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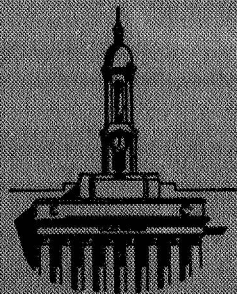
Scientific Report No. 368

COMPETITIVE REACTION OF $O(^3P)$ WITH
OZONE AND CARBONYL SULFIDE

**CASE FILE
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by
D. C. Krezenski
February 15, 1971

IONOSPHERE RESEARCH LABORATORY



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Scientific Report

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Ionosphere Research Laboratory

Submitted by: *J. S. Nisbet* *(aw)*

J. S. Nisbet, Professor of Electrical Engineering
Project Supervisor

Approved by: *A. H. Waynick*

A. H. Waynick, Director
Ionosphere Research Laboratory

The Pennsylvania State University

University Park, Pennsylvania 16802

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ABSTRACT

The competitive reaction of $O(^3P)$ atoms with O_3 and OCS was investigated in the temperature range $197^\circ K - 299^\circ K$. The relative rate constants for the reactions



were determined and found to be independent of irradiation time, absorbed intensity, and the addition of a foreign gas. The absolute value of $k_1 = 1.1 \times 10^{-11} \exp(-4330/RT) \text{ cm}^3/\text{particle-sec}$, was calculated from a pre-determined value of k_3 .

The value of k_3 was determined from a similar competitive study of $O(^3P)$ atoms with 2-trifluoromethylpropene (TMP) and OCS in the temperature range $300^\circ K - 523^\circ K$. The value of $k_3 = 1.63 \times 10^{-11} \exp(-4500/RT) \text{ cm}^3/\text{particle-sec}$, was calculated from the known rate constant of the $O(^3P)$ reaction with TMP.

The value of k_1 determined is in excellent agreement with the value k_1 determined from the collective previous works in the temperature range $300^\circ K - 1150^\circ K$.

CHAPTER I

INTRODUCTION

The photochemistry of atmospheric ozone is one of the more important problems of the stratosphere. It is well known that the vertical distribution of the atmospheric ozone shows large variations with latitude and season and with weather conditions.¹ The maximum of the ozone density is, on the average, located near the altitude of 19.8 km. and the average value of the ozone density is 3×10^{-10} gm/cm³ corresponding to a partial pressure of about 1.2×10^{-4} mm. of Hg.²

The existence of ozone in the atmosphere is due to the photo-dissociation of O₂ molecules into oxygen atoms which subsequently react with oxygen molecules to form ozone. The major route of O₃ disappearance is via O atom attack. Therefore, investigations of the rate laws of these reactions are important in the understanding of the photochemistry of atmospheric ozone.

Previous Investigation of the Rate of Reaction of O(³P) Atoms with O₃

The reaction



has been investigated by several groups. Jones and Davidson³ determined the rate of this reaction directly at high temperatures (around 850°K) through the use of shock tube experiments. Glissman and Schumacher⁴ studied the decomposition of ozone at 373°K. The reaction was further studied by Castellano and Schumacher⁵ who

photolyzed ozone with red light around room temperature. Mathias and Schiff⁶ studied the recombination of oxygen atoms in a stream of discharged oxygen containing a small percentage of atoms, by measuring simultaneously the ozone and oxygen concentrations using a mass spectrometer. A summary of the data obtained from these investigations is shown as an Arrhenius plot in Figure 1.

The data fall mainly into three groups: Jones and Davidson's at about 850°K, Glissman and Schumacher's at about 373°K and Castellano and Schumacher's around 300°K. Collectively the three groups of points cover a wide range of temperature and fall on a straight line. The recommended value⁷ of the rate constant based on the collective data is $k_1 = 2.00 \times 10^{-11} \exp(-4790/RT) \text{ cm}^3/\text{particle-sec}$. Although there is too much scatter to determine an Arrhenius expression from either the Jones and Davidson or the Glissman and Schumacher data, the Castellano and Schumacher data indicate an activation energy considerably lower than the collective data.

Present Investigation of the Rate of Reaction of O(³P) Atoms with O₃

In view of the discrepancies found in the literature values for the activation energy of reaction 1, it seemed appropriate to study this reaction in a different system. In the present study, mixtures of ozone and carbonyl sulfide were irradiated with wavelengths exceeding 4300 Å. The O(³P) atoms produced from the photolysis of O₃ reacted with either the carbonyl sulfide or ozone; thus relative rate constants were obtained. The present study was conducted from

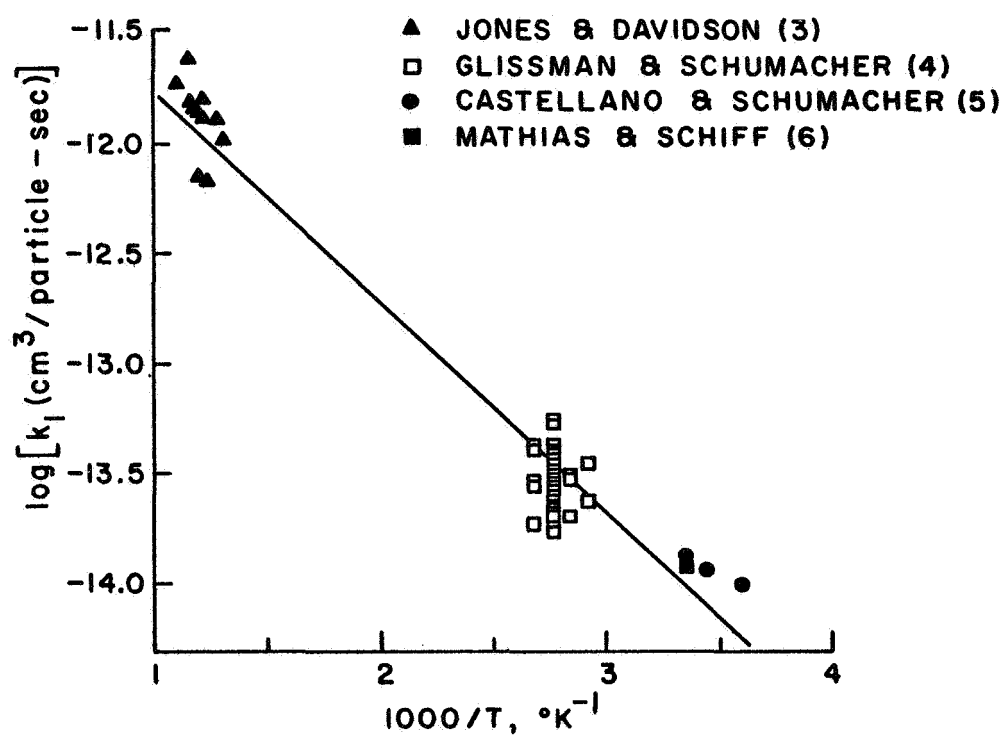


FIGURE 1

OBSERVED VALUES OF k_1

room temperature down to 197°K, while the previous studies were carried out from room temperature up to 850°K. Thus, the reciprocal temperature range was expanded by nearly a factor of two.

Photolysis of Ozone

When ozone is photolyzed in the laboratory or in the atmosphere, it dissociates into an oxygen atom and oxygen molecule. The electronic state of the atom and molecule depend on the wavelength of the photolyzing radiation. The bond dissociation energy is 26 kcal/mole.⁸ Energy in excess of this can cause electronic excitation of the oxygen atom or molecule. The electronic energies of the first few excited states of oxygen atoms and molecules are given in Table 1.

TABLE 1^a
ENERGIES OF THE FIRST FEW ELECTRONIC STATES OF
OXYGEN ATOMS AND MOLECULES

Atomic or Molecular State	Energy Relative to Ground State (kcal/mole)
O(³ P)	0.0
O(¹ D)	45.4
O(¹ S)	96.6
O ₃ (³ Σ _g ⁺)	0.0
O ₂ (¹ Δ _g)	22.5
O ₂ (¹ Σ _g ⁺)	37.5

a. See references 9, 10 and 11,

In the present study the principal lines transmitted through the filter used were 4358 Å, 15% transmission, 64.2 kcal/mole, and 5461 Å, 82% transmission, 51.4 kcal/mole. It can be seen from Table 2 that at these wavelengths, the ground state oxygen atom, $O(^3P)$ is produced. Although it is energetically possible to produce the excited $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^-)$ electronic states, there is no evidence for their formation.¹² The proposed mechanism for the photolysis of ozone at these wavelengths is:



TABLE 2^c

WAVELENGTHS (Å) BELOW WHICH IT IS ENERGETICALLY POSSIBLE TO PRODUCE THE INDICATED SPECIES FROM O_3 PHOTOLYSIS

Species	$O_2(^3\Sigma_g^-)^a$	$O_2(^1\Delta_g)$	$O_2(^1\Sigma_g^+)$	$O_2(^3\Sigma_u^+)$	$O_2(^3\Sigma_u^-)$
$O(^3P)^a$	11,400	5900 ^b	4600 ^b	2300	1700
$O(^1D)$	4,100 ^b	3100	2600	1670 ^b	1500 ^b
$O(^1S)$	2,340 ^b	1960	1790	1290 ^b	1080 ^b

a. Ground State

c. See reference 12

b. Forbidden Transition

Previous Investigation of the Rate of Reaction of $O(^3P)$ Atoms with OCS

The reaction



has been investigated by Westenberg and de Haas¹³ who determined the rate directly over a wide range of temperatures (273° - 808°K), employing a fast flow reactor with ESR detection. The rate constant k_3 was also determined by Hoyer mann, Wagner and Wolfrum¹⁴ over the range 290° - 465°K. The method used was also a fast flow reactor system with ESR detection. Homann, Krome and Wagner¹⁵ determined the rate constant k_3 in the temperature range 300° - 1150°K while investigating the oxidation of CS₂ in an isothermal flow system under reduced pressure and high dilution with inert gas. The observed values of k_3 are summarized in Table 3.

TABLE 3
OBSERVED VALUES OF k_3

k_3 (cm ³ /mole-sec)	Investigators
$1.9 \times 10^{13} \exp(-4530/RT)$	Westenberg and de Haas ¹³
$6.5 \times 10^{13} \exp(-5500/RT)$	Homann, Krome, and Wagner ¹⁴
$1.2 \times 10^{14} \exp(-5800/RT)$	Hoyer mann, Wagner, and Wolfrum ¹⁵
$9.8 \times 10^{12} \exp(-4500/RT)$	This work

Present Investigation of the Rate of Reaction O(³P) Atoms with OCS

The present investigation was conducted to try to resolve the discrepancies in the values found previously for the activation energy of reaction 3 and also to check the self consistency of the rate data obtained for the reaction of O(³P) atoms with 1-butene, 2-trifluoromethylpropene (TMP), and carbonyl sulfide. In this

investigation the $O(^3P)$ atoms were produced by the mercury photosensitized decomposition of nitrous oxide with 2537 Å radiation in the presence of mixtures of TMP and OCS.

Previous Investigation of the Rate of Reaction of $O(^3P)$ Atoms with 2-Trifluoromethylpropene

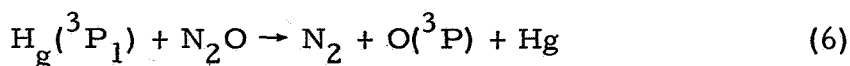
The reaction



where A represents 2-trifluoromethylpropylene oxide and E represents 2-trifluoromethylpropionaldehyde, was studied by Moss and Jennings,¹⁶ who found the reaction to give almost exclusively (> 95 %) the addition products A and E. The rate constant, at room temperature was found to be 0.077 relative to that of 1-butene, whose rate constant is well known. This value is in good agreement with the value obtained by Simonaitis and Heicklen,¹⁷ who extended the temperature range from 298° - 548°K. They found the Arrhenius expression for the rate constant to be equal to $9.1 \times 10^{12} \exp(-2220/RT) \text{ cm}^3/\text{mole-sec.}$

Photolysis of Nitrous Oxide

$O(^3P)$ atoms can be produced by the photolysis of nitrous oxide in the presence of mercury with 2537 Å radiation.¹⁸ The mechanism is:



CHAPTER II

EXPERIMENTAL

The Competitive Reaction of $O(^3P)$ with Ozone and Carbonyl Sulfide

The Vacuum Line

The high vacuum line was constructed of Pyrex glass and was free of mercury and grease; teflon stopcocks (West Glass) were used throughout. Figure 2 illustrates the location of the reaction cell and other components. The pumping system consists of a three-stage oil diffusion pump (Consolidated Vacuum Corporation) and a Welch Duo-Seal oil pump (model 1399). Ozone pressures were measured on a sulfuric acid manometer, and carbonyl sulfide pressures were measured on an alphasatron gauge (NCR, type 530).

Optical System

A cylindrical quartz cell, 10 cm. in length and 5 cm. in diameter, was used as a reaction vessel. A Hanovia medium pressure mercury lamp (model 30620) was used as a source of radiation. A Corning (CS 3-72) filter was used to remove radiation below 4300 Å.

Gas Chromatograph

Gas chromatography was used for the quantitative analysis of CO and CO₂. The gas chromatograph system consisted of a detector (Gow Mac model 10-777), a power supply (Gow Mac model 40-012), and a recorder (Texas Instrument, Servo Riter II). The detector was kept at 0°C and a current of 15 milliamperes was provided by the power supply.

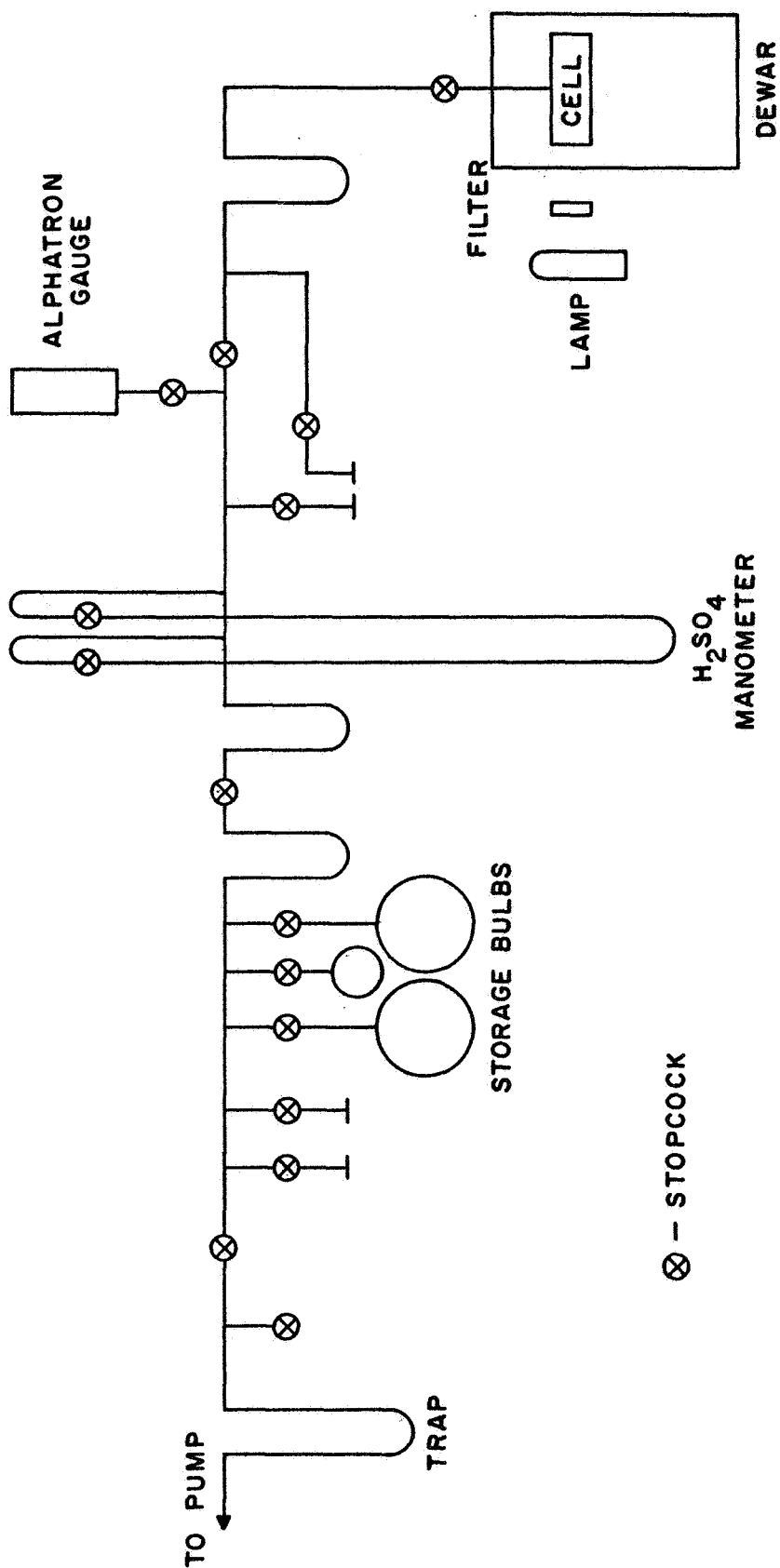


FIGURE 2
MERCURY FREE VACUUM LINE

Helium, passed through indicating drierite and ascarite, was used as the carrier gas.

A porapak (type Q) column, twelve feet long was used to analyze for CO₂, with a carrier gas pressure of twenty-five psi. The CO was analyzed on a molecular sieve (5A) column three and one-half feet long with a carrier gas pressure of fifteen psi.

Reagents

Ozone was prepared by passing an electrical discharge from a tesla coil through the glass walls of the vacuum line containing oxygen (Air Products, research grade). The ozone was condensed in a liquid nitrogen trap and degassed. The discharge process was relatively fast (5-10 minutes) if the oxygen pressure in the line was five to six torr or less. The ozone was distilled twice from liquid argon (-186°C) to liquid nitrogen (-196°C) with continuous pumping.

Carbonyl sulfide was purified by passing it through a one inch diameter glass tube containing about three inches of drierite and about ten inches of ascarite (8-20 mesh) and then distilling it twice at -130°C (n-pentane slush).

The carbon monoxide (chemically pure) and the carbon dioxide (bone dry) used to calibrate the gas chromatograph were from Matheson.

The tetrafluoromethane (Matheson) used to study foreign body effects was purified by passing it through ascarite and distilling it at -160°C (iso-pentane slush).

The helium used to study foreign body effects was the same as that used as the carrier gas in the chromatograph.

Temperature Control

The temperatures were maintained by submerging the cell in an unsilvered dewar filled with a liquid at the desired temperature. The length of the runs were short enough so that the temperature did not vary by more than 1.0 degree. Ice water was used to maintain the temperature at 273°K, with care being taken to keep pieces of ice out of the path of the radiation. Water at 299°K was used to maintain that temperature. The 197°K temperature was maintained with a mixture of dry ice and acetone. Acetone cooled with liquid nitrogen was used to maintain the 228°K temperature.

Procedure

The vacuum line was pumped down to less than one micron on the alphanatron gauge. After degassing the ozone and filling the reaction cell, the carbonyl sulfide was admitted into the cell simultaneously with the opening of the shutter of the lamp. The lamp was previously allowed at least 20 minutes to warm up. At the end of the irradiation period the contents of the cell were allowed to expand into a liquid nitrogen trap, where the ozone, carbon dioxide, and carbonyl sulfide condensed. The carbon monoxide was allowed to expand filling a collecting tube. Fifteen to twenty minutes were allowed for equilibrium of the carbon monoxide after the expansion. The aliquot of carbon monoxide was then removed for analysis. The remaining condensed gases were distilled at -186°C to remove the excess ozone. The carbon dioxide and carbonyl sulfide were then condensed into a liquid nitrogen trap and removed for analysis.

The Competitive Reaction of $O(^3P)$ with 2-Trifluoromethylpropene and Carbonyl Sulfide

The Vacuum Line

The high vacuum line was constructed of Pyrex glass in the usual fashion. Figure 3 illustrates the location of the various components. A mercury diffusion pump and a Welch Duo-Seal oil pump (model 1402) comprised the pumping system. Pressures less than 10 torr were measured on a McLeod gauge (Consolidated Vacuum Corporation), pressures greater than 10 torr were measured on a mercury manometer. A thermocouple gauge was used to monitor the admission of gases to the line.

Optical System

The same cell described earlier was used as a reaction vessel. A Hanovia spiral low pressure mercury resonance lamp was used as a source of radiation. Corning (9-30) filters were used to remove radiation below 2200 Å.

Gas Chromatograph

The gas chromatograph system used was the same as that described earlier.

A molecular sieve (5A) column, seven feet long was used to analyze for nitrogen and carbon monoxide. The carrier gas pressure was twenty psi. A ten foot Kel-F oil number three on Chromosorb P column was used to analyze for 2-trifluoromethylpropionaldehyde and 2-trifluoromethylpropylene oxide. The column was kept at 38°C and a carrier gas pressure of thirty psi was used.

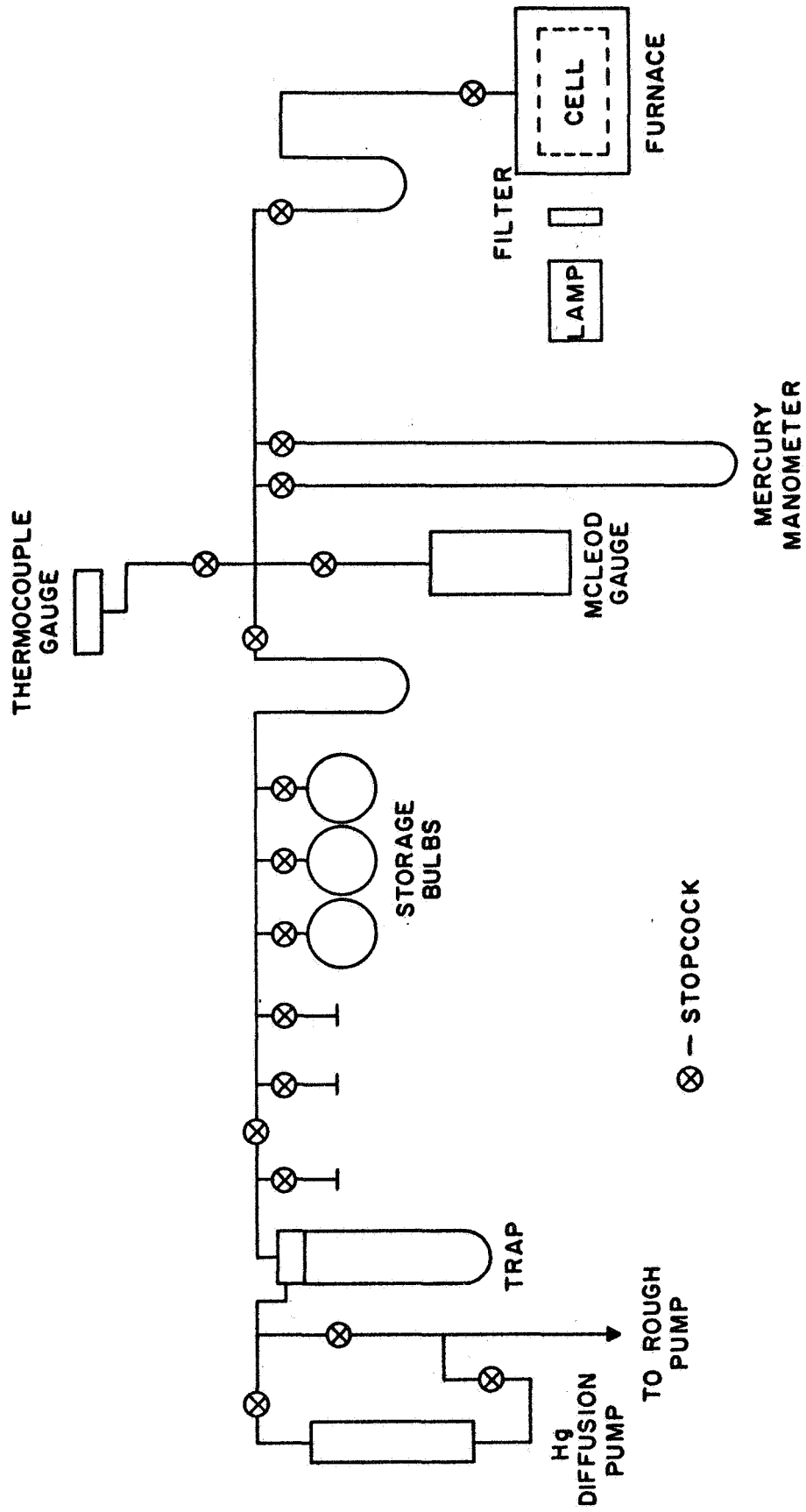


FIGURE 3
VACUUM LINE

Reagents

Trifluoromethylpropene-2 (Peninsular Chem Research, Inc.) was purified by passing it through ascarite and degassing it at -196°C .

The carbonyl sulfide was purified in the same manner as described earlier.

The nitrous oxide (Matheson) was degassed at -196°C .

Temperature Control

The cell was placed inside an aluminum block furnace, where the temperature was maintained by a regulator (Dohrmann, Model 1300), which controlled it to $\pm 0.5^{\circ}\text{C}$.

Procedure

The vacuum line was pumped down to less than one micron. Trifluoromethylpropene-2, carbonyl sulfide, and nitrous oxide were admitted into the reaction cell and irradiated. The lamp was allowed to warm up for at least ten minutes prior to irradiation. At the end of the irradiation period the cell was opened and the contents were allowed to expand into the line through a liquid nitrogen trap which condensed the aldehyde, epoxide, nitrous oxide, and carbonyl sulfide. The non-condensibles, nitrogen, oxygen, and carbon monoxide were collected by a Toepler pump into a tube for analysis. The nitrous oxide and carbonyl sulfide were distilled away at -130°C (n-pentane slush) and the remaining aldehyde and epoxide were condensed into a collecting tube for analysis.

CHAPTER III

RESULTS

Reaction of O(³P) Atoms with O₃ and OCS

The results of the photolysis of mixtures of ozone and carbonyl sulfide, in the temperature range 197°-299°K, are shown in Tables 4-10. Ozone pressures of approximately 3 torr and 12 torr were mixed with OCS pressures varying between 0.5 torr and 223 torr. The products CO and CO₂ were identified and quantitatively analyzed.

The following expression for the theoretical rate of production of CO, R{CO}_t, can be derived from reactions 1-3:

$$R\{CO\}_t = \left[\frac{k_3[OCS]}{k_1[O_3] + k_3[OCS]} \right] I_a$$

where I_a is the absorbed intensity. Since CO is known to react with ozone to produce CO₂, R{CO}_t must be corrected for the CO lost through this reaction. Since one molecule of CO₂ is produced for each molecule of CO lost, R{CO}_t can be written as R{CO} + R{CO₂}, where R{CO} and R{CO₂} represent the measured rates of production of CO and CO₂ respectively. The previous expression for R{CO}_t becomes:

$$R\{CO\} + R\{CO_2\} = \left[\frac{k_3[OCS]}{k_1[O_3] + k_3[OCS]} \right] I_a$$

At constant ozone pressure, the R{CO} + R{CO₂} increased with increasing OCS pressures and then leveled off, approaching a

TABLE 4

PHOTOLYSIS OF OZONE IN THE PRESENCE OF CARBONYL SULFIDE

AT 197°K, $[O_3] = 3$ TORR, AND IRRADIATION TIME = 30 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
2.78	1.01	3.19	0.043	0.6	0.734	0.067	0.251
2.70	2.02	3.1	0.028	0.8	1.17	0.033	0.388
2.94	2.92	3.37	0.022	0.39	1.47	0.267	0.505
2.92	6.0	3.35	0.017	0.4	1.9	0.3	0.658
3.05	21.6	3.5	0.025	1.0	2.63	0.0	0.751

d represents dark reaction

l represents light reaction

 $R\{CO\}$ = rate of CO production $R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

TABLE 5

PHOTOLYSIS OF OZONE IN THE PRESENCE OF CARBONYL SULFIDE
 AT 197°K, $[O_3] = 12$ TORR, AND IRRADIATION TIME = 30 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[\Phi\{CO\} + \Phi\{CO_2\}]^*$
11.69	1.01	10.8	0.11	0.5	0.534	0.367	0.083
11.95	1.5	11.0	0.05	0.545	1.13	0.3	0.133
12.08	2.02	11.1	0.044	0.52	1.43	0.368	0.162
12.0	4.4	11.1	0.027	1.0	2.4	0.0	0.216
12.3	6.3	11.4	0.019	0.75	3.47	0.13	0.316
12.2	28.3	11.3	0.099	0.59	5.16	0.7	0.515

d represents dark reaction

l represents light reaction

$R\{CO\}$ = rate of CO production

$R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

TABLE 6

PHOTOLYSIS OF OZONE IN THE PRESENCE OF CARBONYL SULFIDE

AT 228°K, $[O_3] = 3$ TORR, AND IRRADIATION TIME = 30 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
2.86	1.5	2.86	0.041	1.0	0.766	0.0	0.268
3.02	2.02	3.02	0.031	0.4	1.03	0.1	0.374
2.67	3.81	2.67	0.022	0.63	1.5	0.1	0.6
3.08	22.82	3.08	0.068	0.79	2.3	0.23	0.826

d represents dark reaction

l represents light reaction

 $R\{CO\}$ = rate of CO production $R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

TABLE 7

PHOTOLYSIS OF OZONE IN THE PRESENCE OF CARBONYL SULFIDE

AT 273°K, $[O_3] = 3$ TORR, AND IRRADIATION TIME = 30 MINUTES

$[O_3]$ (torr)	[OCS] (torr)	I_a (μ /min)	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
2.39	1.01	3.22	0.0	0.364	1.03	0.234	0.394
3.03	2.02	4.08	0.039	0.86	1.63	0.067	0.417
2.86	3.63	3.85	0.015	0.82	2.13	0.10	0.578
2.94	7.56	3.96	0.078	0.56	2.36	0.50	0.725
2.94	23.46	3.96	0.147	0.57	2.7	0.70	0.855

d represents dark reaction

l represents light reaction

 $R\{CO\}$ = rate of CO production $R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

TABLE 8

PHOTOLYSIS OF OZONE IN THE PRESENCE OF CARBONYL SULFIDE
 AT 273°K, $[O_3] = 12$ TORR, AND IRRADIATION TIME = 30 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
10.79	1.01	12.85	0.029	1.0	1.13	0.0	0.088
10.8	1.5	12.9	0.06	0.69	1.73	0.3	0.157
10.93	2.02	13.5	0.03	0.56	2.17	0.13	0.174
12.2	3.2	14.55	0.035	0.29	3.7	1.13	0.332
12.1	4.9	14.45	0.027	0.60	4.86	0.4	0.363
11.9	22.5	14.2	0.051	0.93	9.25	0.2	0.666
12.2	81.0	14.55	0.20	0.82	10.9	1.1	0.826

d represents dark reaction

l represents light reaction

$R\{CO\}$ = rate of CO production

$R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

TABLE 9
PHOTOLYSIS OF OZONE IN THE PRESENCE OF CARBONYL SULFIDE
AT 299°K, [O₃] = 3 TORR, AND IRRADIATION TIME = 30 MINUTES

[O ₃] (torr)	[OCS] (torr)	I _a (μ/min)	[CO] _d /[CO] _l	[CO ₂] _d /[CO ₂] _l	R{CO} (μ/min)	R{CO ₂ } (μ/min)	[Φ{CO} + Φ{CO ₂ }] *
2.84	1.01	3.65	0.0	0.91	0.935	0.033	0.265
2.76	1.2	3.54	0.061	1.0	1.03	0.0	0.291
2.87	1.46	3.68	0.03	0.46	1.1	0.30	0.38
2.95	3.0	3.78	0.074	0.89	1.67	0.067	0.46
3.0	6.93	3.85	0.095	0.36	2.23	0.534	0.72
2.95	23.95	3.78	0.316	0.571	2.16	1.20	0.89
3.12	39.38	4.0	0.395	0.585	2.3	1.53	0.96
2.86	70.04	3.67	0.506	0.716	2.3	1.30	0.98

d represents dark reaction

l represents light reaction

R{CO} = rate of CO production

R{CO₂} = rate of CO₂ production

* corrected for dark reaction

TABLE 10

PHOTOLYSIS OF OZONE IN THE PRESENCE OF CARBONYL SULFIDE

AT 299°K, $[O_3] = 12$ TORR, AND IRRADIATION TIME = 30 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
11.39	1.01	12.8	0.051	1.0	1.23	0.0	0.096
11.75	1.5	13.3	0.121	1.0	1.7	0.0	0.128
11.76	2.02	13.2	0.138	0.788	2.3	0.233	0.192
12.1	3.3	13.6	0.118	0.87	3.5	0.133	0.268
11.8	5.2	13.2	0.141	0.75	4.47	0.33	0.363
12.0	24.5	13.5	0.11	0.71	7.6	0.6	0.606
12.3	84.7	13.8	0.285	0.78	9.2	1.53	0.775
12.0	223.	13.5	0.419	0.749	9.49	2.8	0.909

d represents dark reaction

l represents light reaction

 $R\{CO\}$ = rate of CO production $R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

constant value. Thus at high OCS pressures essentially all of the $O(^3P)$ atoms reacted with the OCS, making it possible to use the high OCS/O_3 rate as an actinometer.

At large excess of OCS, $k_1[O_3]$ is negligible compared to $k_3[OCS]$ and hence $I_a = R\{CO\} + R\{CO_2\}$. The quantum yields of CO and CO_2 production, $\Phi\{CO\}$ and $\Phi\{CO_2\}$, could then be determined.

Studies were done in which the irradiation time and the intensity, for otherwise similar conditions, were changed by a factor of six and nine respectively. These variations showed no effect on the $\Phi\{CO\} + \Phi\{CO_2\}$. The experimental conditions for the time and intensity studies are given in Tables 11 and 12 respectively.

When ozone is photolyzed at the wavelengths used, some energy exists in excess of that required for the dissociation of ozone. This energy could be in the form of translational energy of the $O(^3P)$ atom. If a non-reactive foreign gas is included in the mixture of O_3 and OCS, the $O(^3P)$ atoms produced by the photolysis of O_3 will lose translational energy through collisions with the foreign gas. Helium and tetrafluoromethane were used as foreign gases to determine if this loss of translational energy had any effect on the relative rate constants k_1/k_3 .

The results of the addition of helium were inconclusive because the points obtained showed considerable scatter and were not reproducible. The addition of CF_4 as a foreign gas showed no effect on the relative rate constants k_1/k_3 . The experimental conditions for the He and CF_4 experiments may be found in Tables 13 and 14 respectively.

TABLE 11

TIME STUDY OF THE PHOTOLYSIS OF OZONE IN THE PRESENCE OF
CARBONYL SULFIDE AT 299°K AND $[O_3] = 3$ TORR

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ/min)	Irradiation time-min.	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ/min)	$R\{CO_2\}$ (μ/min)	$[R\{CO\} + R\{CO_2\}]^*$
3.31	0.97	3.78	10	0.0	1.0	0.9	0.0	0.238
2.61	1.01	2.98	20	0.0	1.0	0.8	0.0	0.268
2.86	23.89	3.27	10	0.576	0.581	2.3	2.3	1.41
2.84	23.96	3.24	20	0.433	0.625	2.1	1.2	1.02
3.02	24.18	3.45	60	0.242	0.478	1.94	1.16	0.9

d represents dark reaction

l represents light reaction

$R\{CO\}$ = rate of CO production

$R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

TABLE 12

INTENSITY STUDY OF THE PHOTOLYSIS OF OZONE IN THE PRESENCE
OF CARBONYL SULFIDE AT 299°K, $[O_3] = 3$ TORR, AND IRRADIATION

TIME = 285 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_1$	$[CO_2]_d/[CO_2]_1$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
3.21	1.01	0.47	0.369	0.865	0.084	0.011	0.202
2.93	1.99	0.43	0.303	1.0	0.162	0.00	0.376
2.96	4.32	0.434	0.156	0.69	0.266	0.032	0.685
3.1	6.8	0.454	0.21	0.91	0.277	0.007	0.625
2.9	23.8	0.425	0.35	0.56	0.291	0.126	0.982

d represents dark reaction

1 represents light reaction

$R\{CO\}$ = rate of CO production

$R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

TABLE 13

EFFECT OF HELIUM ON THE PHOTOLYSIS OF OZONE IN THE
 PRESENCE OF CARBONYL SULFIDE AT 299°K, $[O_3] = 3$ TORR,
 AND IRRADIATION TIME ≈ 30 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_1$	$[CO_2]_d/[CO_2]_1$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
2.84	1.01	3.25	0.296	1.0	1.03	0.0	0.317
2.77	1.01	3.17	0.33	0.67	0.534	0.1	0.2
3.01	1.46	3.44	0.445	1.0	0.5	0.0	0.145
3.01	1.5	3.44	0.308	1.0	0.6	0.0	0.175
2.84	3.23	3.25	0.419	0.31	1.06	0.3	0.422
3.06	3.01	3.5	0.218	1.0	1.43	0.0	0.457
2.96	4.33	3.49	0.258	0.58	1.43	0.6	0.459
2.82	23.58	3.23	0.596	0.79	1.4	0.43	0.567

d represents dark reaction

* corrected for dark reaction

l represents light reaction

 $[He] = 520$ torr $R\{CO\}$ = rate of CO production $R\{CO_2\}$ = rate of CO_2 production

TABLE 14

EFFECT OF TETRAFLUOROMETHANE ON THE PHOTOLYSIS OF
OZONE IN THE PRESENCE OF CARBONYL SULFIDE AT 299°K,

$[O_3] = 3$ TORR AND IRRADIATION TIME = 30 MINUTES

$[O_3]$ (torr)	$[OCS]$ (torr)	I_a (μ /min)	$[CO]_d/[CO]_l$	$[CO_2]_d/[CO_2]_l$	$R\{CO\}$ (μ /min)	$R\{CO_2\}$ (μ /min)	$[R\{CO\} + R\{CO_2\}]^*$
3.03	0.5	3.37	0.25	0.8	0.4	0.067	0.138
3.09	1.01	3.44	0.241	0.89	0.734	0.033	0.222
3.04	1.5	3.39	0.114	1.0	1.3	0.0	0.385
2.97	3.04	3.31	0.103	0.536	1.73	0.434	0.653
3.04	3.86	3.39	0.312	1.0	1.4	0.0	0.414
2.81	28.0	3.13	0.137	1.0	2.53	0.0	0.813

d represents dark reaction

l represents light reaction

$R\{CO\}$ = rate of CO production

$R\{CO_2\}$ = rate of CO_2 production

* corrected for dark reaction

$[CF_4] = 300$ torr

The present investigation was complicated by a dark reaction which produced both CO and CO₂. The ratio of the rate of CO produced, R{CO}, in the dark runs to the R{CO}, produced in the light runs was found to be less than 10% at OCS pressures less than approximately 15 torr. This ratio was found to increase slightly with ozone pressure and with temperature. The ratio of the rate of CO₂ produced, R{CO₂}, in the dark runs to the R{CO₂}, produced in the light runs was found to average approximately 70%, with no noticeable ozone pressure or temperature effect.

Reaction of O(³P) Atoms with TMP and OCS

The results of the mercury photosensitized decomposition of nitrous oxide in the presence of mixtures of 2-trifluoromethylpropene and carbonyl sulfide in the temperature range 298°-523°K, are shown in Tables 15-17. The products CO, N₂, the aldehyde A, and the epoxide E were identified and quantitatively analyzed.

TMP pressures were held approximately constant at 0.7 torr except in a few cases where the pressure was varied between 2 torr and 4.7 torr. The OCS pressure was varied between 1.4 torr and 18.3 torr, always maintaining a [TMP]/[OCS] ratio between 0.06 and 0.45. At ratios of [TMP]/[OCS] exceeding this range, the rate of CO production, R{CO}, in the absence of OCS became a significant factor, and was measured by photolyzing N₂O and TMP in the absence of OCS. The CO produced in the absence of OCS was generally less than 15% of the total CO produced with OCS present. The ratios [N₂O]/[OCS] > 38 and [N₂O]/[TMP] > 130 were maintained to minimize the quenching of mercury by TMP and OCS.

TABLE 15

MERCURY PHOTOSENSITIZED DECOMPOSITION OF N_2O IN THE
 PRESENCE OF MIXTURES OF CARBONYL SULFIDE AND
 2-TRIFLUOROMETHYLPROPENE AT 298°K

[OCS] (torr)	[TMP] (torr)	[N_2O] (torr)	Irradiation Time (min)	I_a^* (μ /min)	$\Phi\{CO\}$	$\Phi\{E\}$	$\Phi\{A\}$	[TMP]**/[OCS]
0.0	0.770	590	180	1.01	0.022	0.6	0.4	-
7.7	0.680	657	50	1.1	0.267	0.39	0.27	0.085
6.4	0.725	584	50	1.08	0.204	-	-	0.109
2.31	0.290	532	15	2.66	0.218	0.32	0.22	0.117
4.37	0.785	500	163	1.01	0.173	0.45	0.33	0.161
13.3	2.4	500	20	7.2	0.205	0.48	0.34	0.175
3.44	0.760	550	10	8.0	0.131	0.46	0.30	0.182
10.8	2.0	500	52	1.08	0.184	0.41	0.26	0.183
3.66	0.780	544	102	1.08	0.138	0.44	0.31	0.197
2.85	0.760	523	25	8.0	0.123	0.54	0.37	0.232
18.3	4.7	610	120	1.05	0.163	0.51	0.36	0.253

TABLE 15 cont'd

[OCS] (torr)	[TMP] (torr)	[N ₂ O] (torr)	Irradiation Time (min)	I _a [*] (μ/min)	Φ{CO}	Φ{E}	Φ{A}	[TMP] ^{**} /[OCS]
1.93	0.715	490	225	1.04	0.098	0.53	0.40	0.309
1.43	0.725	555	20	11.9	0.080	0.60	0.39	0.425
5.65	2.55	516	119	1.03	0.093	0.51	0.42	0.44

* Pressure based on calibrations at 298°K

** Average value of [TMP] used to calculate ratio

TABLE 16

MERCURY PHOTOSENSITIZED DECOMPOSITION OF N_2O IN THE
 PRESENCE OF MIXTURES OF CARBONYL SULFIDE AND
 2-TRIFLUOROMETHYLPROPENE AT 398°K

[OCS] (torr)	[TMP] (torr)	[N_2O] (torr)	Irradiation Time (min)	I_a^* (μ /min)	$\Phi\{CO\}$	$\Phi\{E\}$	$\Phi\{A\}$	[TMP]**/[OCS]
0.0	0.630	587	227	1.61	0.075	0.6	0.4	-
9.36	0.640	571	21	1.61	0.474	0.26	0.17	0.067
5.95	0.655	663	20	1.6	0.475	0.21	0.19	0.107
7.2	0.840	592	20	1.6	0.422	0.29	0.19	0.119
3.66	0.740	664	40	1.62	0.288	0.36	0.31	0.193
2.46	0.640	669	20	1.6	0.250	0.53	0.4	0.254
8.65	2.35	574	35	1.57	0.294	0.46	0.46	0.269
1.92	0.780	710	70	1.59	0.193	0.46	0.36	0.378

* Pressure based on calibration at 298°K

** Average value of [TMP] used to calculate ratio

TABLE 17

MERCURY PHOTOSENSITIZED DECOMPOSITION OF N₂O IN THE
 PRESENCE OF MIXTURES OF CARBONYL SULFIDE AND
 2-TRIFLUOROMETHYLPROPENE AT 523°K

[OCS] (torr)	[TMP] (torr)	[N ₂ O] (torr)	Irradiation Time (min)	I _a [*] (μ/min)	Φ{CO}	[TMP]**/[OCS]
0.0	0.740	620	181	1.82	0.11	-
6.94	0.760	621	20	1.85	0.568	0.107
5.07	0.835	647	15	1.85	0.512	0.162
3.11	0.790	593	15	1.86	0.465	0.25
2.26	0.745	647	15	1.86	0.401	0.323
2.1	0.900	677	20	1.87	0.341	0.42
1.54	0.665	550	17	1.87	0.346	0.422

* Pressure based on calibrations at 298°K

** Average value of [TMP] used to calculate ratio

The absorbed intensity, I_a was taken equal to the rate of production of N_2 . The I_a was varied from 1 μ /min to 11.9 μ /min (pressures based on calibrations at 298°K) with no effect on the quantum yield, $\Phi\{CO\}$. The irradiation time was varied from 15 to 227 minutes with no effect on $\Phi\{CO\}$.

The quantum yields of E and A were measured at 298°K and 398°K. Examination of Tables 15 and 16 show that all of the $O(^3P)$ atoms reacted either with TMP or OCS, since the sum of the quantum yields of A, E, and CO are, within experimental error, equal to one. As the ratio of $[TMP]/[OCS]$ was increased, the $R\{CO\}$ decreased.

CHAPTER IV.

DISCUSSION

Reaction of $O(^3P)$ Atoms with O_3 and OCS

The reaction scheme proposed is:



The SO produced in reaction 3 is known to react rapidly with O_3 to produce SO_2 and O_2 , thus eliminating the possibility of $O(^3P)$ atoms being lost to the SO.

If the previous expression:

$$R\{CO\} + R\{CO_2\} = \left[\frac{k_3[OCS]}{k_1[O_3] + k_3[OCS]} \right] I_a$$

is divided through by I_a , the following expression for the sum of the quantum yields of CO and CO_2 , $\Phi\{CO\} + \Phi\{CO_2\}$ is obtained.

$$\Phi\{CO\} + \Phi\{CO_2\} = \frac{k_3[OCS]}{k_1[O_3] + k_3[OCS]}$$

A more convenient expression is obtained by taking the reciprocal, giving:

$$\left[\Phi\{CO\} + \Phi\{CO_2\} \right]^{-1} = 1 + \frac{k_1[O_3]}{k_3[OCS]}$$

A plot of this expression yields a straight line whose slope is equal to k_1/k_3 and whose intercept is equal to one. Plots at each ozone pressure and temperature studied are shown in Figures 4-10.

From Figures 9, 11, and 12 it can be seen that k_1/k_3 is independent of the absorbed intensity, the irradiation time, and the addition of a foreign gas.

The relative rate constants k_1/k_3 were found to be independent of the ozone pressure used. The small differences in the value of k_1/k_3 at 3 torr and 12 torr ozone were averaged to obtain the value at each temperature. The observed and average values are shown in Table 18.

TABLE 18
OBSERVED VALUES OF k_1/k_3

	197°K	228°K	273°K	299°K
3 torr O ₃	1.05	1.05	0.934	0.938
12 torr O ₃	0.92	-	0.915	0.865
average	0.98	1.05	0.925	0.901

An Arrhenius plot of k_1/k_3 is shown in Figure 13. The points show considerable scatter, thus the error in determining the difference in activation energy is large, $E_3 - E_1 = 170 \pm 70$ cal/mole. However, a large error would be expected since $E_3 - E_1$ is small compared to E_3 or E_1 . The relative pre-exponential factor $A_1/A_3 = 0.671 \pm .076$.

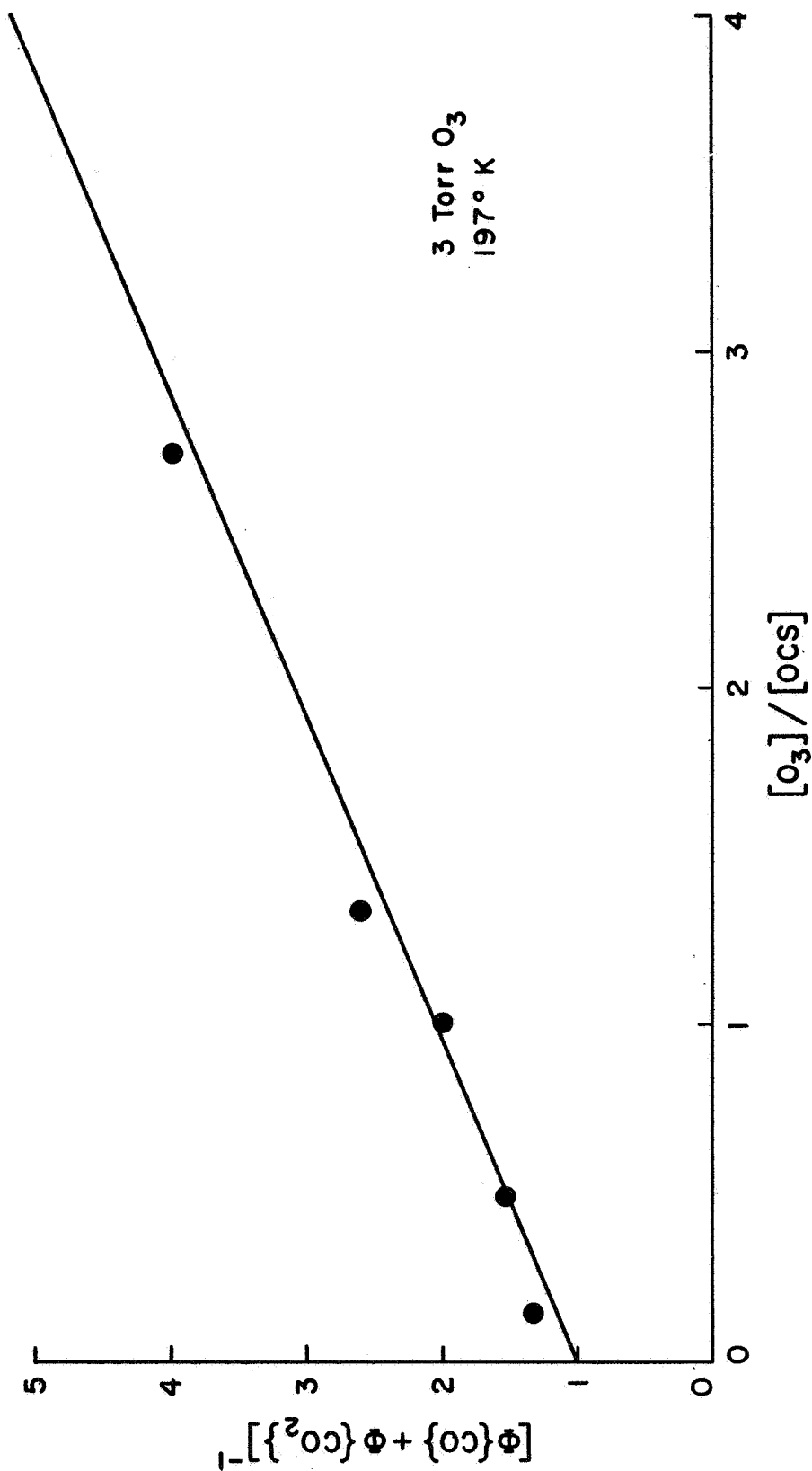


FIGURE 4
 $[\Phi\{CO\} + \Phi\{CO_2\}]^{-1}$ AS A FUNCTION OF
 $[O_3]/[OCS]$ AT 197°K AND $[O_3] = 3$ TORR

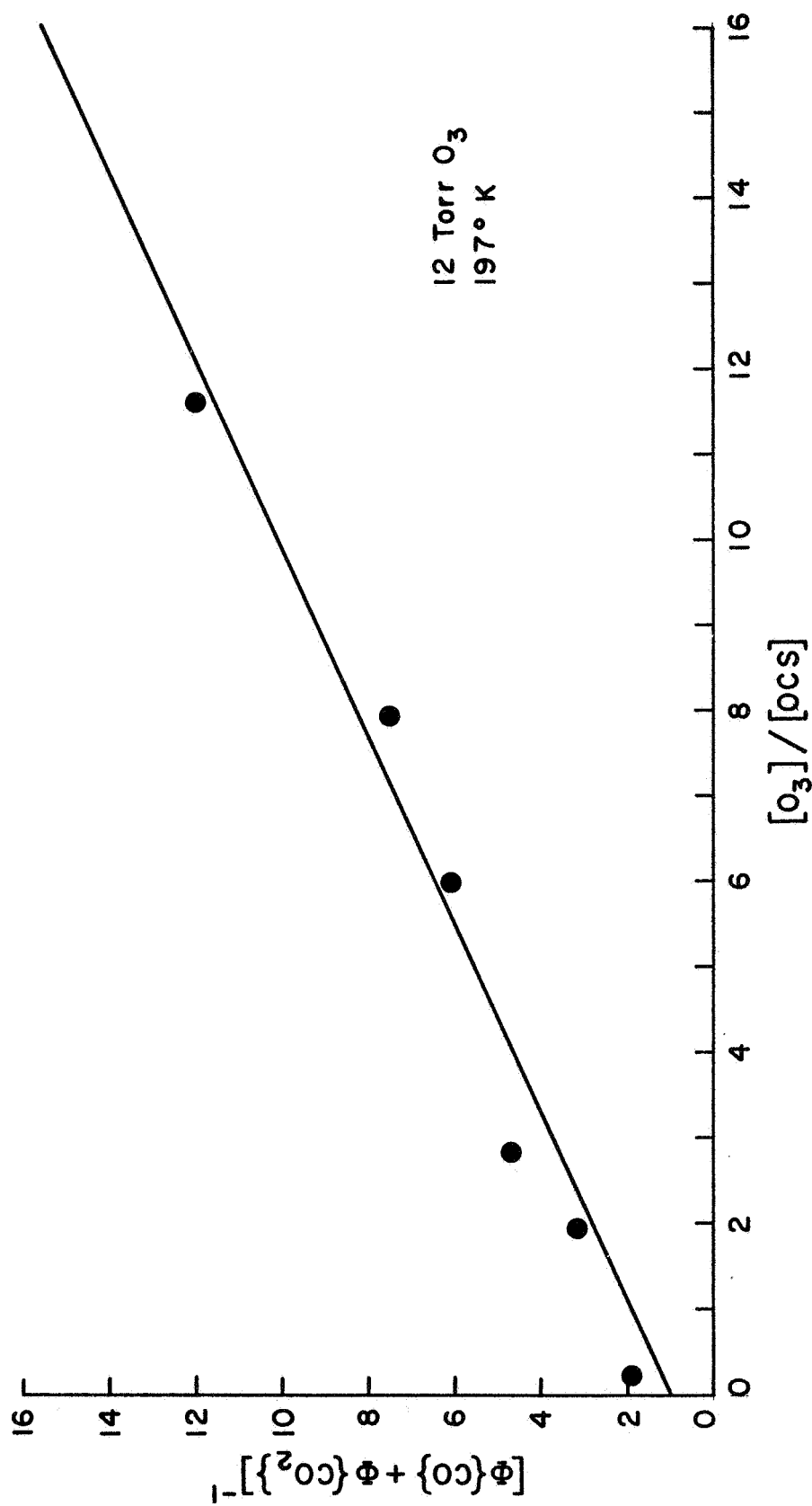


FIGURE 5

$[\Phi\{\text{CO}\} + \{\text{CO}_2\}\Phi]^{-1}$ AS A FUNCTION OF
 $[\text{O}_3]/[\text{OCS}]$ AT 197°K AND $[\text{O}_3] = 12$ TORR

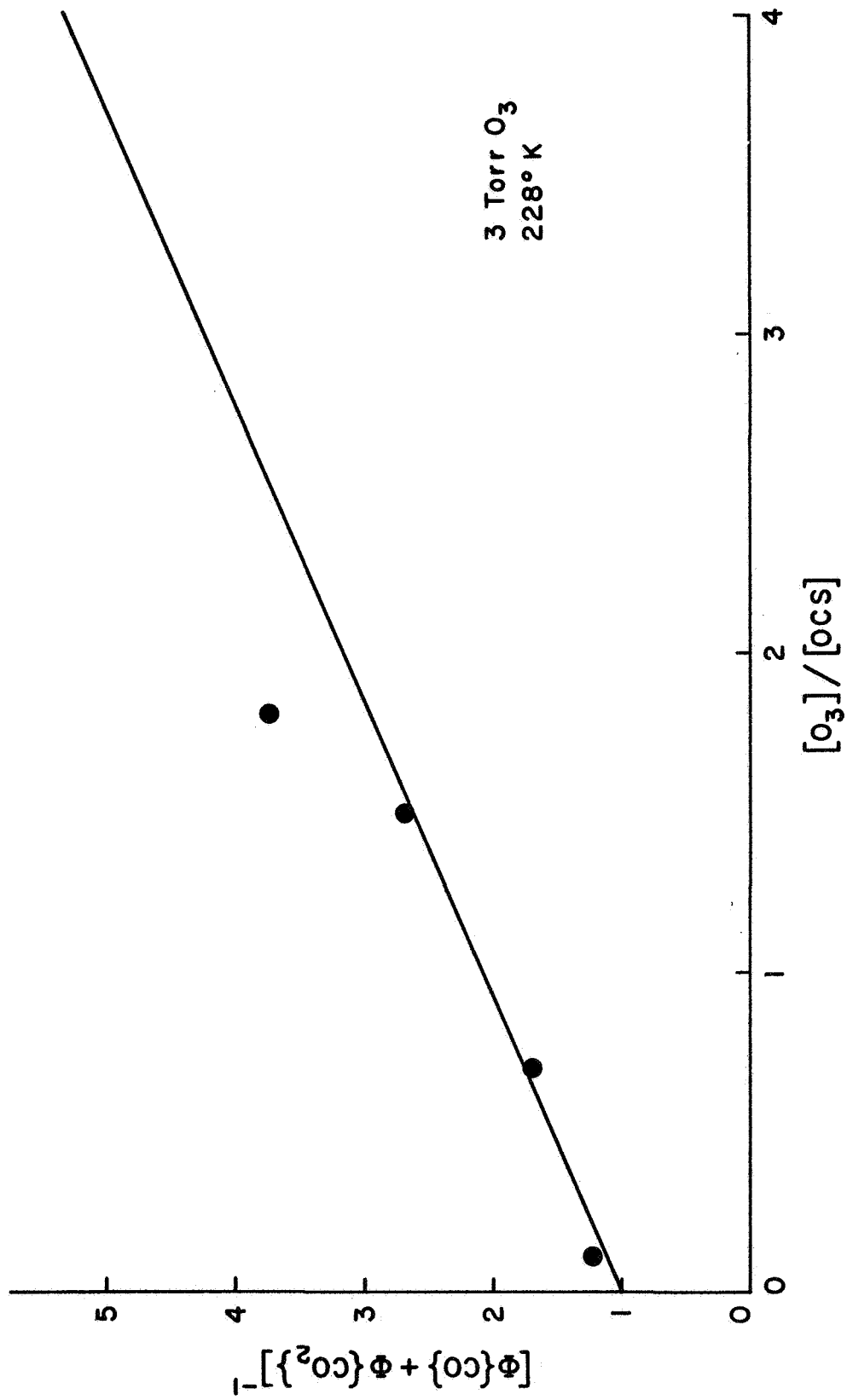


FIGURE 6
 $[\Phi\{CO\} + \Phi\{CO_2\}]^{-1}$ AS A FUNCTION OF
 $[O_3]/[OCS]$ AT 228°K AND $[O_3] = 3$ TORR

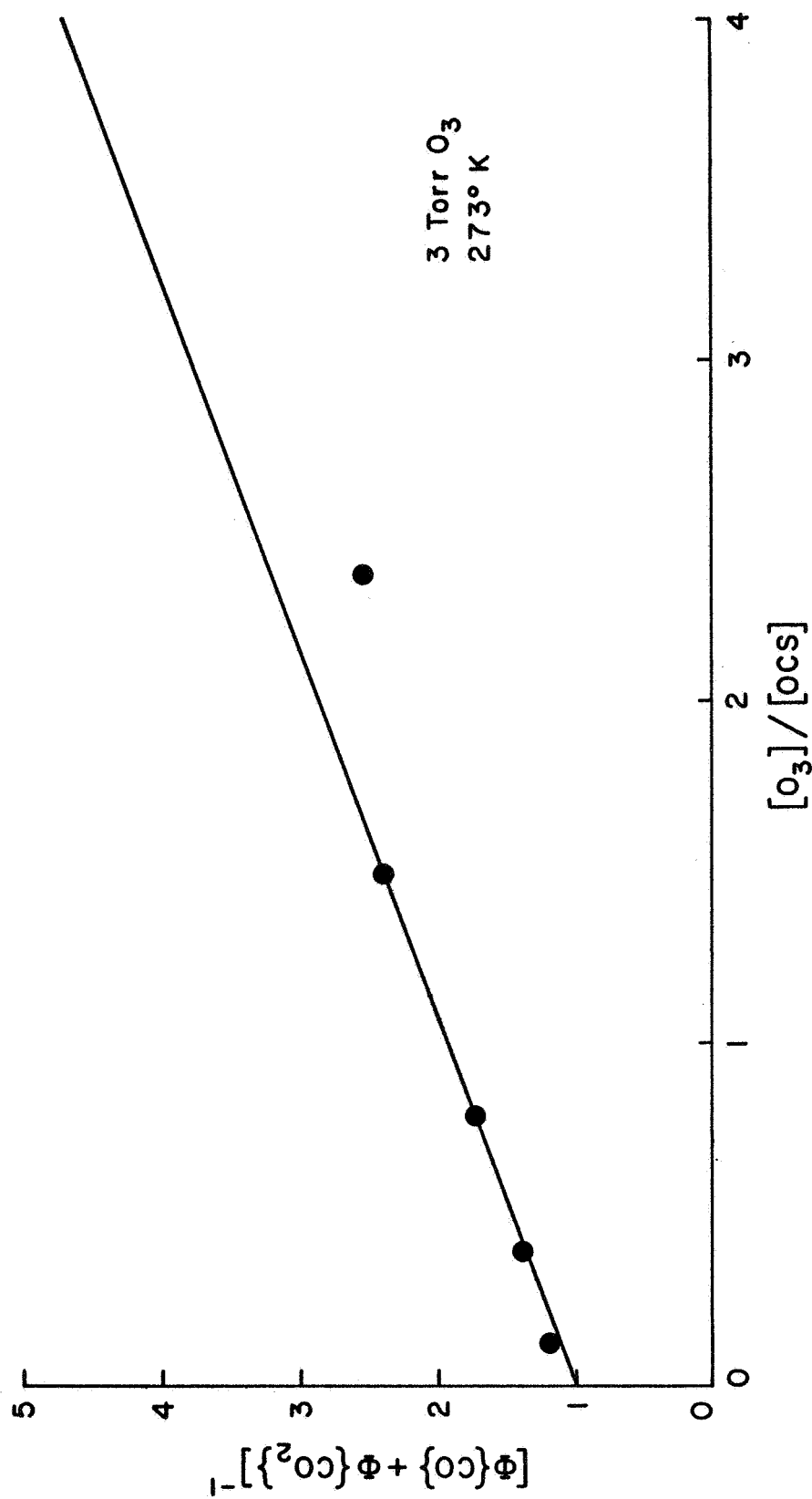


FIGURE 7

$[\Phi\{CO\} + \Phi\{CO_2\}]^{-1}$ AS A FUNCTION OF
 $[O_3]/[OCS]$ AT 273°K AND $[O_3] = 3$ TORR

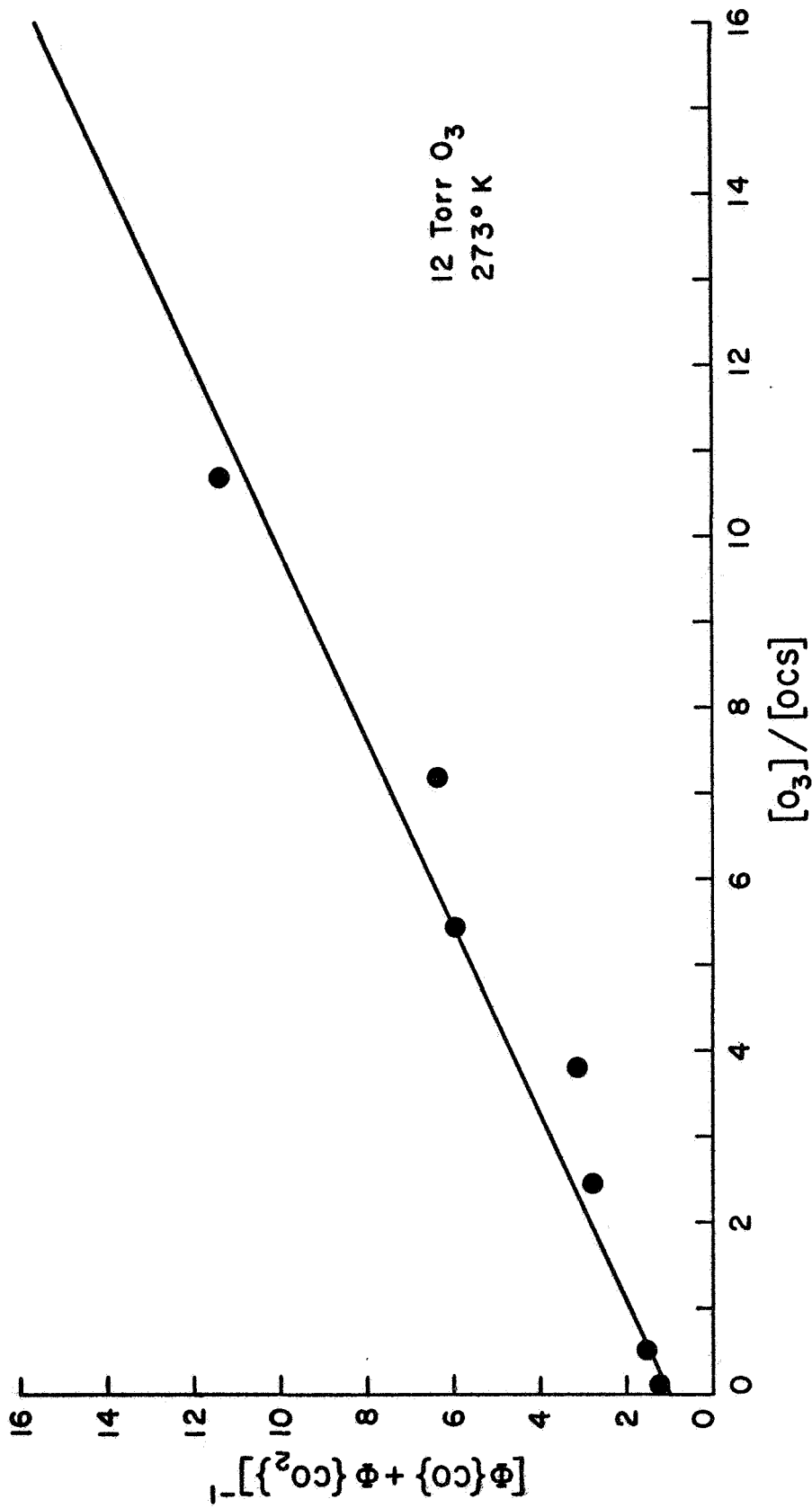


FIGURE 8
 $[\Phi\{CO\} + \Phi\{CO_2\}]^{-1}$ AS A FUNCTION OF
 $[O_3]/[OCS]$ AT 273°K and $[O_3] = 12$ TORR

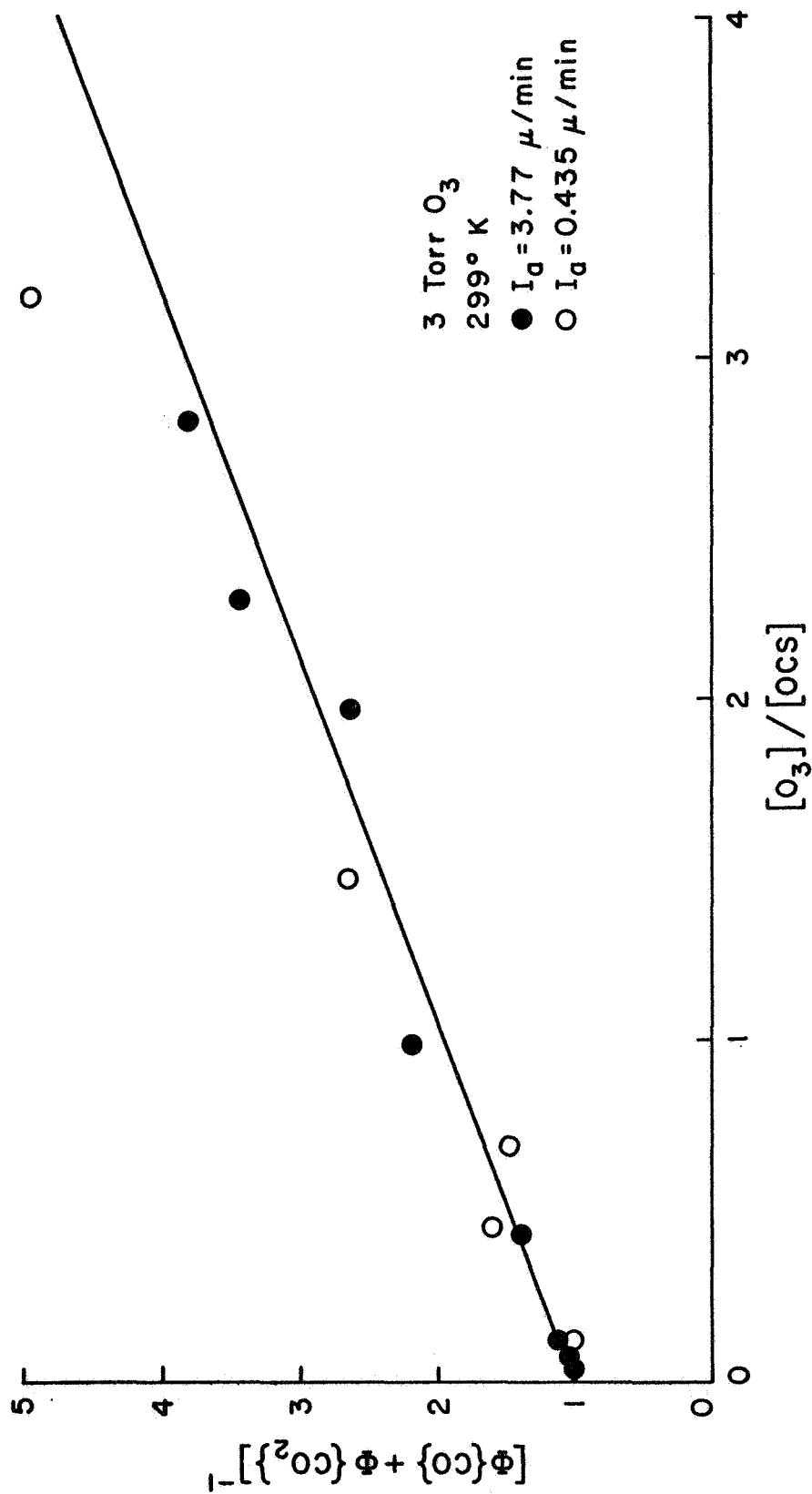


FIGURE 9
[$\Phi\{CO\} + \Phi\{CO_2\}$]⁻¹ AS A FUNCTION OF
[O₃]/[OCS] AT 299°K AND [O₃] = 3 TORR

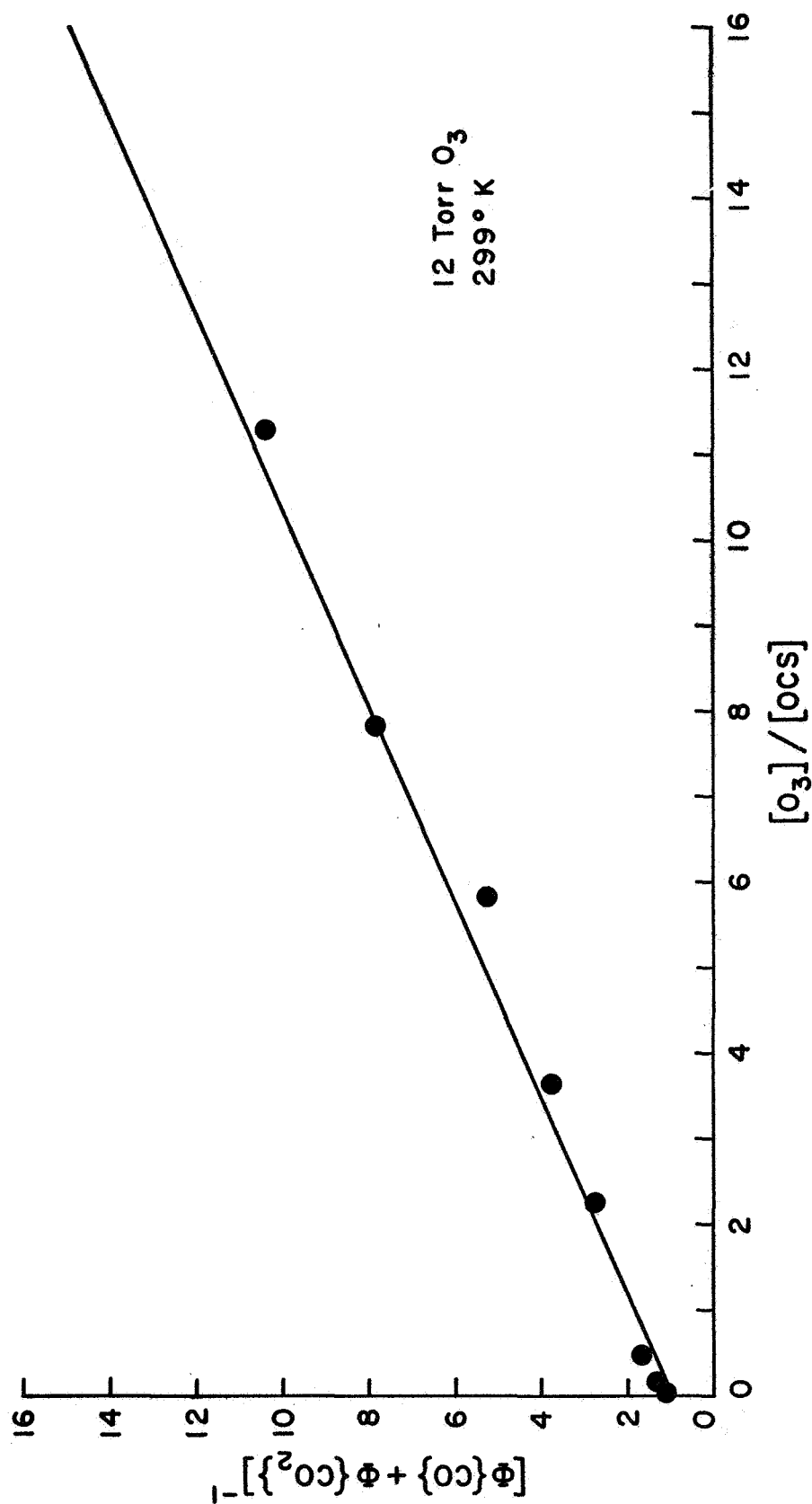


FIGURE 10

$[\Phi\{\text{CO}\} + \Phi\{\text{CO}_2\}]^{-1}$ AS A FUNCTION OF
 $[\text{O}_3]/[\text{OCS}]$ AT 299°K AND $[\text{O}_3] = 12$ TORR

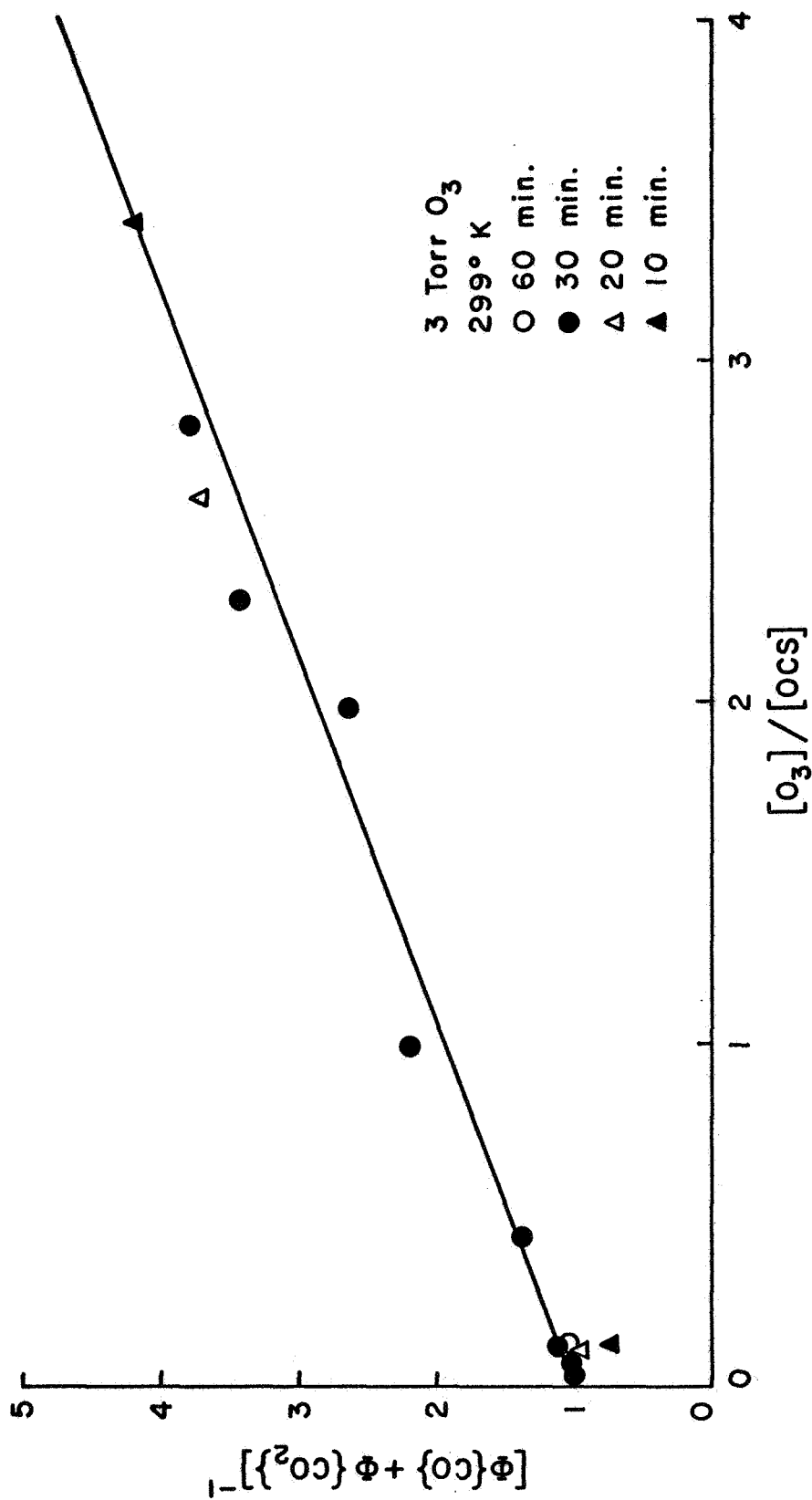


FIGURE 11

$[\Phi\{\text{CO}\} + \Phi\{\text{CO}_2\}]^{-1}$ AS A FUNCTION OF $[\text{O}_3]/[\text{OCS}]$ AT 299°K,
 $[\text{O}_3] = 3$ TORR AND VARYING IRRADIATION TIMES

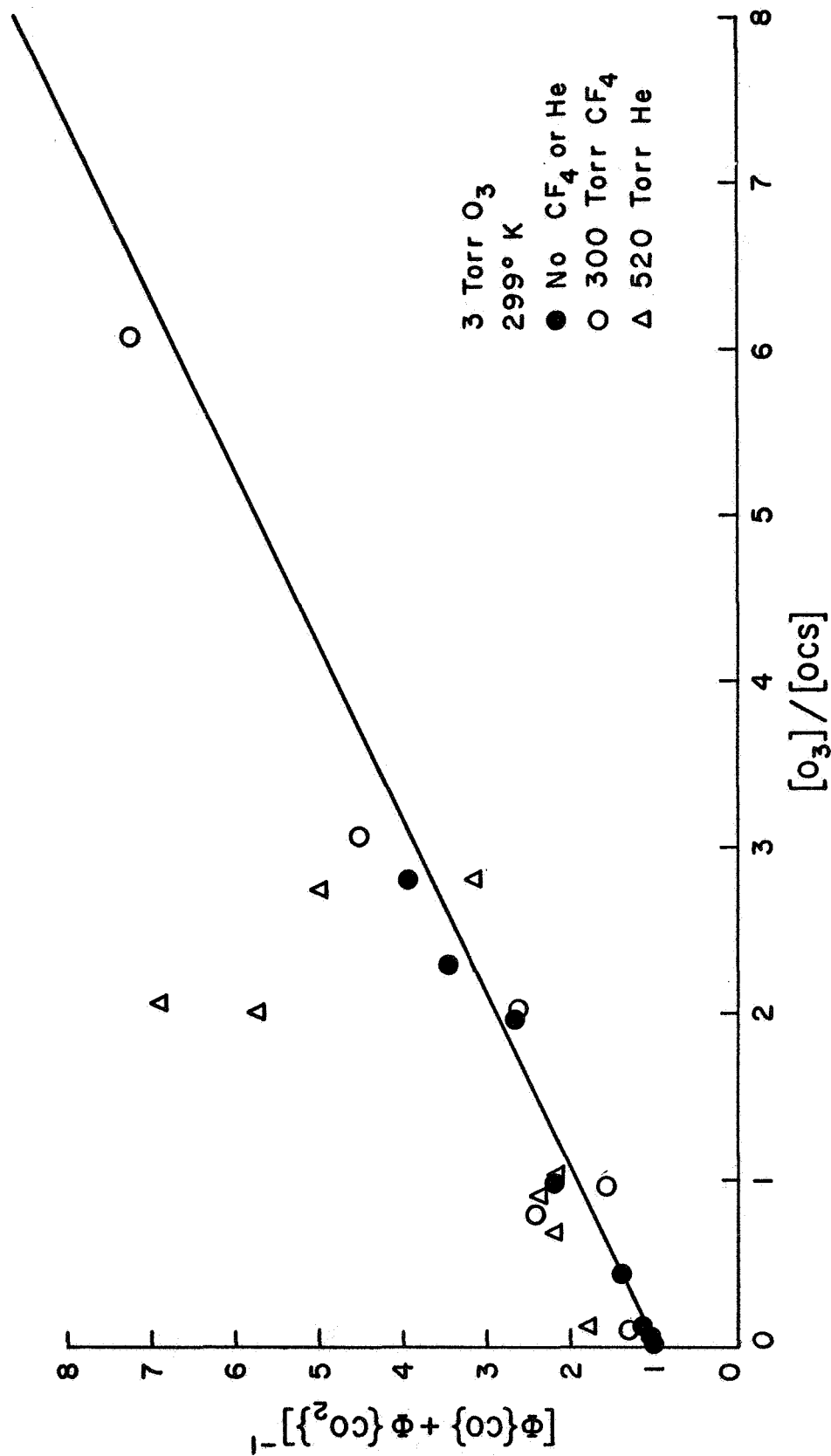


FIGURE 12

$[\Phi\{CO\} + \Phi\{CO_2\}]^{-1}$ AS A FUNCTION OF $[O_3]/[OCS]$ AT 299°K,
 $[O_3] = 3$ TORR, WITH He OR CF₄ ADDED

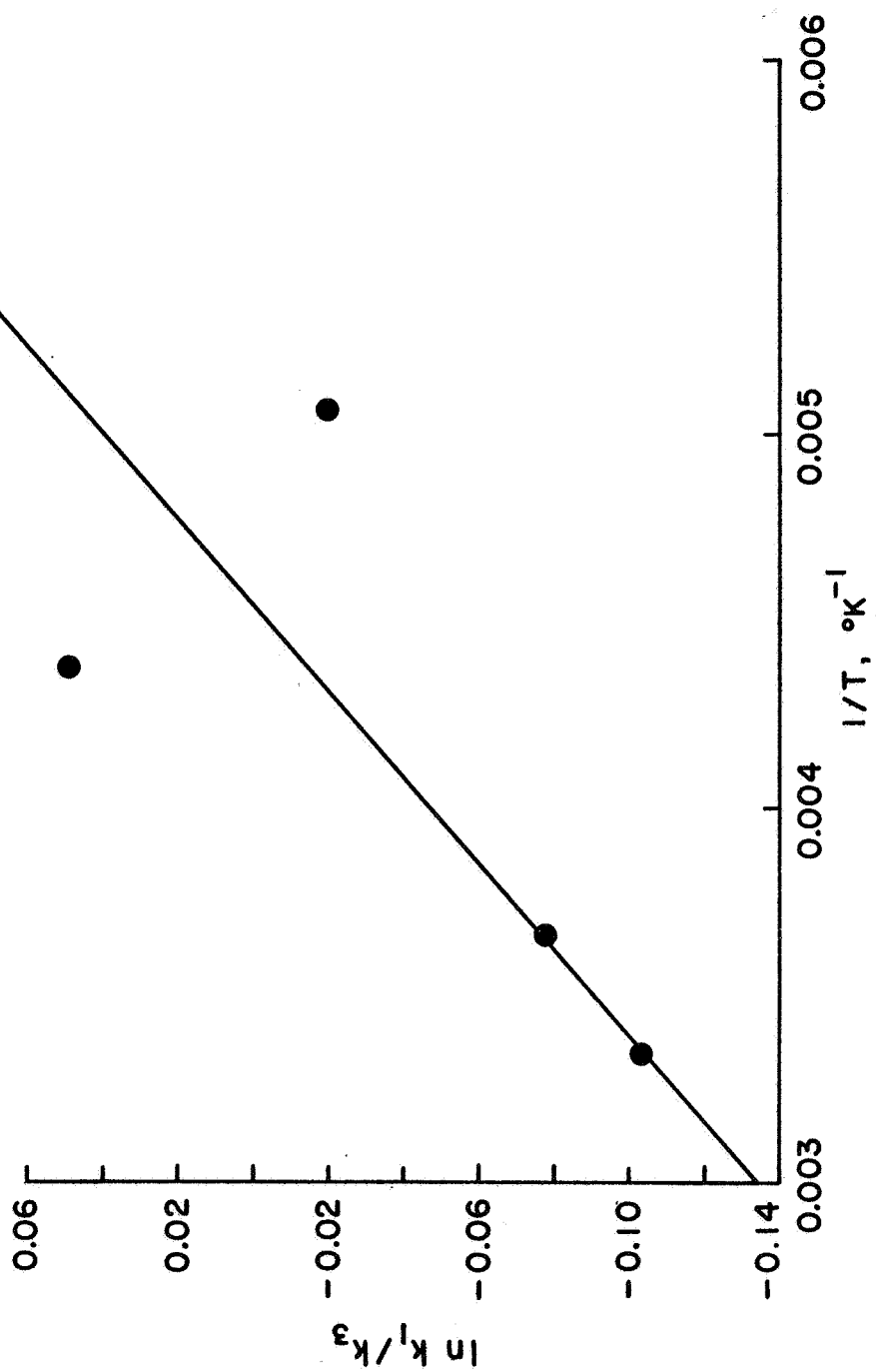
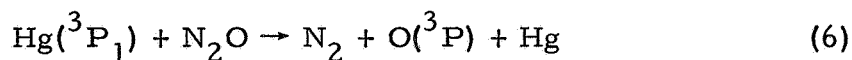
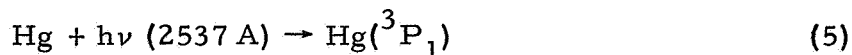


FIGURE 13
ARRHENIUS PLOT OF k_1/k_3

Reaction of O(³P) Atoms with TMP and OCS

The reaction scheme proposed is:



The reactions listed are well known and have been reported in numerous studies. In reaction 4, A and E represent 2-trifluoromethylpropionaldehyde and 2-trifluoromethylpropylene oxide respectively. The SO produced in reaction 3 can react with O(³P) atoms to produce SO₂. However, it can be seen from Tables 15 and 16 that the sum of the quantum yields of CO, A, and E, within experimental error, equal one, indicating that O(³P) atoms were not lost to the SO under the conditions studied. At higher intensities, the quantum yields of CO were considerably higher, possibly due to a complex reaction involving SO, which is known to be removed in wall reactions.¹⁹

The following expression for the $[\Phi\{\text{CO}\}]^{-1}$ can be derived from reactions 3-6.

$$[\Phi\{\text{CO}\}]^{-1} = 1 + \frac{k_4[\text{TMP}]}{k_3[\text{OCS}]}$$

Since CO was produced as a result of the photolysis of N₂O and TMP in the absence of OCS it was necessary to make a correction

to the measured quantum yield of CO, $\Phi\{\text{CO}\}$. The correction was calculated, at each set of conditions, from the measured quantum yield of CO produced in the absence of OCS and was found to be generally less than 15%. The quenching of mercury by the OCS also resulted in the production of CO and necessitated a second correction to $\Phi\{\text{CO}\}$. The ratio of quenching cross-sections of OCS and N_2O , found to equal 1.7, by Yarwood, Strausz, and Gunning²⁰ was used to calculate the quantum yield of CO produced from the quenching of mercury by OCS. This correction to the measured $\Phi\{\text{CO}\}$ was less than 30%.

A plot of the corrected $[\Phi\{\text{CO}\}]^{-1}$ as a function of $[\text{TMP}]/[\text{OCS}]$ yields a straight line with intercept equal to one and a slope equal to k_4/k_3 . Plots at 298°K, 398°K, and 523°K are shown in Figure 14, and the observed values of k_4/k_3 obtained from these plots are shown in Table 19. The relative rate constants k_4/k_3 were found to be independent of the irradiation time and absorbed intensity in the range of pressures of N_2O , TMP, and OCS studied.

TABLE 19
OBSERVED VALUES OF k_4/k_3

Temperature	k_4/k_3
298°K	42.4
398°K	18.7
523°K	8.1

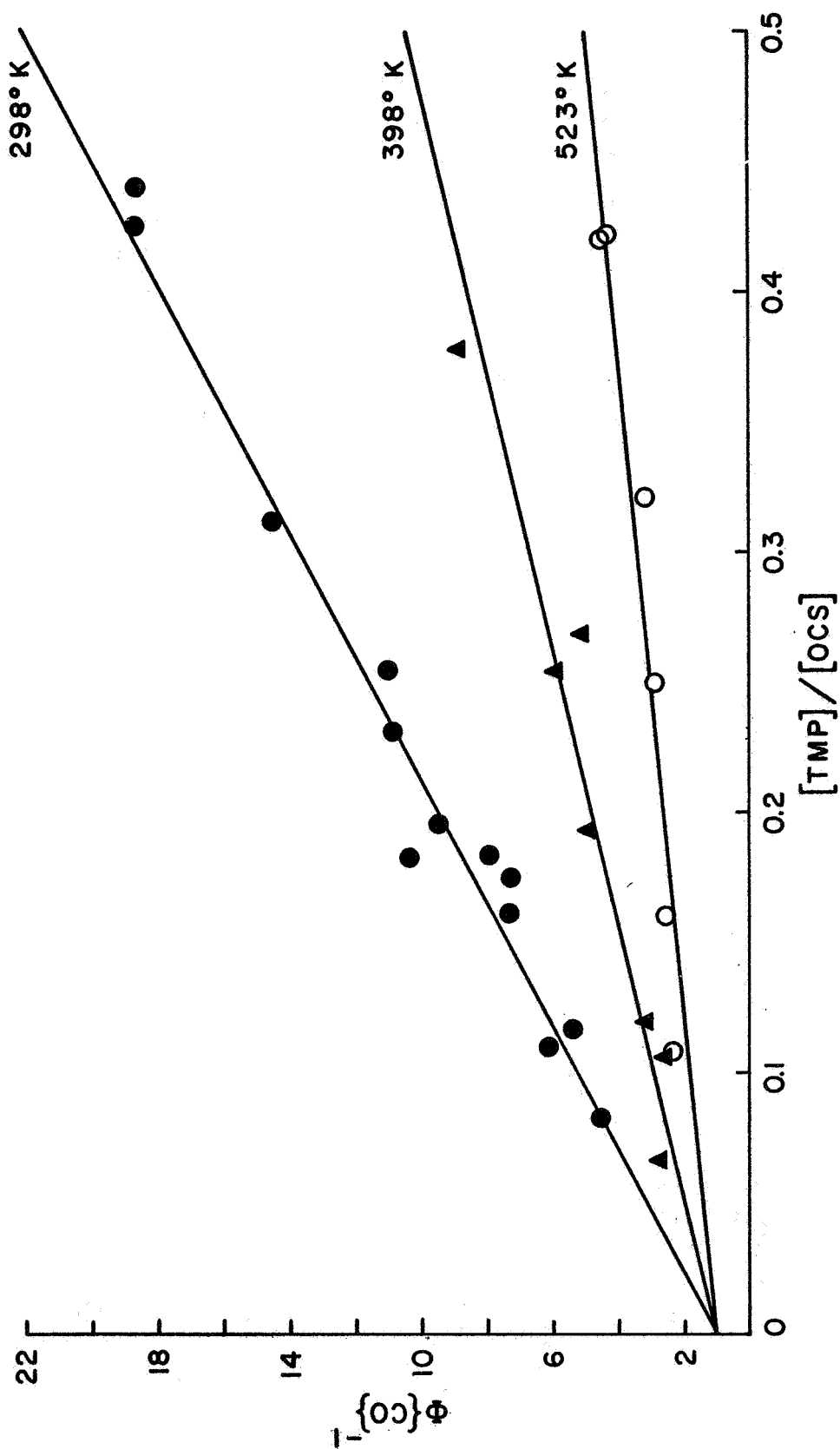


FIGURE 14
 $\Phi\{\text{CO}\}^{-1}$ AS A FUNCTION OF $[\text{TMP}]/[\text{OCS}]$

An Arrhenius plot of k_4/k_3 is shown in Figure 15. The points fall on a straight line whose slope gives the difference in activation energy $E_3 - E_4 = 2280$ cal/mole and whose intercept gives the pre-exponential factor $A_4/A_3 = 0.928$. From these values and the expression $k_4 = 1.51 \times 10^{-11} \exp(-2220/RT)$ cm³/particle-sec found by Simonaitis and Heicklen,¹⁷ the absolute value of $k_3 = 1.63 \times 10^{-11} \exp(-4500/RT)$ cm³/particle-sec was determined. The value of k_3 found in this work is compared with previously observed values of k_3 in Table 3.

Determination of the Absolute Value of k_1

Since relative rate constants k_1/k_3 were determined, the absolute value of k_1 is dependent on the absolute value of k_3 . Table 20 shows the absolute values of k_1 determined from the relative pre-exponential factors, $A_1/A_3 = 0.691 \pm .076$, the difference in activation energy, $E_3 - E_1 = 170 \pm 70$ cal/mole, and the different observed values of k_3 .

TABLE 20
VALUES OF k_1 CALCULATED FROM
OBSERVED VALUES OF k_3

k_1 (cm ³ /particle-sec)	Observed Value of k_3 Used
$(1.1 \pm .2) \times 10^{-11} \exp(-4330 \pm 70/RT)$	This work
$(2.12 \pm .2) \times 10^{-11} \exp(-4360 \pm 70/RT)$	Westenberg and de Haas ¹³
$(7.25 \pm .2) \times 10^{-11} \exp(-5330 \pm 70/RT)$	Homann, Krome and Wagner ¹⁴
$(1.34 \pm .2) \times 10^{-10} \exp(-5630 \pm 70/RT)$	Hoyermann, Wagner and Wolfrum ¹⁵

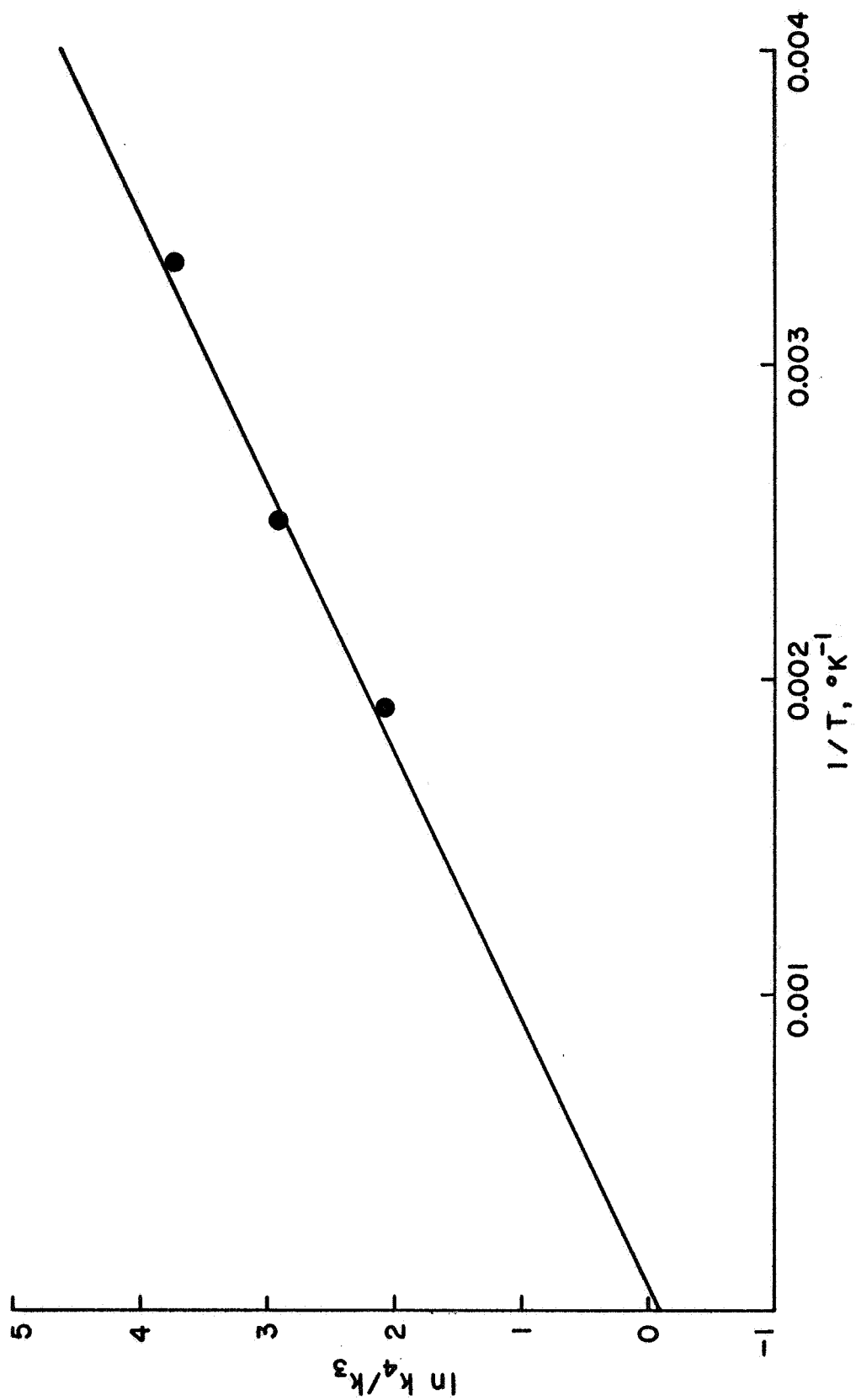


FIGURE 15
ARRHENIUS PLOT OF k_4/k_3

At any given temperature in the range studied, all of the Arrhenius expressions for k_1 yield rate constants which are in good agreement with each other. However, only the Arrhenius expressions for k_1 calculated from the Westenberg and deHaas value of k_3 and the present investigation value of k_3 indicate activation energies, E_1 , for reaction 1, which are in good agreement with E_1 determined from the previous collective investigations of k_1 . Although E_1 determined from the present investigation of k_3 , is in very good agreement with the value of E_1 , determined from the Westenberg and de Haas value of k_3 , the Westenberg and de Haas pre-exponential factor is higher by nearly a factor of two. Since relative rate constants k_4/k_3 were determined in the present investigation, the value of k_3 depends on the accuracy of the value of k_4 which in turn is based on the rate constant for the reaction of 1-butene with $O(^3P)$ atoms. Any inaccuracy in the value of k_4 or the rate constant for 1-butene would be reflected in the accuracy of k_3 found in the present investigation. On the other hand, Westenberg and de Haas assumed an O/OCS stoichiometry equal to one, under the conditions of their experiment. If in fact the stoichiometry was higher, their value of k_3 would be lower and in closer agreement with the value found in the present investigation.

The value of $k_1 = 1.1 \times 10^{-11} \exp(-4330/RT) \text{ cm}^3/\text{particle-sec}$ found in this investigation, provides the best agreement with the previously obtained collective data for k_1 . Figure 16 shows an Arrhenius plot of k_1 determined in the present and previous investigations. From this plot the value of $k_1 = 1.65 \times 10^{-11} \exp(-4400/RT) \text{ cm}^3 \cdot \text{particle-sec}$ was obtained.

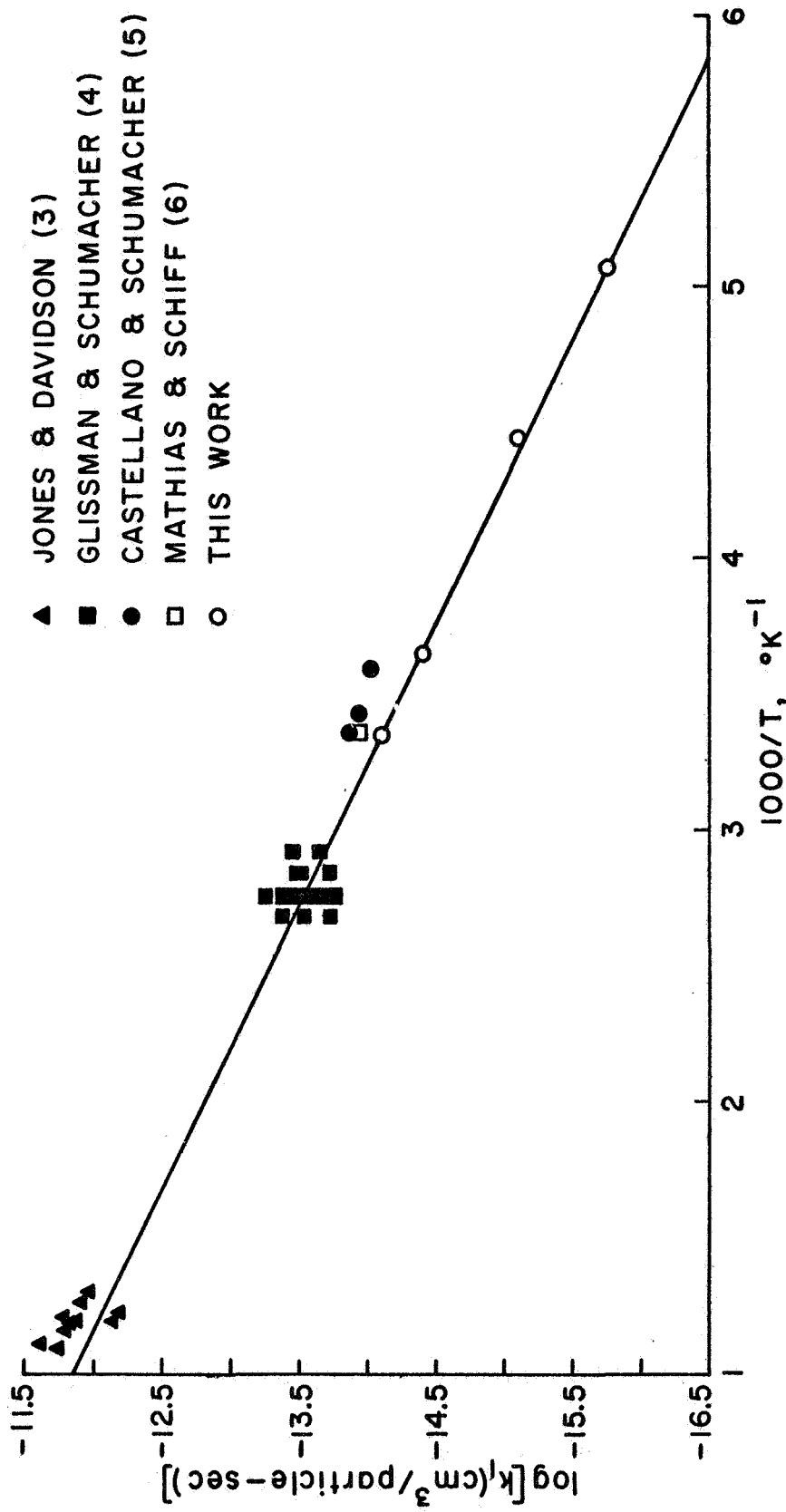


FIGURE 16
ARRHENIUS PLOT OF k_1

CHAPTER V

SUMMARY

In this study the competitive reaction of $O(^3P)$ atoms with O_3 and OCS was investigated in the temperature range $197^{\circ}K$ - $299^{\circ}K$. The relative rate constants for the reactions



were determined and found to be independent of irradiation time, absorbed intensity, and the addition of a foreign gas. The absolute value of $k_1 = 1.1 \times 10^{-11} \exp(-4330/RT) \text{ cm}^3/\text{particle-sec}$, was calculated from a pre-determined value of k_3 .

The value of k_3 was determined from a similar competitive study of $O(^3P)$ atoms with 2-trifluoromethylpropene (TMP) and OCS in the temperature range $300^{\circ}K$ - $523^{\circ}K$. The value $k_3 = 1.63 \times 10^{-11} \exp(-4500/RT) \text{ cm}^3/\text{particle-sec}$, was calculated from the known rate constant of the $O(^3P)$ reaction with TMP.

The value of k_1 determined, is in excellent agreement with the value of k_1 determined from the collective previous works in the temperature range $300^{\circ}K$ - $1150^{\circ}K$.

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