[H_2]}{[CO]}$	$\frac{[HCOOH]}{[CO]-[H_2]}$
244[a]	234	0	9.57	-	30.0	-	-	-	-	-	0.79	5.30
304[a]	62	232	9.68	5.29	72.0	2.63	1.80	0.44	10.3	-	0.77	7.17
305[a]	62	233	9.54	-	5.4	-	-	-	-	-	0.84	3.25
305[a]	63	237	5.01	3.53	22.0	2.05	3.78	0.50	11.3	-	0.87	3.45
306	62	234	10.00	7.72	31.0	2.73	2.54	0.46	10.3	0.04	0.82	4.95
306[a]	62	234	10.10	6.87	11.1	3.74	4.20	0.61	8.22	-	0.85	2.28
307[a]	63	239	4.91	-	78.0	-	-	-	-	-	0.80	6.54
307[a]	62	235	10.00	7.64	9.7	4.19	4.20	0.81	13.6	-	0.81	4.01
310	63	237	10.00	5.89	84.0	2.51	1.75	0.33	9.70	0.05	0.81	6.82
310[a]	63	237	10.10	6.50	15.0	3.59	3.72	0.58	9.80	-	0.85	3.11
310	63	237	10.20	9.22	10.0	3.11	2.89	0.56	13.5	0.06	0.81	5.78

a) Cell was flamed before this run.

Table 22. Product quantum yields in the photolysis of formaldehyde in the presence of O_2 and N_2 at ∿ 22°C using filter no. 2. (See Tables 14 and 15). All pressures are in Torr.

[M]	$[O_2]$	$[N_2]$	$[H_2CO]$ initial	$[H_2CO]$ average	Time min.	I_a, mTorr/min.	$\Phi\{CO\}$	$\Phi\{H_2\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$	$\Phi'\{CO\}^a$	$\frac{[CO']-[H_2]^a}{[CO']}$	$\frac{[HCOOH]}{[CO]-[H_2]}$
35	30	0	5.20	4.75	155	0.155	4.58	1.61	5.00	0.17	3.91	0.59	1.68
35	30	0	5.17	4.22	213	0.160	5.82	-	6.80	0.12	5.19	-	-
41	31	0	10.00	9.25	80	0.290	6.68	-	5.20	0.15	5.55	-	-
41	31	0	10.10	9.39	80	0.296	5.27	1.22	7.70	0.21	4.32	0.72	1.90
44	34	0	9.92	9.08	85	0.352	4.35	0.90	3.30	-	3.50	0.74	0.97
63	11	42	10.00	8.88	137	0.301	5.10	1.53	7.80	0.18	4.20	0.64	2.18
65	11	43	10.00	8.51	215	0.300	4.18	1.41	7.40	0.02	3.32	0.57	2.68
83	73	0	9.92	8.41	204	0.321	3.21	0.99	7.00	0.32	3.36	0.59	3.17
310	64	241	5.06	3.77	315	0.125	4.81	1.75	14.2	0.10	4.22	0.59	4.63
313	64	239	9.94	7.23	207	0.288	4.61	1.62	17.4	0.13	3.86	0.58	5.84
315	64	241	10.00	7.84	158	0.253	5.00	1.61	17.1	0.10	4.13	0.61	5.05
615	605	0	10.00	7.92	197	0.241	4.21	1.13	4.10	0.08	3.23	0.66	1.34
622	129	483	10.00	7.64	255	0.283	3.19	1.01	11.8	0.06	2.40	0.59	5.41
645	635	0	10.30	8.39	197	0.285	3.57	0.68	12.7	0.07	2.70	0.75	4.40
646	641	0	5.12	3.84	393	0.158	4.20	1.03	15.4	0.06	3.67	0.72	4.82

a) Corrected for CO which was produced as a result of reaction 44.

Filter No. 3, ∿ 22°C: [M] from 85 to 321 Torr, $[O_2]$ from 16 to 66 Torr, $[N_2]$ from 59 to 250 Torr, initial $[H_2CO]$ from 4.66 to 10.1 Torr, average $[H_2CO]$ from 3.78 to 8.43 Torr, irradiation time from 360 to 499 minutes, and I_a from 0.109 to 0.227 mTorr/minute.

$\Phi\{CO\}$ ranged from 2.56 to 3.57 and averaged 2.97. $\Phi\{H_2\}$ ranged from 0.54 to 0.66 and averaged 0.60. $\Phi\{HCOOH\}$ ranged from 4.80 to 9.20 and averaged 6.96. $\Phi\{CO_2\}$ ranged from 0.10 to 0.46 and averaged 0.20. $[HCOOH]/([CO] - [H_2])$ ranged from 1.81 to 4.24 and averaged 3.00. See Table 23.

Filter No. 4, ∿ 22°C: [M] from 94 to 100 Torr, $[O_2]$ from 18 to 19 Torr, $[N_2]$ from 68 to 71 Torr, initial $[H_2CO]$ from 5.86 to 10.2 Torr, average $[H_2CO]$ from 4.73 to 8.77 Torr, irradiation time from 146 to 365 minutes and I_a from 0.230 to 0.452.

$\Phi\{CO\}$ ranged from 1.84 to 2.80 and averaged 2.38, $\Phi\{H_2\}$ ranged from 0.21 to 0.46 and averaged 0.31. $\Phi\{HCOOH\}$ ranged from 5.4 to 11.3 and averaged 7.53. $\Phi\{CO_2\}$ was not measured. $[HCOOH]/([CO] - [H_2])$ ranged from 2.43 to 6.91 and averaged 3.87. See Table 24.

Filter No. 5, ∿ 22°C: [M] from 95 to 664 Torr, $[O_2]$ from 18 to 166 Torr, $[N_2]$ from 67 to 517 Torr, initial $[H_2CO]$ from 1.14 to 10.3 Torr, average $[H_2CO]$ from 0.81 to 8.36 Torr, irradiation time from 10 to 126 minutes, and I_a from 0.481 to 5.20 mTorr/minute.

$\Phi\{CO\}$ ranged from 1.90 to 5.10 and averaged 3.32. $\Phi\{H_2\}$ ranged from 0.38 to 1.00 and averaged 0.61. $\Phi\{HCOOH\}$ ranged from 4.80 to 23.0 and averaged 10.8. $\Phi\{CO_2\}$ ranged from 0.04 to 0.21 and averaged 0.09. $[HCOOH]/([CO] - [H_2])$ ranged from 2.81 to 5.01 and averaged 3.75. There may be a total pressure dependence on $\Phi\{CO\}$ and $\Phi\{H_2\}$. See Table 25.

Table 23. Product quantum yields in the photolysis of formaldehyde in the presence of O_2 and N_2 at ∿ 22°C using filter no. 3. (See Tables 14 and 15). All pressures are in Torr.

[M]	$[O_2]$	$[N_2]$	$[H_2CO]$ initial	$[H_2CO]$ average	Time min.	I_a, mTorr/min.	$\Phi\{CO\}$	$\Phi\{H_2\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$	$\Phi'\{CO\}^a$	$\frac{[CO']-[H_2]}{[CO']}^a$	$\frac{[HCOOH]}{[CO]-[H_2]}$
85	16	59	10.00	8.43	368	0.227	2.94	0.66	5.60	0.18	1.96	0.66	2.44
86	17	63	5.54	4.77	375	0.134	3.29	0.62	4.80	0.20	2.42	0.74	1.81
91	18	67	6.28	5.24	499	0.153	2.82	0.62	4.90	0.16	2.08	0.70	2.25
95	18	67	10.10	7.74	410	0.186	2.56	0.62	7.03	0.46	1.57	0.60	3.62
311	64	242	5.09	4.11	360	0.109	3.57	0.57	8.50	0.13	2.88	0.80	2.85
313	64	242	7.48	5.71	411	0.171	2.71	0.54	9.20	0.19	1.95	0.72	4.24
321	66	250	4.66	3.78	360	0.114	2.92	0.60	8.70	0.10	2.30	0.74	3.74

a) Corrected for CO which was produced as a result of reaction 44.

Table 24. Product quantum yields in the photolysis of formaldehyde in the presence of O_2 and N_2 at ∿ 22°C using filter no. 4. (See Tables 14 and 15). All pressures are in Torr.

[M]	$[O_2]$	$[N_2]$	$[H_2CO]$ initial	$[H_2CO]$ average	Time min.	I_a, mTorr/min.	$\Phi\{CO\}$	$\Phi\{H_2\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$	$\Phi'\{CO\}^a$	$\frac{[CO']-[H_2]}{[CO']}^a$	$\frac{[HCOOH]}{[CO]-[H_2]}$
94	18	70	5.86	4.73	365	0.230	2.44	0.21	5.40	-	1.89	0.89	2.43
96	18	68	9.76	7.48	323	0.412	1.84	0.21	11.3	-	1.20	0.82	6.91
96	18	68	10.20	8.77	146	0.452	2.42	0.36	7.00	-	1.70	0.79	3.41
100	19	71	10.00	7.93	342	0.365	2.80	0.46	6.40	-	2.07	0.79	2.71

a) Corrected for CO which was produced as a result of reaction 44.

Table 25. Product quantum yields in the photolysis of formaldehyde in the presence of O_2 and N_2 at ∿ 22°C using filter no. 5. (See Tables 14 and 15). All pressures are in Torr.

[M]	$[O_2]$	$[N_2]$	$[H_2CO]$ initial	$[H_2CO]$ average	Time min.	I_a, mTorr/min.	$\Phi\{CO\}$	$\Phi\{H_2\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$	$\Phi'\{CO\}^a$	$\frac{[CO']-[H_2]}{[CO']}^a$	$\frac{[HCOOH]}{[CO]-[H_2]}$
95	18	67	9.84	6.89	43	3.33	4.51	0.84	11.7	0.06	4.30	0.80	3.20
95	19	71	5.10	4.19	20	2.67	2.81	0.62	7.70	0.07	2.67	0.77	3.52
96	18	68	10.00	8.36	10	5.20	3.85	0.83	10.6	0.04	3.65	0.77	3.50
97	18	69	9.84	7.97	23	4.91	3.94	0.66	9.20	0.06	3.74	0.82	2.81
104	21	78	5.40	3.42	53	2.02	3.83	-	7.90	0.08	3.67	-	-
108	21	77	9.84	8.33	10	4.48	4.80	1.00	17.3	0.19	4.59	0.78	4.55
314	64	240	10.30	7.80	25	4.08	3.28	-	15.6	0.04	3.02	-	-
330	67	253	9.76	7.15	20	4.02	5.10	0.51	23.0	0.21	4.90	0.90	5.01
461	24	436	1.17	0.81	123	0.493	1.90	0.38	4.80	0.11	1.84	0.79	3.15
466	97	364	5.18	4.20	20	2.50	2.61	0.46	10.3	0.06	2.46	0.81	4.81
478	24	453	1.14	0.81	126	0.481	1.90	0.38	5.00	-	1.84	0.79	3.26
510	25	484	1.15	0.82	118	0.487	1.91	0.38	5.60	0.11	1.84	0.79	3.64
664	166	517	10.10	7.73	18	4.66	2.74	-	11.8	0.04	2.47	-	-

a) Corrected for CO which was produced as a result of reaction 44.

Filter No. 6, ∿ 22°C: [M] from 95 to 312 Torr, [O_2] from 19 to 63 Torr, [N_2] from 71 to 239 Torr, initial [H_2CO] from 4.95 to 10.0 Torr, average [H_2CO] from 3.93 to 7.83 Torr, irradiation time from 196 to 487 minutes, and I_a from 0.153 to 0.316 mTorr/minute.

$\Phi\{CO\}$ ranged from 1.97 to 2.50 and averaged 2.21. $\Phi\{H_2\} = 0.42$ (two runs), $\Phi\{HCOOH\}$ ranged from 3.17 to 8.19 and averaged 4.99. $\Phi\{CO_2\}$ ∿ 0.06, and [HCOOH]/([CO] - [H_2]) ranged from 2.06 to 3.94 and averaged 3.00. See Table 26.

Filter No. 5, ∿ 40°C: [M] ranged from 115 to 390 Torr, [O_2] from 22 to 80 Torr, [N_2] from 83 to 300 Torr, initial [H_2CO] from 5.19 to 10.16 Torr, average [H_2CO] from 3.79 to 9.99 Torr, irradiation time from 20 to 41 minutes, and I_a from 2.16 to 5.45 mTorr/minutes.

$\Phi\{CO\}$ ranged from 2.26 to 2.56 and averaged 2.37. $\Phi\{H_2\}$ ranged from 0.41 to 0.57 and averaged 0.50. $\Phi\{HCOOH\}$ ranged from 2.21 to 3.38 and averaged 2.65. $\Phi\{CO_2\}$ ranged from 0.39 to 1.17 and averaged 0.75. [HCOOH]/([CO] - [H_2]) ranged from 1.27 to 1.66 and averaged 1.41. See Table 26.

The light intensity through the cell was constantly monitored and it was found to decrease during a run.

A few runs were done in which CO was substituted for N_2. More CO_2 was produced in these runs than in similar runs with N_2.

Table 26. Product quantum yields in the photolysis of formaldehyde in the presence of O_2 and N_2 at ∿ 22° and ∿ 40°C using filters no. 6 and 5. (See Tables 14 and 15). All pressures are in Torr.

[M]	$[O_2]$	$[N_2]$	$[H_2CO]$ initial	$[H_2CO]$ average	Time min.	I_a, mTorr/min.	$\Phi\{CO\}$	$\Phi\{H_2\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$	$\Phi'\{CO\}^a$	$\frac{[CO']-[H_2]^a}{[CO']}$	$\frac{[HCOOH]}{[CO]-[H_2]}$
						Filter no. 6, ∿ 22°C							
95	19	71	4.95	3.93	487	0.153	1.97	-	3.17	0.07	1.31	-	-
100	19	71	9.92	8.45	280	0.316	2.17	0.42	3.62	0.07	1.34	0.69	2.06
312	63	239	10.00	7.83	196	0.270	2.50	0.42	8.19	0.05	1.70	0.75	3.94
						Filter no. 5, ∿ 40°C							
115	22	83	10.00	9.99	24	5.45	2.56	0.57^b	3.38	0.39	2.13	0.73	1.66
125	25	95	5.36	4.37	41	2.42	2.34	0.49^b	2.70	0.69	2.06	0.76	1.46
336	70	261	5.19	3.79	41	2.16	2.26	0.41	2.32	1.17	2.00	0.80	1.26
390	80	300	10.16	7.14	20	3.97	2.30	0.52	2.21	-	1.94	0.73	1.24

a) Corrected for NO which was produced as a result of reaction 44.
b) ± 20%.

DISCUSSION

Formaldehyde has an absorption band extending from ∿ 2300 to ∿ 3530 A which is associated with a transition from the ground state ($^1A_1$) to the first excited state ($^1A_2$) (Herzberg, 1966, p. 612). This transition, which is forbidden by electric dipole selection rules, is made allowed by vibronic interactions (Job, Sethurman, and Innes, 1969).

$$H_2CO\ (^1A_1) + h\nu \rightarrow H_2CO\ (^1A_2) \qquad 78$$

The $^1A_2$ state can undergo fluorescence.

$$H_2CO\ (^1A_2) \rightarrow H_2CO\ (^1A_1) + h\nu' \qquad 79$$

can be collisionally deactivated to a lower energy triplet,

$$H_2CO\ (^1A_2) + M \rightarrow H_2CO\ (^3A_2) + M \qquad 80$$

or to the ground state,

$$H_2CO\ (^1A_2) + M \rightarrow H_2CO\ (^1A_1) + M \qquad 81$$

or can be converted to a highly vibrationally excited ground state molecule by internal conversion.

$$H_2CO\ (^1A_2) \rightarrow H_2CO\ (^1A_1^v) \qquad 82$$

The triplet formaldehyde might also react directly with O_2.

$$H_2CO\ (^3A_2) + O_2 \rightarrow HO_2 + HCO \qquad 83a$$

$$H_2CO\ (^3A_2) + O_2 \rightarrow OH + HCO_2 \qquad 83b$$

$$H_2CO\ (^3A_2) + O_2 \rightarrow H + HCO_3 \qquad 83c$$

Since each of these states might have different branching ratios for the production of H_2 + CO and H + HCO, and since the relative population of these states depends on the total pressure, it is logical to expect that the overall branching ratio might depend on the total pressure.

The study done in the mercury vacuum line was done to measure the relative importance of reactions 75 and 76 as a function of total pressure and I_a.

$H_2CO + h\nu \rightarrow HCO + H$ Rate = αI_a 75

$H_2CO + h\nu \rightarrow H_2 + CO$ Rate = βI_a 76

In the presence of O_2 the following mechanism was considered.

$HCO + O_2\ (+M) \rightarrow HCO_3\ (+M)$ 33a

$HCO + O_2 \rightarrow CO + HO_2$ 33b

$HCO + O_2 \rightarrow CO_2 + OH$ 33c

$H + O_2 + M \rightarrow HO_2 + M$ 77

$HCO_3 + H_2CO \rightarrow HCO_3H + HCO$ 41

$HCO_3H \rightarrow HCOOH + (1/2)O_2$ on the wall 42

$2HO_2 \rightarrow H_2O_2 + O_2$ 43

$HO_2 + H_2CO \rightarrow H_2O_2 + HCO$ 44

$OH + H_2CO \rightarrow H_2O + HCO$ 45

This mechanism predicts that one H_2 molecule will be produced each time reaction 76 occurs. The HCO produced by reaction 75 can react in three different ways with O_2 according to reaction 33. However, two of these, reactions 33a and 33c, produce radicals that react to regenerate HCO radicals <u>via</u> reactions 41 and 45. Reaction 33b, which produces a CO molecule, is the only termination reaction for HCO radicals. Thus one CO molecule is produced not only each time reaction 76 occurs, but also each time reaction 75 occurs. However, there is another source of HCO radicals, namely reaction 44. The mechanism predicts that one CO molecule will also be produced each time reaction 44 occurs. The importance of reaction 44 is proportional to $[H_2CO](\alpha/I_a)^{1/2}$. Thus, at low formaldehyde pressures and high I_a, reaction 44 is relatively unimportant and the following approximation can be made.

$$\frac{[CO] - [H_2]}{[CO]} \approx \frac{\alpha}{\alpha + \beta} = \frac{\phi_{75}}{\phi_{75} + \phi_{76}} \qquad \text{XXI}$$

These measurements were made and are reported in Table 17. $([CO] - [H_2])/[CO]$ ranged from 0.72 to 0.79 and averaged 0.76 from the data in Table 17.

Since $\alpha + \beta \leq 1.0$, a value of 0.76 was taken as a first approximation of α. (This value was used to correct the CO yields in Tables 18 and 22 to 26 for the CO which was produced as a result of reaction 44. This correction was not made in Table 21 because reaction 44 is much less important at 0°C, $k_{44} = 1.7 \times 10^{-12} \exp\{-8000/RT\}$, and the largest correction would have been less than 3%).

The corrected CO yields, $[CO']$, can be used to determine $\alpha/(\alpha + \beta)$.

$$\frac{[CO'] - [H_2]}{[CO']} = \frac{\alpha}{\alpha + \beta} \qquad \text{XXII}$$

The results listed in Table 18 show that this ratio ranged from 0.62 to 0.82 and averaged 0.69.

The $([CO] - [H_2])/[CO]$ ratios reported in Table 19 are somewhat lower than those reported in Table 17. As the O_2 and total pressure are reduced, reaction 77 decreases in importance and reaction 84 begins to play a role.

$$H + H_2CO \rightarrow H_2 + HCO \qquad 84$$

The $([CO] - [H_2])/[CO]$ ratio was calculated for the runs listed in Table 19 using 0.76 for $\alpha/(\alpha + \beta)$ obtained above and 5.6×10^{-32} cm.^{6}/sec. and 5.4×10^{-14} cm.^{3}/sec. for k_{77} and k_{84} (Garvin and Hampson, 1974) respectively.

The agreement between the measured and calculated ratios is good. Thus, it was found that ([CO] - [H_2])/[CO] has a dependence on the O_2 and total pressure at very low O_2 and total pressure, and that this dependence can be explained by the inclusion of reaction 84 in the mechanism.

The quantum yield of CO_2 was found to be small and somewhat variable. A few runs were done with CO instead of N_2. This was done to scavenge the OH radicals produced in reaction 33c. If the CO_2 were coming from reaction 33c, and if all the OH's reacted with CO to produce CO_2, and if nothing else oxidized CO, the amount of CO_2 produced in a run with CO should be twice that produced in a similar run with N_2. The results are presented in Table 20. Since the CO_2 ratio is greater than two, it is concluded that some other radical, perhaps HCO_3 oxidizes CO.

The quantum yield of CO was measured and corrected for CO which was produced as a result of reaction 44. A value of 1.0 is expected for the corrected quantum yield, $\Phi'\{CO\}$, unless some state is reached by the formaldehyde molecule that doesn't produce either CO or HCO. If this happens $\Phi'\{CO\}$ should be less than one, and again the value may be a function of the total pressure. The results are listed in Table 18. The values obtained are scattered, show no trend with total pressure, and averaged approximately 0.9. It must be mentioned that the I_a values listed in Table 18 were obtained by using the average formaldehyde pressures. These were calculated by making appropriate corrections for the CO, CO_2, and HCOOH produced. (The results presented in Chapter II were used to calculate the amount of HCOOH produced). No account was made of any formaldehyde that might have polymerized, but it was thought that this might account for at least some of the scatter in the data.

It was at this point in time that the study presented in Chapter II was done. This was to check the mechanism presented above, and in particular to check that one CO molecule was produced for each HCO radical produced in the photolytic act. The mechanism was borne out and the intercept of 1 in Figure 11 indicates that one CO molecule was produced for each primary HCO radical (at least at room temperature).

It was decided to go back and restudy the photolysis of the formaldehyde/air system, in the hope of getting more consistent values for $\Phi'\{CO\}$. Since the mercury line used before had been disassembled, the study was done in the mercury free line used for the HCO oxidation study. The data and results are presented in Tables 21 to 26.

The first study done was at 0°C and is presented in Table 21. The light intensity through the cell was monitored and it was observed to decrease during the course of a run. If the $\log(I_o/I_t)$ was plotted vs. time, a plot was obtained that was linear for ∿ 15 to ∿ 20 minutes and showed an induction time of from ∿ 1.5 to ∿ 4.5 minutes. (There were 4 plots). The intensity decreased at the same rate if the light was shut off (measurements taken periodically for 7.5 minutes, one run) and the most linear plot was linear for a decrease in transmitted intensity from 100 to 13.5 arbitrary units. The slopes of the lines, however, were not reproducible.

The transmitted light intensity didn't return to its initial value when the cell was evacuated, but did return to its initial value when the cell was flamed. Therefore, the reduction in transmitted light intensity was attributed to the formaldehyde polymerizing on the walls of the cell.

Carruthers and Norrish (1936b) observed a reduction of pressure in the photochemical oxidation of formaldehyde which was induced by the light, but continued on extinguishing the light. They showed that the polymerization was due to the formic acid which was produced in the photolysis.

Their observations correlate very well with the observations just described from this study. The induction period was necessary to allow enough formic acid to be produced to cause the polymerization, and the polymerization was seen to continue in the dark in both studies.

It is necessary to know the formaldehyde pressure during a run to calculate I_a and thus quantum yields. The average formaldehyde pressure was obtained in the following way. At the end of a run the gases were passed through a spiral trap immersed in liquid nitrogen. The noncondensables were analyzed for H_2 and CO, after which the line was evacuated. The liquid nitrogen was replaced with an acetone slush and the H_2CO, CO_2, and H_2O_2 were distilled off.

The pressure of these gases was then measured with the silicone oil manometer in a portion of the line whose volume relative to the cell was known. From this the final H_2CO pressure in the cell was calculated, assuming that the H_2O_2 pressure was negligible. This gas sample was then condensed in the gas chromatograph loop and analyzed for CO_2, which was always found to be negligible compared to the amount of formaldehyde left. The sample condensed in the acetone slush was transferred to the ir cell and analyzed for formic acid.

The assumption that the H_2O_2 pressure was negligible is reasonable according to the mechanism. The assumption that the formaldehyde didn't farther polymerize on condensation is showed to be fairly good by the following consideration.

The average formaldehyde pressure, calculated as (initial pressure + final pressure)/2 was usually about 70% of the initial formaldehyde pressure. Since it is known that some of the formaldehyde polymerized in the cell, the maximum average error must be less than 30%.

The average formaldehyde pressures reported in Tables 21 to 26 were obtained in this way, and they were used to calculate I_a. As stated earlier, no correction was made for any formaldehyde polymerization that may have occurred in the study done in the mercury line.

The incident light intensity, I_o, from which I_a was calculated, decreased during a run due to the polymer deposition. The light transmitted through the cell at 0°C decreased by as much as 50%. Thus the cell was usually flamed between runs.

It was decided to try some runs without flaming the cell. It was thought that CO might be produced at "active sites" on the cell wall and that the polymer might "deactivate" these "active sites". It was hoped that the CO quantum yield would thus fall to 1.0 or below as required by the mechanism. The results are presented in Table 21. There is no significant difference between the runs done in the flamed or unflamed cell.

The amount of light attenuated during runs done at room temperature and above (usually less than 10%) was much less than at 0°C. Also the polymer that was formed usually pumped away, and flaming the cell was unnecessary.

The $\Phi\{CO\}$ values listed in Table 21 and the $\Phi'\{CO\}$ values listed in Tables 22 to 26 are significantly greater than 1.0 and most $\Phi\{HCOOH\}$ are significantly greater than 5 ± 1. This indicates that there is a source of radicals in this system not yet accounted for in the mechanism. Possible sources of radicals will be discussed and where possible an estimation will be made of their probable importance.

One possible source of radicals is the photolysis of the polymer deposited on the cell wall. The average value of $\Phi\{CO\}$ (=3.11) from Table 21, under conditions of heavy polymer formation, is comparable to the average value of $\Phi'\{CO\}$ from Table 22 (=3.60) and Table 25 (=3.15) which were obtained under conditions of light polymer formation. This, and the similarity of the $\Phi\{CO\}$'s in the flamed and unflamed cell in Table 21, indicates that the formation of radicals from the photolysis of the polymer is not important. Also, the polymer alone and in the presence of air was photolized and no H_2, CO, or HCOOH was formed.

The photolysis of HCOOH and H_2O_2 was considered. HCOOH has no absorption band at 3130 A (Herzberg, 1966, p. 624) and can be disregarded. H_2O_2 photolizes to produce two OH radicals (Calvert and Pitts, 1966, p. 202). Two runs were done in which the N_2 was replaced by CO, so that any OH radicals produced in the system would react with CO to form CO_2. If it is assumed that only OH reacts with CO to form CO_2, there was enough OH in one run to increase $\Phi'\{CO\}$ by 0.36 and in another to increae it by 0.32. These numbers are significant when compared to $\Phi'\{CO\}$ values of 1.84 from similar runs with N_2 listed in Table 25. This correction is not enough however, to reduce $\Phi'\{CO\}$ to 1.0. It must also be remembered that this correction is too large if anything else, HCO_3 for example, oxidizes CO. Thus the production of OH may be significant, but not enough to account completely for the high values of $\Phi'\{CO\}$. It is doubtful that the hydrogen peroxide's pressure and extinction coefficient are large enough to account for a significant amount of OH radicals. If OH radicals are indeed present, they probably originate in some other way.

It is not known what the ultraviolet absorption spectrum of performic acid is, but the primary processes are probably reactions 85 and/or 86.

$$HCOOOH + h\nu \rightarrow HCO + HO_2 \qquad 85$$

$$HCOOOH + h\nu \rightarrow HCO_2 + OH \qquad 86$$

Either of these processes could account for the high CO yields.

The influence of surface has been recognized as being important in the oxidation of formaldehyde (Horner and Style, 1954; Norrish, 1966; Purcell and Cohen, 1967), the amount of H_2O_2 measured in a run being dependent on the nature of the surface. Perhaps H_2O_2 reacts with the polymer or HCOOOH on the wall to produce radicals (HO_2, OH, or HCO) which diffuse from the surface to react in the gas phase.

Nalbandyan, Oganessyan, Vardanyan, and Griffiths (1975), have recently shown that peracetic acid decomposes on surfaces to produce radicals. This suggests that performic acid might decompose on the cell surface.

$$HCOOOH \rightarrow HCO + HO_2 \quad \text{on the wall} \qquad 87$$

$$HCOOOH \rightarrow HCO_2 + OH \quad \text{on the wall} \qquad 88$$

The fact that this complication didn't occur in the study in Chapter II (at least at room temperature) does not eliminate any of the last four possibilities. The photolysis of H_2O_2 and/or HCOOH might occur at 3130 A but not at 3660 A.

Different cells were used in these two studies. Thus the surfaces might have been different even though both cells were made of quartz. Also, the chlorine used in the first study might have altered the surface in some way. The time difference between the two studies might also be a factor. The time scale of the chlorine study was minutes, while the time scale of the present study was hours. There might have not been enough time for surface reactions to make a significant contribution in the chlorine work at room temperature.

Radical scavenging experiments were attempted twice, once using HBr and once using diethylhydroxylamine. Both attempts failed because the radical scavengers rapidly polymerized the formaldehyde.

There are several possible sources of radicals. Without a complete understanding of the mechanism the amount of information that can be obtained from this study is limited.

The values of $([CO'] - [H_2])/[CO']$ obtained in the mercury free line don't equal $\alpha/(\alpha + \beta)$, and great doubt is placed on the results obtained in the mercury line.

Figure 16 shows plots of $\Phi'\{CO\}$ vs. [M] from Tables 22 and 25. The intercepts, slopes, and correlation coefficients are 4.3, -0.0020, -0.60 and 4.2, -0.0035, and -0.67 respectively.

Figure 17 shows plots of $\Phi\{H_2\}$ vs. [M] from Tables 22 and 25. The intercepts, slopes, and corrleation coefficients are 1.5, -0.00078, -0.50, and 0.87, -0.0010, and -0.87 respectively. (The method of least squares was used to obtain the lines in Figures 16 and 17).

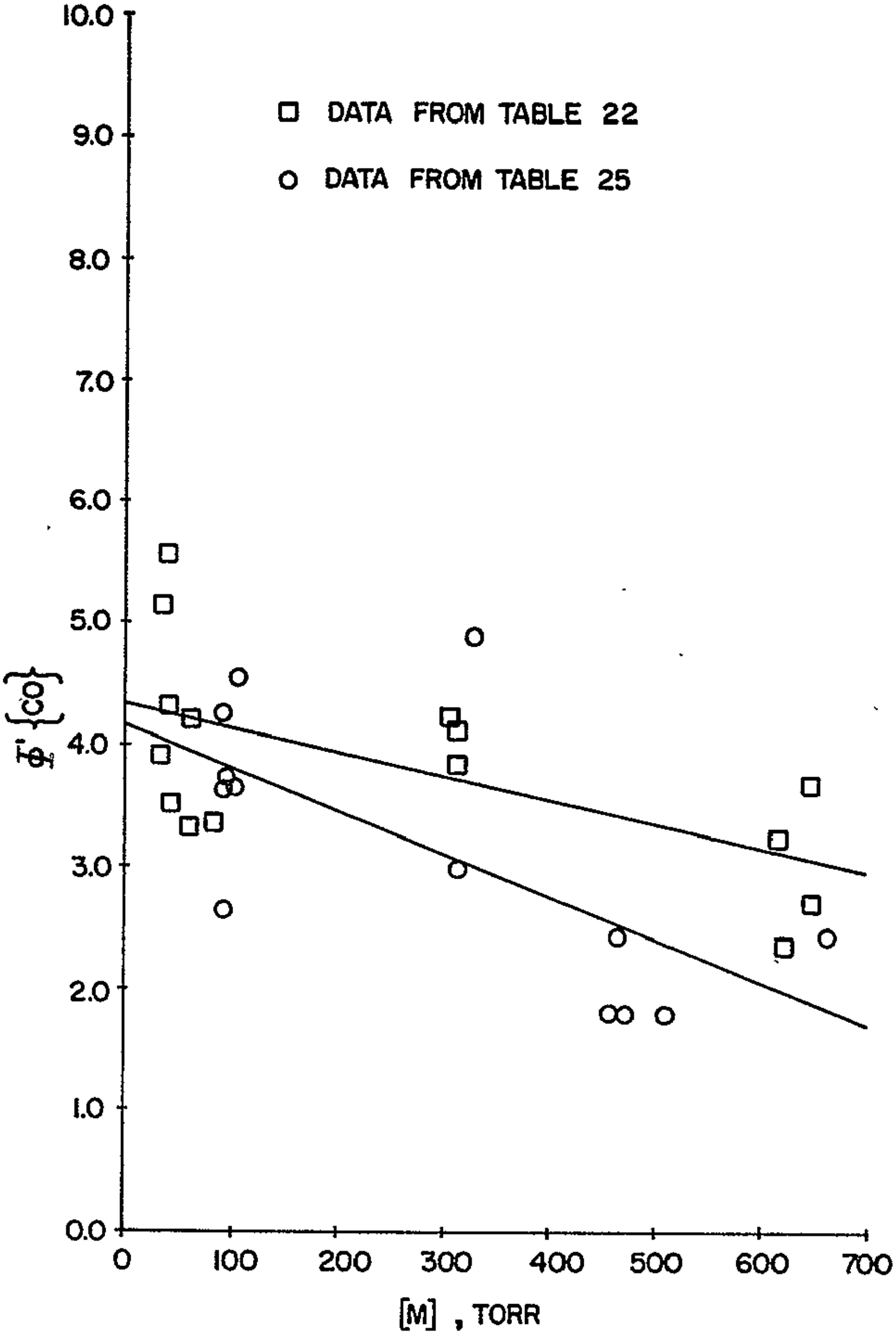


Figure 16. Plot of Φ'{CO} vs. [M] in the photolysis of H_2CO in the presence of N_2 and O_2.

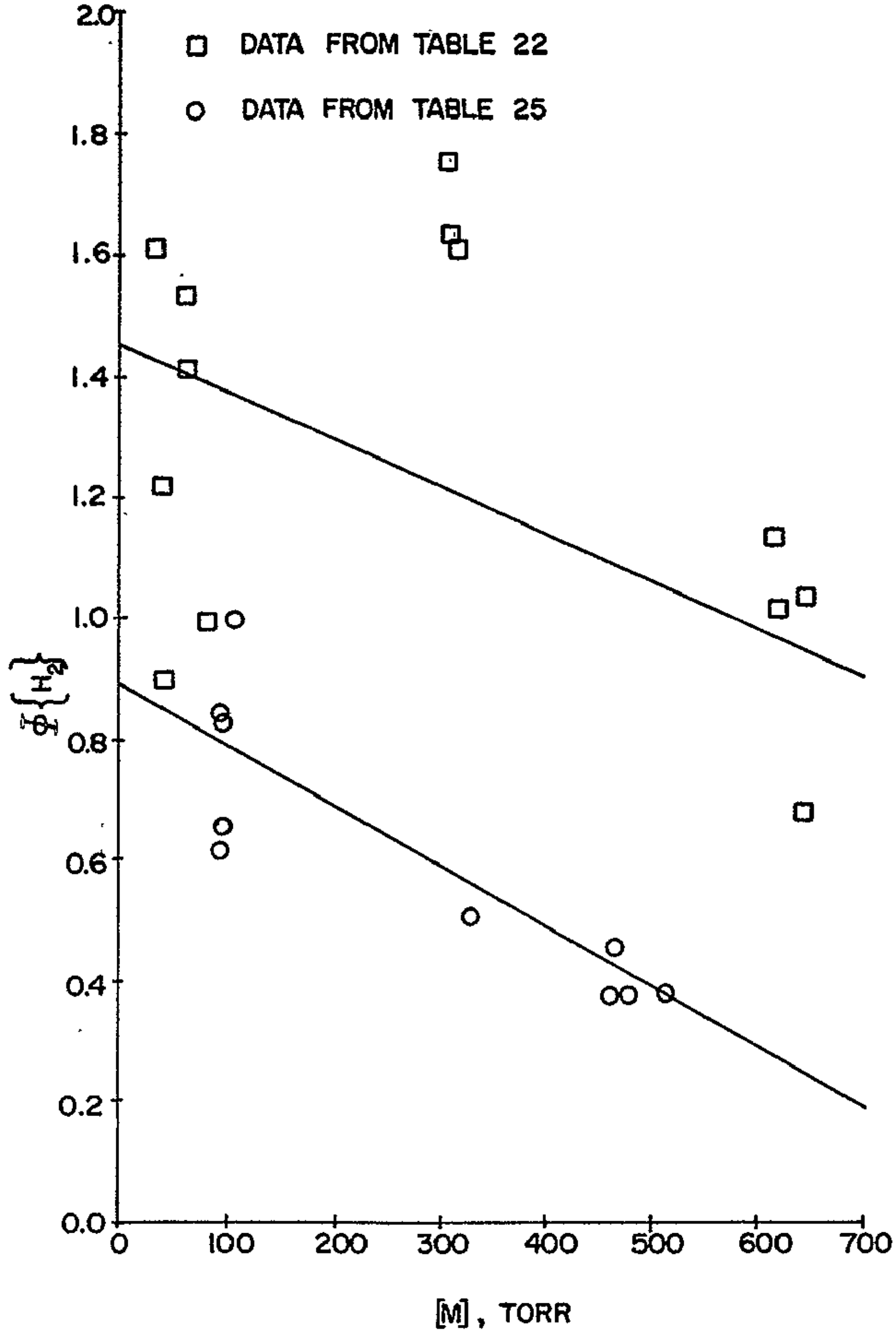


Figure 17. Plot of $\Phi\{H_2\}$ vs. [M] in the photolysis of H_2CO in the presence of N_2 and O_2.

It is impossible to tell if these trends of reduction of $\Phi'\{CO\}$ and $\Phi\{H_2\}$ are due to pressure dependencies of reactions 75 and 76 or not.

If it is assumed that hydrogen is produced only from reaction 76 (an assumption that is contradicted by the fact that the hydrogen quantum yields listed in Table 22 are greater than 1.0. However, even if this is not true, the error introduced will not be over 30% because the average $[H_2]/[CO]$ ratio is 0.3.) and CO is produced only from reactions 76 and 33b, equation XXIII can be obtained. (See DISCUSSION OF RESULTS AT ROOM TEMPERATURE AND -7 ± 1°C of Chapter II for a complete discussion of the pressure dependence of reaction 33a).

$$\frac{[CO] - [H_2]}{[HCOOH]} = \frac{k_{33b}k_{33a2}}{k_{33a3}k_{33a1}[M]} + \frac{k_{33b}}{k_{33a1}} \qquad \text{XXIII}$$

Figure 18 shows a least squares plot of equation XXIII for the data from Table 22, except for two points which are clearly out of line with the rest. The line has a correlation coefficient of 0.98, an intercept of 0.17, and a slope of 15 Torr. The intercept gives a "high pressure" value of 5.9 for k_{33a}/k_{33b}, which agrees well with the value of 5 ± 1 reported in Chapter II. The slope to intercept ratio gives k_{33a2}/k_{33a3} = 88 Torr, which is the half quenching pressure for reaction 33a. This suggests that the change in $k_{33} = k_{33a'} + k_{33b}$ measured by Washida, Martinez, and Bayes (1974) would be even smaller than suggested in Chapter II.

The average "high pressure" values for k_{33a}/k_{33b} (= $[HCOOH]/([CO] - [H_2])$) from Tables 21, 23, and 25 are 4.8, 3.7, and 4.0 respectively. Again these values are in good agreement with the value 5 ± 1 reported

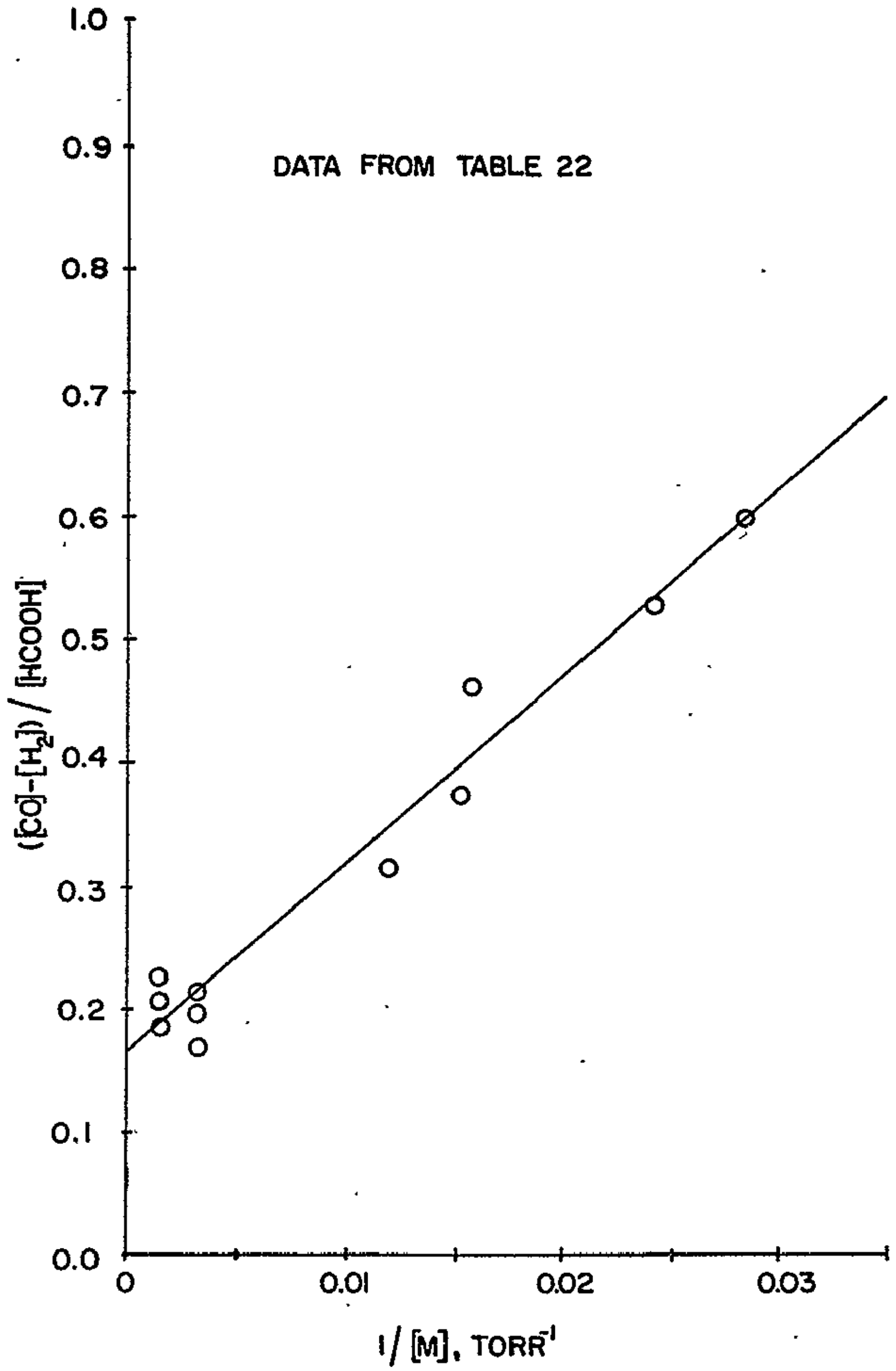


Figure 18. Plot of ([CO] - [H_2])/[HCOOH] vs. 1/[M] in the photolysis of H_2CO in the presence of N_2 and O_2.

earlier. The values at 40°C reported in Table 26 are much lower, the average being 1.4. This result is surprising because the earlier study showed this ratio had little or no temperature dependence.

The values of $\Phi\{CO_2\}$ were usually small, which agrees with the earlier work.

The average values of $\Phi\{H_2\}$ can be placed in three groups. Those around 0.55 (0.54, 0.60, 0.61, 0.42, and 0.50 from Tables 21, 23, 25, 26, and 26 respectively), those around 0.30 (0.31 and 0.27 from Tables 24 and 18 respectively), and at 1.27 from Table 22. These differences might be due, at least in part, to the pressure dependence suggested by Figure 17. However, if it is assumed that $\Phi\{H_2\} = \phi_{76}$ the values of $\Phi\{H_2\}$ at about 0.55 are in good agreement with the value of 0.52 obtained by DeGraff and Calvert (1967) when they photolized H_2CO and D_2CO in the presence of added olefin and with the value of 0.50 obtained by McQuigg and Calvert (1969) when they flashed H_2CO, D_2CO, HDCO, and mixtures of H_2CO and D_2CO. The values at about 0.30 are in fair agreement with the value of 0.20 obtained by Sperling and Toby (1973) when they photolized H_2CO.

CONCLUSION

The rate constant ratios $(k_{14} + k_{14}a)/k_{12a}$ (= 0.56 ± 0.10), k_{12}/k_{12a} (= 2.2 ± 0.4), and k_{11}/k_{15} (= 0.63 ± 0.10 at 25°C and 0.98 ± 0.20 at 72°C) were measured.

$OH + CH_3OH \rightarrow H_2O + R$ 11

$O(^1D) + CH_3OH \rightarrow OH + R$ 12a

$\rightarrow$ products 12

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

$\rightarrow 2NO$ 14b

$OH + CO \rightarrow CO_2 + H$ 15

When this value for k_{11}/k_{15} is combined with the value of 0.0235 for $k_{OH + N_2}/k_{15}$ (Sie, Simonaitis, and Heicklen, 1976a), and $k_{OH + H_2} = 7.1 \times 10^{-15}$ cm.^{3}/sec. (Garvin and Hampson, 1974) a value of $\sim 1.9 \times 10^{-13}$ cm.^{3}/sec. is obtained for k_{11} at 25°C.

A value of $\sim 5.9 \times 10^{-10}$ cm.^{3}/sec. is obtained for k_{12a} from $(k_{14} + k_{14}a) = 3.3 \times 10^{-10}$ cm.^{3}/sec. (Garvin and Hampson, 1974) and $(k_{14} + k_{14}a)/k_{12a} = 0.56$. Thus, k_{12} is found to be $\sim 1.3 \times 10^{-9}$ cm.^{3}/sec.

These rate coefficients can be used to better estimate the importance of these reactions in the atmosphere.

Formyl radical chemistry was also studied,

$HCO + O_2\ (+M) \rightarrow HCO_3\ (+M)$ 33a

$HCO + O_2 \rightarrow CO + HO_2$ 33b

$HCO + O_2 \rightarrow CO_2 + OH$ 33c

$HCO + Cl_2 \rightarrow HClCO + Cl \rightarrow HCl + CO + Cl$ 40a

$HCO + Cl_2 \rightarrow HCOCl_2 \rightarrow$ termination 40b and the following rate constant ratios were found to be $k_{40}b/k_{33}b$ = 6 (+7, −2), $k_{33}a/k_{33}b = 5 \pm 1$, $k_{33}c/k_{33}b \leq 0.19$, and $k_{40}a/k_{40}b \sim 7.5$. The value obtained for $k_{33}a/k_{33}b$ (= 5 ± 1) represents the high pressure value. A half quenching pressure of 88 Torr was found for reaction 33a.

In light of these results the chemistry of the HCO_3 radical must be studied so that the role it plays in atmospheric chemistry can be determined.

The photolysis of H_2CO is important not only in polluted city air, but also in the stratosphere. The production of H, OH and HO_2 in the stratosphere depends on A, (Nicolet, 1975) where

$$A = 1 - X \qquad \text{XXIV}$$

and

$$X = \frac{2J\{H - HCO\}}{J\{H - HCO\} + J\{H_2 - CO\} + k_{45}[OH]} \qquad \text{XXV}$$

$$OH + H_2CO \rightarrow H_2O + HCO \qquad 45$$

Since X is compared to 1, it can be seen that the values of

$$H_2CO + h\nu \rightarrow HCO + H \qquad 75$$

$$\rightarrow H_2 + CO \qquad 76$$

ϕ_{75} and ϕ_{76}, from which the J's are determined, must be known with much more accuracy than was obtained in this study.

APPENDIX I.

TABLE OF NOMENCLATURE

A - Angstrom = 10^{-8} cm.

Chain reaction - A cycle of reactions which continues to form product and regenerate reactant.

I_a - Absorbed light intensity.

ir - Infrared

I_o - Luminous intensity before the light passes through an absorbing species.

o. d. - Outside diameter.

$\Phi\{X\}$ - Quantum yield of X.

Photochemical oxidation - Oxidation under the influence of radiant energy, especially light.

Photolysis - Chemical decomposition by the action of radiant energy, especially light.

Propogation reaction - A reaction that produces as many reactive species as it removes.

Quantum yield - (Molecules of B formed per unit volume per unit time)/(quanta of light absorbed by A per unit volume per unit time) where $A + h\nu \rightarrow B$.

$R\{X\}$ - Rate of production of X.

Termination reaction - A reaction that removes more reactive species than it produces.

TMP - 2-trifluoromethylpropene.

Volume mixing ratio - In a homogeneous mixture or solution of gases the mols of a component divided by the sum of the mols of all components.

APPENDIX II.

DATA ON "UNKNOWN"

The infrared spectrum of the "unknown" which was discussed in Chapter II is presented in Figure 19. This spectrum was taken on a Perkin-Elmer 521 Grating Infrared Spectrophotometer. The absorbance at $\sim$ 1180 $cm.^{-1}$ (as measured on a Beckman Microspec Spectrometer) is listed in Table 27, along with the reactant pressures, I_a, irradiation time, and product quantum yields. The amount of "unknown" produced should be directly proportional to the absorbance.

A run was performed by adding the reactants, cooling the cell and irradiating the chlorine. Cooling was stopped and the cell allowed to warm for $\sim$ 25 minutes after the irradiation was stopped. The contents of the cell were then passed through a spiral trap immersed in liquid nitrogen. After the noncondensables were removed, the liquid nitrogen was replaced by a -130°C or a -95°C slush. The sample was pumped on for $\sim$ 30 minutes when the -130°C slush was used and for $\sim$ 1.5 minutes when the -95°C slush was used. The contents left in the spiral trap were then transferred to another cell for infrared analysis.

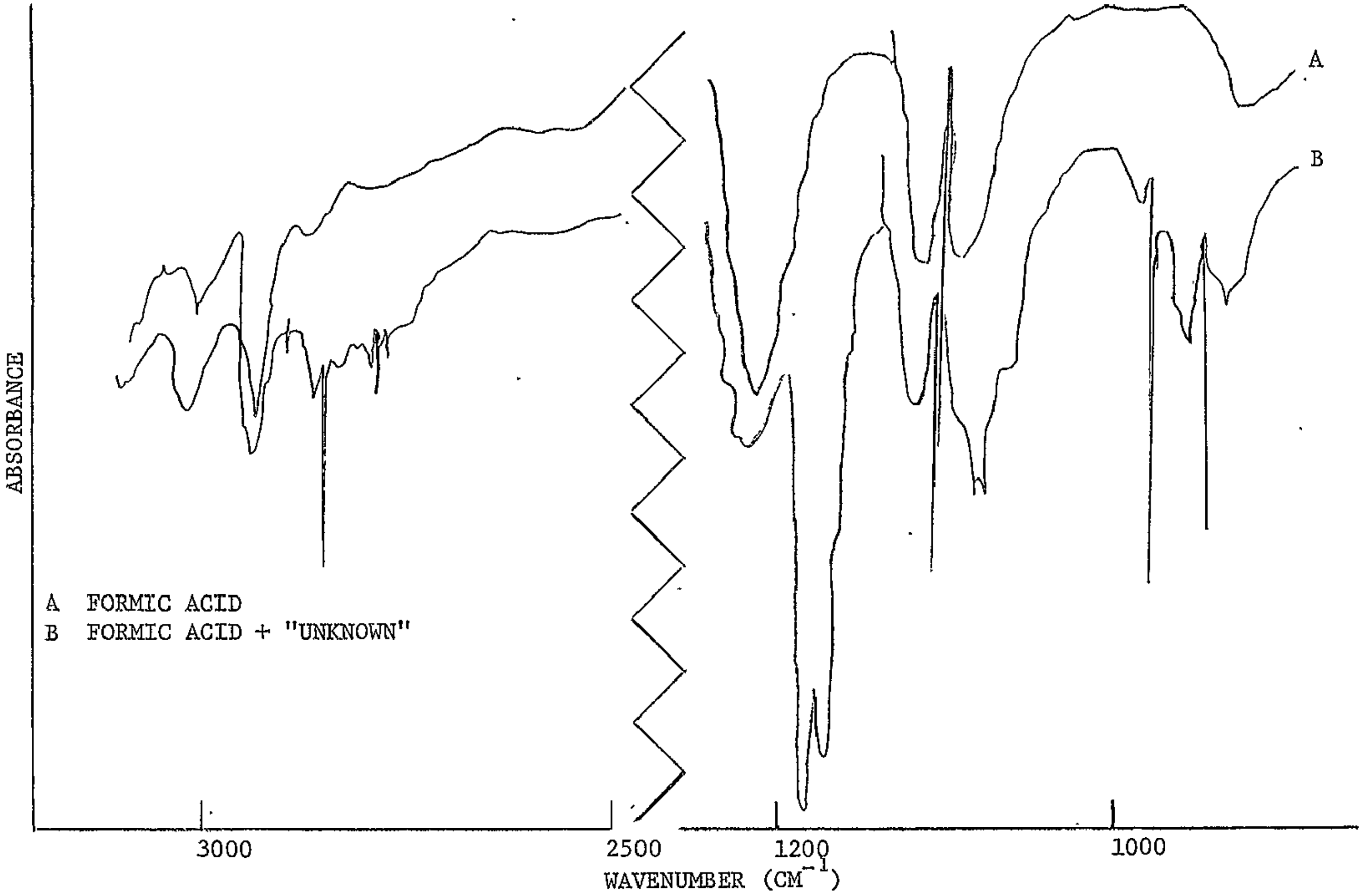


Figure 19. Infrared spectrum of "unknown".

Table 27. Yield of "unknown". Runs done at -7 ± 1°C, pressures reported at room temperature.

A^a	$[Cl_2]$, Torr	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	$\Phi\{CO\}$	$\Phi\{HCOOH\}$	$\Phi\{CO_2\}$
.293	1.49	2.13	2.84	329	9.40	2.0	8.83	–	0.16
.253	1.46	625	3.07	0	8.66	8.0	2.37	8.25	0.13
.245	1.43	645	3.37	0	8.85	8.0	2.30	–	0.21
.232	4.41	52.2	3.11	286	27.3	1.0	–	–	0.33
.199	4.38	56.5	3.07	282	27.8	1.0	–	–	–
.192^b	4.41	48.4	3.05	299	0	0	–	–	–
.135^b	1.32	14.2	5.46	314	7.90	11.25	6.22	8.95	–
.118^b	1.46	29.3	4.90	309	8.86	8.0	4.18	9.90	–
.118^b	1.40	14.6	4.54	321	8.95	7.0	6.20	11.8	0.02
.117	1.45	628	2.94	0	9.28	8.0	2.84	9.33	0.11
.112	1.33	609	9.80	0	8.33	8.0	3.27	11.5	–
.079	1.50	7.44	9.96	326	9.50	3.0	9.37	–	0.14
.074	1.37	67.6	9.50	350	9.37	5.0	4.12	13.7	0.06
.039	1.51	16.2	9.18	314	9.90	3.0	6.30	–	0.17
.039	4.25	55.9	9.28	282	27.9	1.0	–	–	–

Table 27 (Continued)

A^a	$[Cl_2]$, Torr	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	Φ{CO}	Φ{HCOOH}	$Φ\{CO_2\}$
.037	1.39	1.53	8.70	323	9.06	2.0	15.1	–	0.11
.030	1.34	1.84	8.87	324	9.04	1.5	13.4	–	0.37
.010	1.45	6.99	7.72	324	9.50	3.0	9.46	9.12	0.27
0^b	1.46	570	10.5	0	0	0	–	–	–
0^b	4.47	340	9.88	0	0	0	–	–	–
0	1.54	52.0	9.45	297	0	0	–	–	–
0	1.49	594	2.98	0	0	0	–	–	–
0	1.47	619	9.74	0	0	0	–	–	–
0	4.69	45.8	8.04	281	30.6	1.0	–	–	0.06
0	4.59	49.1	9.30	288	30.0	3.0	–	13.4	–
0	4.57	47.2	10.3	280	29.3	1.0	–	–	0.10
0^b	4.24	330	10.1	0	26.5	3.0	–	11.2	0.03
0^b	1.51	66.2	9.72	262	9.69	16.0	3.94	11.2	0.07
0	1.48	662	3.18	0	9.64	8.0	2.82	9.71	0.08
0	1.41	603	9.80	0	9.37	8.0	3.46	8.66	0.03
0^b	1.42	558	3.46	0	8.24	12.0	2.22	–	–

Table 27 (Concluded)

A^a	$[Cl_2]$, Torr	$[O_2]$, Torr	$[H_2CO]$, Torr	[He], Torr	I_a, mTorr/min.	Irradiation time, min.	Φ{CO}	Φ{HCOOH}	$Φ\{CO_2\}$
0^b	1.32	65.4	6.17	276	8.35	17.1	3.75	10.8	0.08
0^b	1.16	338	7.65	0	7.19	16.0	3.48	11.8	0.04
0	1.13	65.2	6.94	275	7.18	60.0	3.17	6.77	0.15

a) Absorbance at ∿ 1180 $cm.^{-1}$ as measured on a Beckman Microspec Spectrometer.
b) A -95°C bath was used. A -130°C bath was used in unmarked runs.

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Mixtures of Cl_2, O_2, H_2CO, and sometimes N_2 or He were irradiated at 3660 A at several temperatures to photodecompose the Cl_2. The chlorine atoms abstract a hydrogen atom from H_2CO to produce HCO radicals which can react with O_2.

$$HCO + O_2 (+M) \rightarrow HCO_3 (+M) \qquad 33a$$
$$HCO + O_2 \rightarrow CO + HO_2 \qquad 33b$$
$$HCO + O_2 \rightarrow CO_2 + OH \qquad 33c$$

The HCO_3 radical ultimately becomes HCOOH, so that HCOOH, CO, and CO_2 become measures of the relative importance of the three reaction paths. It was found that $k_{33a}/k_{33b} = 5 \pm 1$ and $k_{33c}/k_{33b} \leq 0.19$ at ~ 23°C (total pressure = 62 to 704 Torr) and -78°C (total pressure = 344 to 688 Torr). Values could not be obtained at -37 or -50°C because of changes in the mechanism.

At the upper two temperatures $k_{40a}/k_{40b} \sim 7.5$ and $k_{40b}/k_{33b} = 6\ (+7, -2)$.

THE PHOTOCHEMICAL OXIDATION OF FORMALDEHYDE

Formaldehyde in the presence of N_2 and/or O_2 (usually dry air) was photolyzed with a medium pressure Hg lamp used in conjunction with various filters which transmit different relative amounts of Hg lines from 2894 A to 3660 A. It was hoped to measure the following branching ratios as functions of total pressure, temperature, I_a, and wavelength,

$$H_2CO + h\nu \rightarrow HCO + H \qquad Rate = \alpha I_a \qquad 75$$
$$H_2CO + h\nu \rightarrow H_2 + CO \qquad Rate = \beta I_a \qquad 76$$

Osif, Terry Lee, The Reactions of $O(^1D)$ and OH with CH_3OH, Oxidation of the HCO Radical, and the Photochemical Oxidation of Formaldehyde, The Ionosphere Research Laboratory, Electrical Engineering East, University Park, Pennsylvania, 16802, 1976

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1.9.2 Chemical Aeronomy

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but lack of a complete understanding of the mechanism prohibits an unambiguous interpretation of the results.

The results suggest that reaction 75 and 76 might decrease with increasing total pressure. The application of very reasonable assumptions leads to a high pressure value of 5.9 for k_{33a}/k_{33b} and a half quenching pressure of 88 Torr for reaction 33a. This contradicts the results presented above that k_{33a} was pressure independent for total pressures down to 62 Torr. However, in that study only one run was done at 62 Torr. The half quenching pressure of 88 Torr obtained in this study is based on several experiments done over a total pressure range of 646 to 35 Torr. Thus, this result is believed to be more reliable.

The average values obtained for ϕ_{75} from eight separate studies were 1.27 (one study), ~ 0.55 (five studies), and ~ 0.30 (two studies). The value of ~ 0.55 is in very good agreement and the value of ~ 0.30 is in fair agreement with values found by others in the photolysis of formaldehyde in the absence of O_2.

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