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KINETICS OF THE OZONATION OF DIMETHYL SULFIDE IN THE GAS PHASE

by

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I am also grateful to Mr. Bill Samsel for his considerable help and to my fellow graduate students, especially Larry Schmitz, for their suggestions during this project.

NOMENCLATURE

Symbol or Term	Definition
DMS	Dimethyl Sulfide
Laminar Flow	A flow which has negligible turbulance. The Reynolds number is less than 2300.
Initial Rates	Method of kinetic study in which less than ten percent completion of the reaction results.
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
RSH	Alkyl or Aromatic Mercaptan
RSR	Alkyl or Aromatic Sulfide
RSSR	Alkyl or Aromatic Disulfide
H_2S	Hydrogen Sulfide
DMSO	Dimethyl Sulfoxide
g.l.c.	Gas-Liquid Chromatography
KI	Potassium Iodide
$Na_2S_2O_3$	Sodium Thiosulfate
CH_2Cl_2	Methylene Chloride
I_2	Iodine
$DMSO_2$	Dimethyl Sulfone
K	Rate Constant
$d(O_3)/dt$	Change in ozone concentration with respect to time

E_a	Activation Energy
A	Arrhenius Factor
ΔS	Change in Entropy
EPR	Electron Paramagnetic Resonance

CHAPTER I

INTRODUCTION

The fact that dimethyl sulfide (DMS) does react with ozone under laboratory conditions, and that the products are water soluble bring up the questions: Do ozone and dimethyl sulfide react fast enough to enter into the photochemical smog cycle? Does oxidation with ozone warrant further investigation as a pollution control device? The purpose of this research, therefore, was to determine the stoichiometry and the kinetics for the gas phase reaction of DMS and ozone and to answer the above questions. To achieve this, a tubular, laminar flow gas reactor was designed so as to allow the kinetics to be studied by the method of initial rates.

OZONE

Studies in the late 1940's made on Los Angeles smog showed that polluted air could have oxidizing properties.[1,2] The proof that ozone was the primary oxidant in this smog came several years later when analysis by long path infrared spectroscopy revealed the presence of ozone in concentrations of a few tenths of a part per million. Since ozone is emitted from natural sources in concentrations too low to account for that found, another source of ozone had to be present in polluted air. Nitrogen dioxide, a common pollutant of urban air, was found to dissociate into nitric oxide and an oxygen atom on absorption of ultraviolet rays from sunlight. The oxygen atom in turn quickly reacts with molecular oxygen to form ozone (see below) with M being any body which can absorb the energy of the reaction. This reaction,

$$NO_2 \dashrightarrow NO + O$$
$$O + O_2 + M \dashrightarrow O_3 + M$$
$$NO_2 + O_2 \dashrightarrow NO + O_3$$

however, is reversible and a "dynamic equilibrium" is set up in minutes at an ozone concentration which still does not account for the existing concentrations. Therefore, still another reaction, one which converts NO to NO_2 without using ozone, has to be present. Hydrocarbon oxidation, in which the intermediate peroxy radicals lose an oxygen atom to NO to form NO_2, turns out to be the necessary reaction for ozone accumulation (see Figure 1).

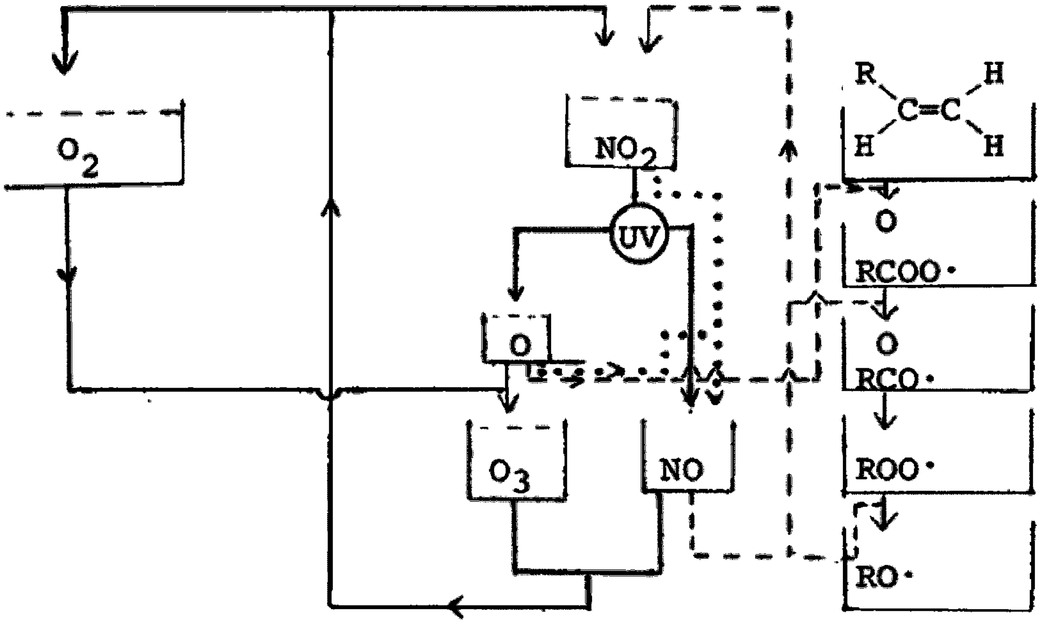


FIGURE 1

THE STEADY STATE FORMATION OF OZONE
(taken from Ref. 1).

While the O_2/NO_2/hydrocarbon cycle acts as the principal source of ozone in urban atmospheres, the much greater ozone concentrations found at high altitudes are due to another reaction.[3] The ozonosphere, a region extending from approximately 6 miles high up to nearly 35 miles, is produced by the direct absorption of ultraviolet light by oxygen. This absorption causes the molecular oxygen to split into two atoms each of which reacts with another molecule of O_2 to form ozone.

$$O_2 + UV \longrightarrow 2O$$

$$2O + 2O_2 \longrightarrow 2O_3$$

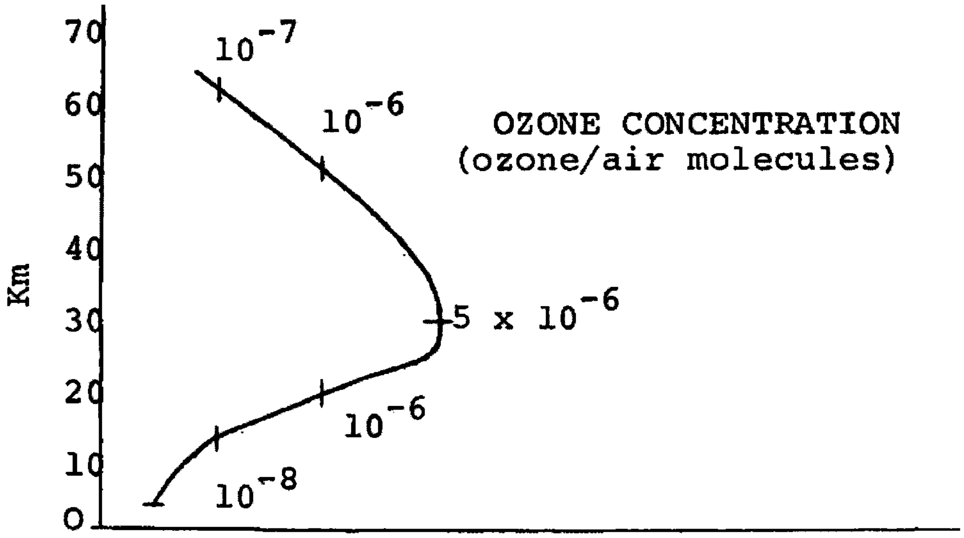


FIGURE 2

OZONE CONCENTRATIONS AT VARIOUS ALTITUDES

DIMETHYL SULFIDE

Dimethyl sulfide is a malodorous, water insoluble sulfide whose ozone oxidation products, dimethyl sulfoxide and dimethyl sulfone, are odorless and water soluble. Although the sulfide is not normally found in appreciable amounts in polluted air, its presence is definitely noticeable where Kraft pulp mills operate. Akamatsu's studies[4,5,6] show that the recovery process losses plus blow gas emissions constitute the major sources, although not the only sources of the malodorous pollutants; MeSH, Me_2S, Me_2S_2 and H_2S (see Table 1).

Akamatsu's work also reveals that sulfide emission variations from mill to mill (see Table 1) depend on the type of wood used and the pulping conditions (see Table 2).

TABLE 2

SULFIDE EMISSION VARIATIONS

Wood type	Pulping Condition	CH_3SCH_3, mg/g. wood Sulfidity %		
		14.7	22.2	30.5
Pine	180°C, 1 hr	0.18	-----	0.30
Spruce	180°C, 1 hr	0.12	0.21	0.31
Maple	180°C, 2 hrs	0.92	0.82	1.36
Pine	170°C, 2 hrs	0.17	0.23	0.33
Pine	180°C, 2 hrs	0.46	0.57	0.74
Spruce	180°C, 3 hrs	0.75	1.00	1.27
Spruce	180°C, 4 hrs	1.07	1.25	1.77
Maple	180°C, 4 hrs	1.62	2.01	2.84

TABLE 1

GASEOUS SULFUR LOSS* BALANCE SHEET FOR SOUTHERN KRAFT MILL A

Source	Form of gas emission					Total, lb/ton	% from each source
	SO_2	H_2S	RSH	RSR	RSSR		
Recovery	6.71	12.97	3.98	2.01	0.04	25.71	85.00
Dissolving tank	0.07	0.04	0.15	0.06	0.01	0.23	1.10
Lime kiln	0.05	0.09	0.31	0.16	0.05	0.66	2.20
Digester	----	0.01	0.02	0.22	0.46	0.70	2.30
Blow tank	----	0.02	0.33	0.74	0.44	1.53	5.01
Pulp washer vent	0.01	0.01	0.18	0.01	0.01	0.19	0.60
Evaporator non-condensable	0.01	0.12	0.13	0.07	0.01	0.32	1.10
Bark boiler	0.16	0.67	0.01	0.01	0.01	0.83	2.70
Total	6.99	13.91	5.10	3.26	1.00	30.26	
% of total in each form of sulfur	23.10	46.00	16.80	10.80	3.70		100.00

* lb S--/ton airdried pulp.

TABLE 1 CONTINUED

GASEOUS SULFUR LOSS* BALANCE SHEET FOR SOUTHERN KRAFT MILL B

Source	Form of gas emission					Total, lb/ton	% from each source
	SO_2	H_2S	RSH	RSR	RSSR		
Recovery	1.20	3.61	0.30	0.00	0.15	5.26	41.90
Dissolving tank	0.00	0.02	0.07	0.02	0.00	0.11	0.90
Kiln	0.15	0.24	0.26	0.00	0.09	0.74	5.90
Digester	----	0.01	0.03	0.83	0.15	1.02	8.10
Blow	----	0.10	0.50	1.40	2.05	4.05	32.20
Evaporator	----	0.03	0.01	0.02	0.00	0.06	0.50
Tall oil							
Acidification	----	0.27	0.01	0.00	0.01	0.29	2.30
Neutralization	----	1.01	0.02	0.00	0.00	1.03	8.20
Total	1.35	5.29	1.20	2.27	2.45	12.56	
% of total in each form of sulfur	10.70	42.10	9.60	18.10	19.50		100.00

* lb S--/ton airdried pulp

CORRELATION

It is reasonable to assume that dimethyl sulfide, along with the other pollutants, can pass up through the lower levels of the atmosphere and eventually reach the ozonosphere. This movement would result in mixtures of DMS and ozone being exposed to varying conditions of concentration and temperature making it feasible that reaction could occur.

CHAPTER II

HISTORY

The first oxidation of an organic sulfide was reported in 1910 by Fichter and Sjostedt.[7] In a mixture of glacial acetic acid and concentrated HCl, benzyl sulfide was electrolyzed at 25°C to give a 92.7% yield of the sulfoxide. Further electrolytic oxidation to the sulfone proved unsuccessful, however, under identical conditions phenyl sulfide was converted to the sulfone in a 93.5% yield.

The control of H_2S odor through oxidation to sulfur, water and sulfuric acid had been known since the early 1900's,[8,9,10] and sulfide oxidation work for the next thirty years dealt with the solution and vapor phase oxidation of this compound. No mention was made of organic sulfides until 1933. In that year Maneck[11] ozonized benzyl sulfide in CCl_4 and reported initial reaction products to be the sulfoxide and sulfone. Prolonged ozonation oxidized these initial products to sulfuric acid, carbon dioxide, and benzoic acid.

In 1942, Bohme and Fischer[12] ozonized several organic sulfides, including dimethyl sulfide, in chloroform. A nearly quantative yield of the sulfone was obtained for the compounds Me_2S, Et_2S, $(ClCH_2CH_2)_2S$, $Me\phi S$, $EtSCH_2\phi$, and $(\phi CH_2)_2S$. That the sulfoxide is formed as a precursor to the sulfone was shown by the isolation of benzyl sulfoxide from the sulfide when an insufficient amount of ozone was used. For some sulfides, i.e., chloromethyl ethyl sulfide, the sulfoxide is the final product.

While studying the possibility of the use of ozone as a titrimetric agent for quantitative determination of olefinic unsaturation in petroleum fractions, Boer and Kooyman[13] ozonized several sulfides to determine the effect of their presence in the olefinic mixtures. The dialkyl sulfides were reported to consume from 1/4 to 3/4 mole of ozone per mole of sulfur compound. Benzothiophene consumed exactly one mole of ozone, while thiophene and dibenzothiophene did not interfere with the reaction.

In 1954, Bateman and Cunneen[14] studied the autoxidizability of several monosulfides at temperatures ranging from 45° - 75°C and found that saturated alkyl and phenyl sulfides absorb no oxygen during 24 hours at 75°C. Similarly inert were the benzyl and diphenylmethyl substituted sulfides (see below for compounds tested).

$Bu^n \cdot S \cdot Me$

$Bu^n \cdot S \cdot Bu^n$

cyclo $C_6H_{11} \cdot S \cdot Me$

CH_2-CEtMe
S
CH_2-CHBr

$\text{Ø} \cdot S \cdot \text{Ø}$

$\text{Ø-CH}_2 \cdot S \cdot Pr^n$

$\text{Ø-CH}_2 \cdot S \cdot CH_2\text{-Ø}$

Ø-CHMe · S · Me

Ø-CH · S · Me

While the benzyl sulfides undergo photo-oxidation, the dialkyl sulfides oxidize only when catalyzed by $\alpha\,\alpha'$-azo-bis-isobutyronitrile. The diphenyl sulfides are inert to all autoxidation.

Barnard[15] found that monosulfide-ozone reactions in solution at -25°C yielded not only the sulfoxide and sulfone but other products as well. For the reaction:

$$R' \cdot S \cdot R'' + 2O_3 \dashrightarrow R' \cdot SO_2 \cdot R'' + 2O_2$$

less than the theoretical amount of ozone was needed for a nearly quantative yield of the sulfone. The ozonation, run just to completion, of di-n-butyl sulfide gave a 100% yield of the sulfone "smelling of butyraldehyde and butyric acid and reacting acid to litmus." The reactivity of the sulfides (see Table 3) indicates that the most easily oxidized sulfides required the least ozone.

TABLE 3

REACTIVITY OF ORGANIC SULFIDES

SULFIDE	OZONE REQUIRED FOR SULFONE	DECREASE IN REACTION RATE
Di-n-butyl	1.40	↓
Cyclyhexyl methyl	1.53	
2-ethyl-2-methyl isopropyl-thiophan	1.70	
Dibenzyl	1.75	
Mathyl phenyl	1.85	

Since saturated alkyl sulfides and several aryl sulfides are inert to molecular oxygen without a catalyst, Barnard speculated that the ozone must either catalyze the sulfide-ozone oxidation or produce, after loss of an oxygen atom, activated oxygen molecules of which some participate in the oxidation of the sulfide or sulfoxide depending on their ease of oxidation.

Barnard's ozone uptake curves indicate oxidation occurs in two stages to give first the sulfoxide and then the sulfone (see Figure 3). By following the ozonolysis of cyclohexyl methyl sulfide with infrared spectroscopy, he was able to show that at least 98-99% of the sulfide was converted to the sulfoxide before any sulfone was detected. This indicates the rate of sulfoxide formation is 50-100 times faster than that of the sulfone.

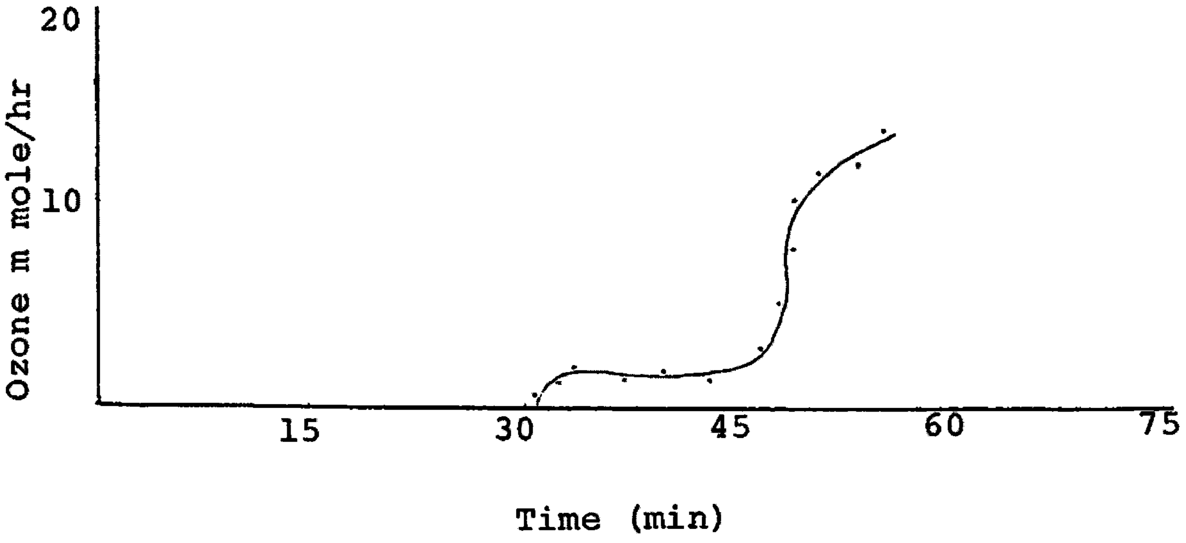


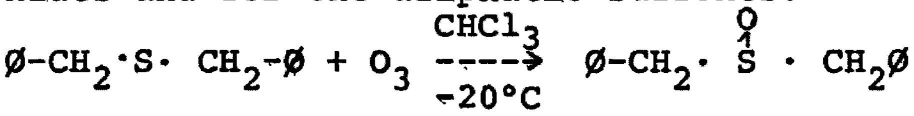
FIGURE 3

OZONOLYSIS OF DI-n-BUTYL SULFIDE IN CCl_4

More recently, Maggiolo and Blair[16] found that ozone reacted with dialkyl and diarly sulfides according to the equation:

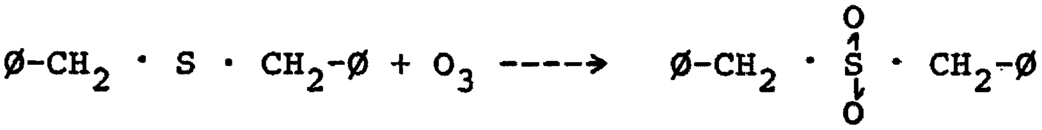
$$R_2S \xrightarrow{O_3} O_2 + R_2SO \xrightarrow{O_3} R_2SO_2 + O_2$$

When the reaction was run in a nonpolar solvent, it was found to be stoichiometric for the aliphatic and aromatic sulfoxides and for the aliphatic sulfones.



$$\emptyset\text{-}CH_2\cdot S\cdot CH_2\text{-}\emptyset + O_3 \xrightarrow[-20°C]{CHCl_3} \emptyset\text{-}CH_2\cdot \overset{O}{\overset{\uparrow}{S}}\cdot CH_2\emptyset$$

10.7g (.0499) 2.33g (.0485) 11.3g (.0491)



$$\emptyset\text{-}CH_2\cdot S\cdot CH_2\text{-}\emptyset + O_3 \longrightarrow \emptyset\text{-}CH_2\cdot \overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}\cdot CH_2\text{-}\emptyset$$

10.7g (.0499) 4.71g (.0981) 12.0g (.0487)

Horner, Schaefer and Ludwig[17] also found that sulfides react in ethyl chloride with ozone according to Maggiolo and Blair's equation to give sulfoxides and sulfones in 80-100% yield. In the study by Horner, <u>et</u> <u>al</u>., aliquots of a di-n-butyl sulfide (20 m mole) - ozonation were analyzed to determine sulfoxide-sulfone conversion (see below).

Time (min)	O_3 observed in m mole	O_3 observed in m mole corrected	O_3%	Yield Sulfoxide
12	5.40	5.40	100	10
24	10.80	10.80	100	
42	18.90	18.90	100	
45	20.19	19.96	92	20*
48	21.40	20.94	75	
60	26.16	25.65	87	15
78	33.21	32.67	86	
90	37.79	37.20	82	3.5
96	39.95	39.28	77	
102	41.72	40.54	48	
108	42.57	40.90	13	

The aliquot taken after 45 minutes indicated a complete conversion of the sulfide to the sulfoxide before any sulfone was formed.

Six years later, work by Hughes, McMinn, and Burleson[18] lent still further support to Maggiolo and Blair's stoichiometry by obtaining stoichiometric yields of sulfoxide and sulfone when Bis (B-hydroxyethyl) sulfide was ozonized at 100°C.

Research was carried out in this laboratory on the ozonation of dimethyl sulfide in methylene chloride at -78°C.[19] Nuclear magnetic resonance analysis of aliquots taken during the reaction revealed dimethyl sulfone formation after only 1% of the reaction was completed. While this would seem to indicate a DMSO/O_3 reaction considerably faster than that for DMS and ozone, it is also possible, due to poor mixing in the reaction vessel, that pockets of high ozone concentration could occur and that the sulfone resulted from the slow oxidation of the DMSO trapped in these areas. Product analysis indicated an uptake of 1.86 moles of ozone per mole of sulfide for conversion to the sulfone.

Not until 1966 was there any work done on the vapor phase ozonation of dimethyl sulfide. In that year, pollution control work resulted in two studies by Akamatsu, _et al._,[20] on the removal of dimethyl sulfide from pulping processes by vapor phase ozonation. This work showed that dimethyl sulfide oxidized with oxygen containing 7% ozone gave 75% dimethyl sulfoxide and 25% dimethyl sulfone. Another project of Akamatsu[21] revealed that an 85% yield of the sulfoxide could be obtained when dimethyl sulfide and oxygen containing 20% ozone were fed into a reactor in a 3:7 ratio at 30°C.

CHAPTER II

EXPERIMENTAL

INSTRUMENTATION

The stoichiometric data were obtained using a Packard Model 7300 gas-liquid chromatograph equipped with dual flame ionization detectors, dual electrometers, and a Vidar 6300 Autolab digital integrator. The column employed was a 5' x 1/4" glass 5% GE XE 60 on Chrom Q. Triple-distilled butyl benzoate was utilized as an internal standard for determination of product yields.

Product identification was achieved by comparison of product g.l.c. retention times with those of known compounds under identical conditions and by mass spectroscopy using a Varian Mat III GS/MS system.

EXPERIMENTAL APPARATUS

A Welsbach T-408 electric discharge ozonator was used to produce the ozone. The ozone flow rate was determined by passing the ozone-oxygen (nitrogen) stream through a KI solution for a known time and titrating the solution, on acidification, with a .005 N solution of sodium thiosulfate.

The equation for the flow rate is:

$$\frac{N \cdot V \cdot .024}{t \cdot 48} = \text{moles } O_3/\text{min}$$

V = milliliters of $Na_2S_2O_3$ used

N = normality of $Na_2S_2O_3$ used

t = time in minutes that O_3 was passed into KI trap

In this study, the carrier gas was simply passed through the Welsbach ozonator, split to decrease the O_3 concentration, brought to the desired temperature of either 25°C or 35°C and introduced into the mixing chamber.

The ozone stream was split in order to decrease concentrations to those desired. Attempts to decrease ozone concentrations to those required by decreasing the current on the ozonator yielded inconsistent ozone flow rates.

After the ozone stream was split, the flow rate of the resulting stream was measured by a Fischer and Porter "Tri Flat" rotometer. The nitrogen flow rate was determined by a Gilmont Model R795 rotometer.

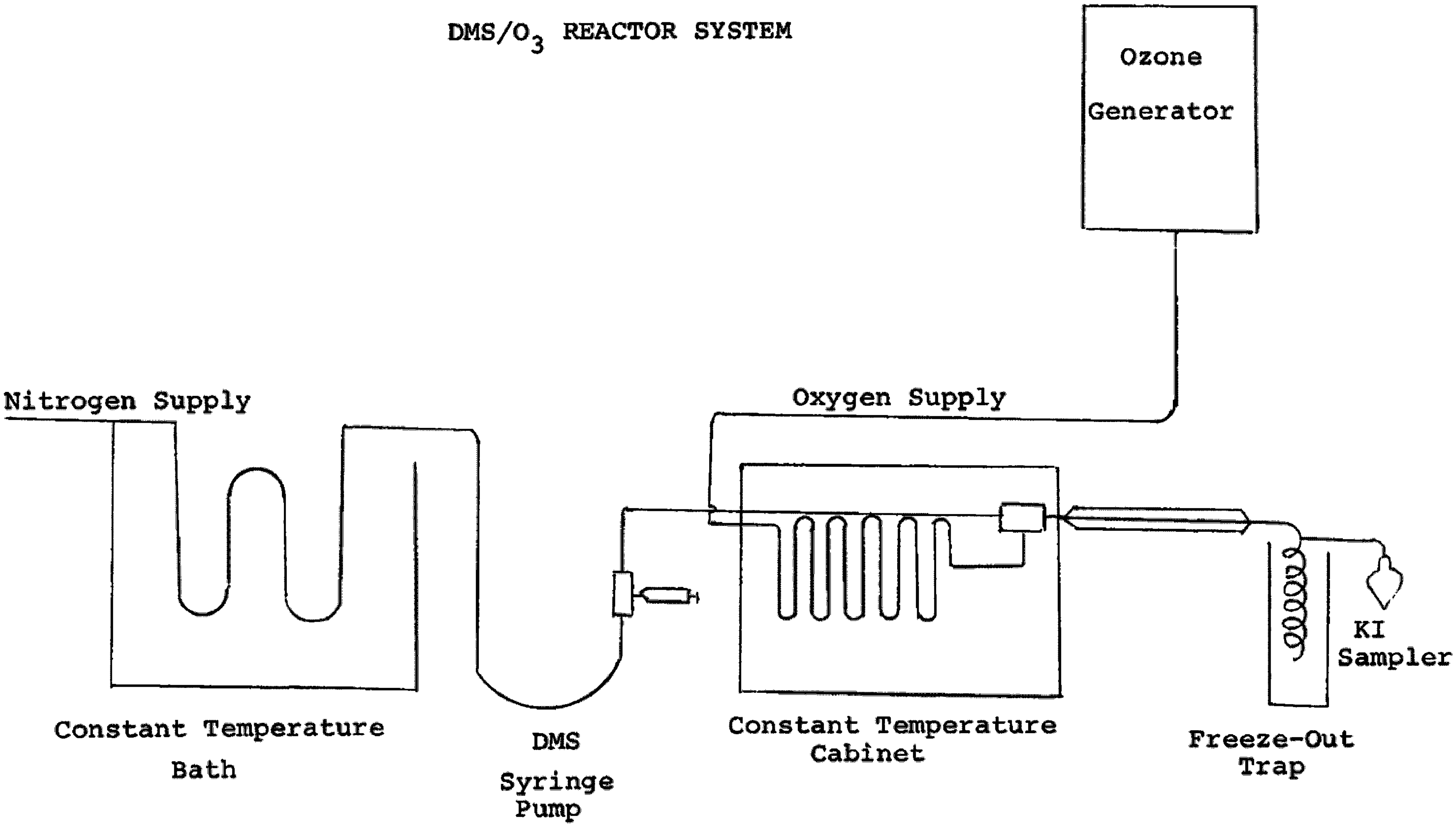
Dimethyl sulfide was introduced into the nitrogen stream by a .1 ml Hamilton gas-tight syringe driven by a Sage model 341 syringe pump. Flow rates for the DMS were varied from .0003 to .00006 ml/min.

DMS-O_3/O_2 Reactor System

Before the DMS was injected, the nitrogen stream was brought to the desired temperature in a constant-temperature water bath. In order to achieve complete DMS vaporization and to prevent the liquid DMS from splashing on the walls, the injection chamber was expanded, the diameter of the

FIGURE 4

DMS/O_3 REACTOR SYSTEM



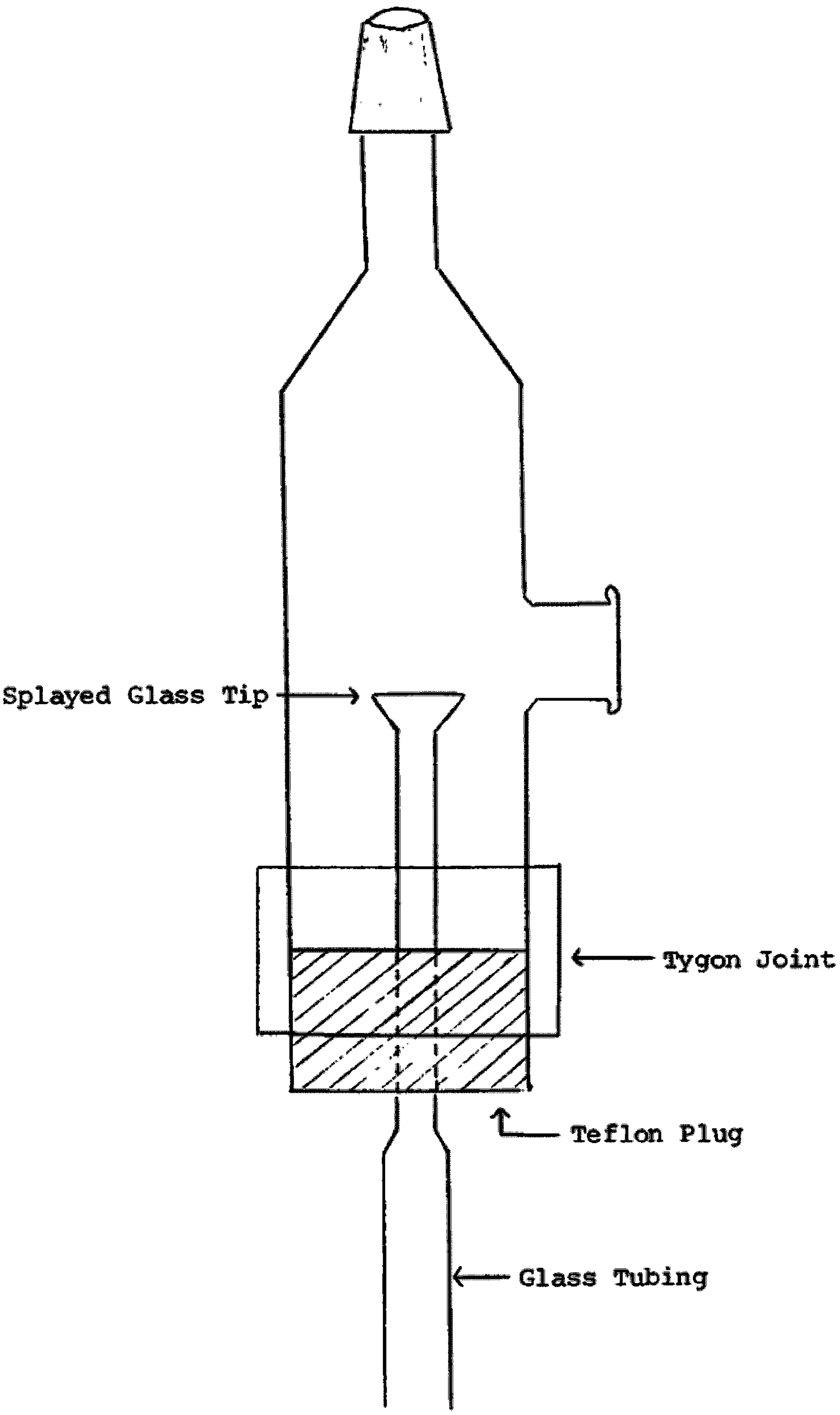


FIGURE 5

DMS INJECTION SYSTEM

glass tubing carrying the nitrogen was decreased and the end was splayed. After injection, both the N_2/DMS and the O_3/O_2 streams entered a styrofoam constant temperature cabinet, passed through 1' and 17' of glass tubing respectively, came together in the gas mixing chamber and then entered into the reactor. The mixing chamber was designed according to Hale's specifications[22] and consisted of a Teflon collar mounted within a stainless steel sleeve. The O_3/O_2 stream passed into the sleeve and proceeded into the reactor through four 5 mm radial holes drilled in the collar. The boundaries between the collar and the sleeve were kept gas-tight using Viton "O" rings. The reactor was constructed of precision-bore Pyrex tubing having an inside diameter of 1/8" ± .0002" and had an inside volume of 1.988 milliliters. The reactor temperature was controlled by means of a water jacket.

Extreme care was taken in cleaning the reactor and associated glassware. The procedure followed for cleaning the reactor was that of Hales.[23]

1. Wash and rinse with soap and tap water
2. Allow to stand for 1 hour in hot concentrated cleaning solution ($Na_2Cr_2O_7/H_2SO_4$)
3. Rinse with tap water
4. Allow to stand for 1 hour in hot concentrated KOH
5. Rinse with tap water
6. Rinse with dilute HCl

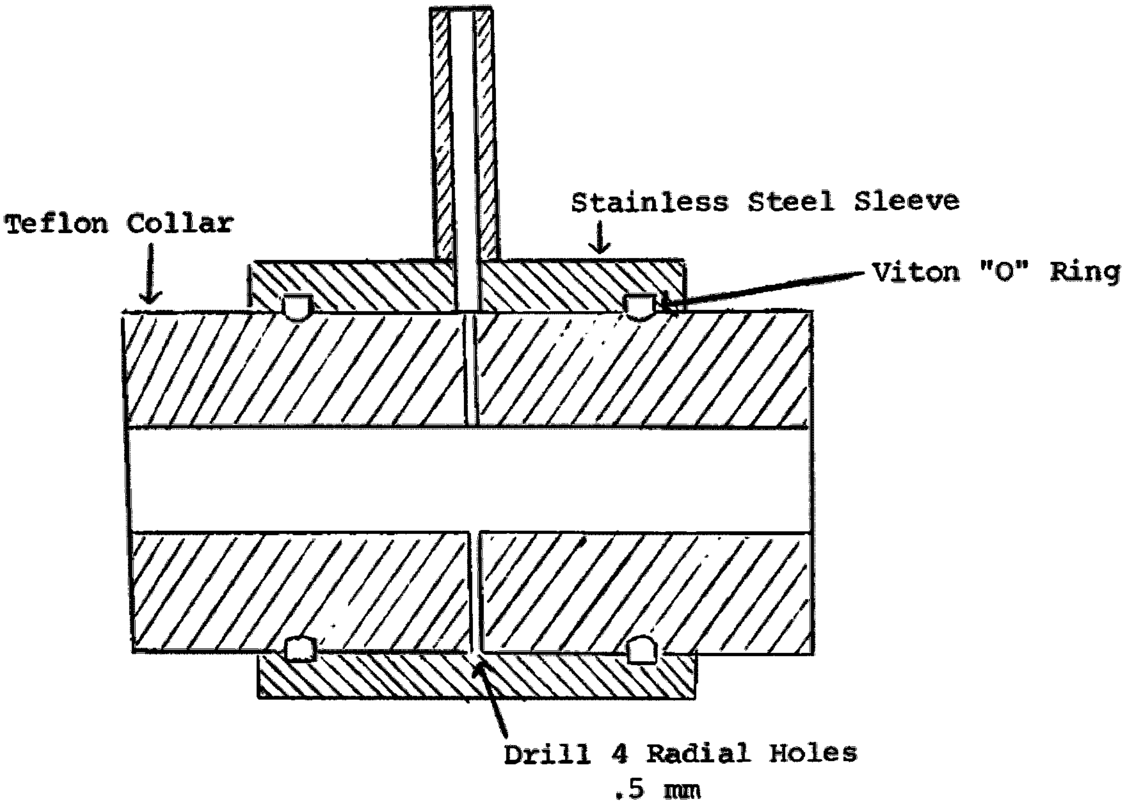


FIGURE 6

GAS MIXING CHAMBER

7. Rinse repeatedly with distilled water

8. Cover and allow to dry

The traps and the evaporation glassware were washed in the following manner:

1. Wash and rinse with soap and tap water
2. Soak in concentrated cleaning solution
3. Rinse with tap water
4. Rinse repeatedly with distilled water
5. Cover and oven dry

The reaction products were collected by means of a freeze-out trap consisting of a glass spiral connected to an adapted 10 ml pear-shaped two neck flask. Products were then removed from the trap by warming to room temperature and washing three times with three milliliter portions of methylene chloride. A 1 ml volumetric flask was attached to the bottom of the flask in order to obtain accurate 1 ml volumes of CH_2Cl_2-product solutions on evaporation. The trap was immersed in a Dewar containing a solid-liquid slush of n-pentane. Two other solid-liquid slushes were tried; however, tests proved that product loss resulted when either the dry ice/acetone or the isooctane/liquid nitrogen slushes were used. Since the amount of product was small, the 10 ml of methylene chloride needed to wash out the trap resulted in product concentrations too low to be analyzed. Vapor pressure data for DMSO and CH_2Cl_2 were obtained from Karchmer's[24] <u>The Analytical Chemistry of Sulfur and Its Compounds</u>

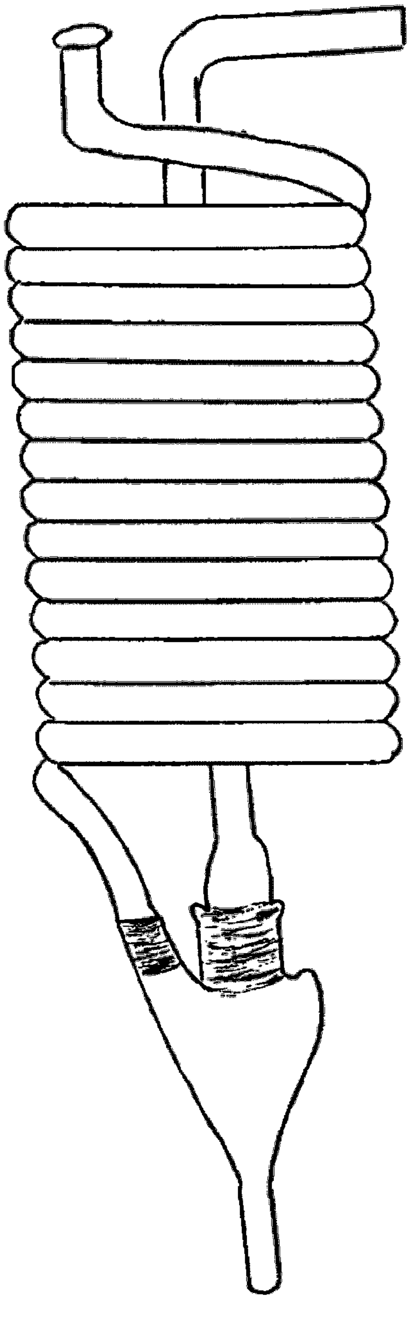


FIGURE 7

FREEZE-OUT TRAP

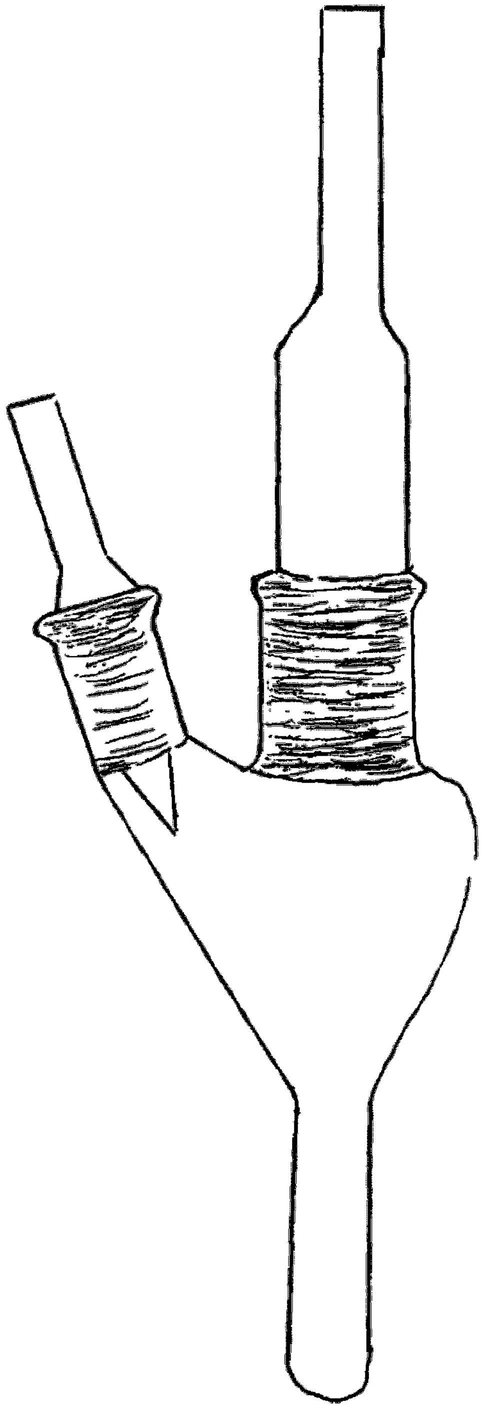


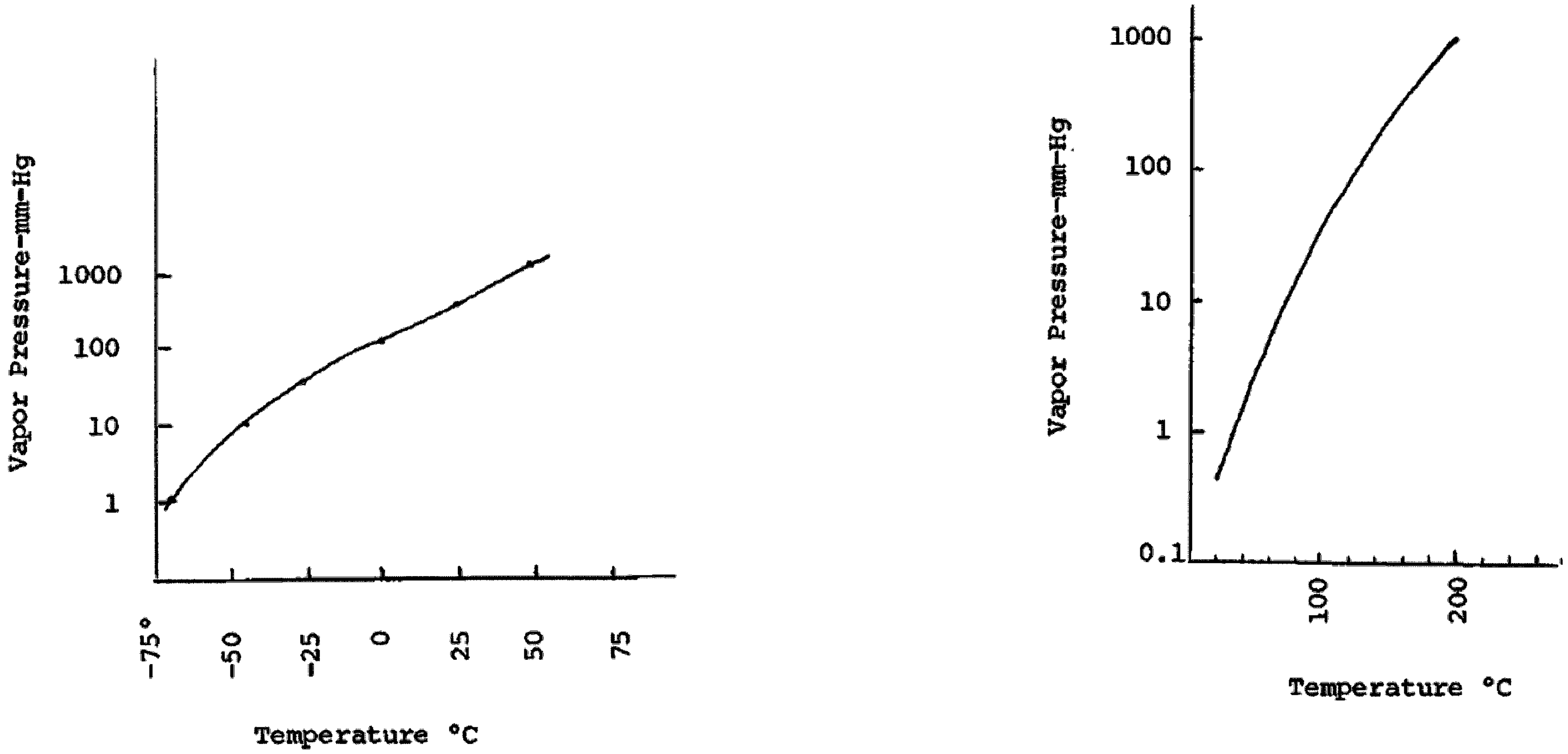
FIGURE 8

EVAPORATION TRAP

and from the Handbook of Chemistry and Physics[25] respectively (see Figure 9). Extrapolation of Karchmer's data yielded a vapor pressure for DMSO of less than .1 mm of Hg at 0°C. A value of .0896 mm of Hg was obtained using the values of Jose *et al.*[26] Methylene chloride's vapor pressure at this temperature was approximately 129 mm of Hg. Since methylene chloride's vapor pressure was almost 1500 times that of DMSO's, evaporation without product loss appeared quite feasible as a means of obtaining product concentrations which could be analyzed. This evaporation was carried out by removing the 10 ml flask from the rest of the CH_2Cl_2-washed trap and attaching a condenser and a nitrogen source. This was then placed in an ice bath and nitrogen was passed over the solution until a volume of 1 ml was reached.

In order to determine the ozone uptake of the reaction, ozone concentrations were measured before and during the reaction by means of a KI sampler attached to the freeze-out trap. It was found that a normal glass frit would hold varying amounts of I_2, causing inaccuracy in the determination of the O_3 concentration. It was not possible to divert the ozone stream in order to wash the frit, since this caused a pressure change and a resulting fluctuation in the ozone flow rate. Studies indicated that it took as long as an hour to restablish the prior O_3 flow. This problem was solved by exchanging the frit with a glass tip consisting of a tapered end and four side openings for a 5-way disper-

FIGURE 9



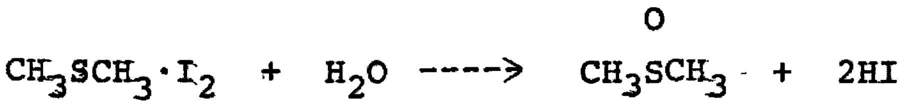
VAPOR-PRESSURE CURVE FOR CH_2Cl_2

VAPOR-PRESSURE CURVE FOR DIMETHYL SULFOXIDE sion of the gas.

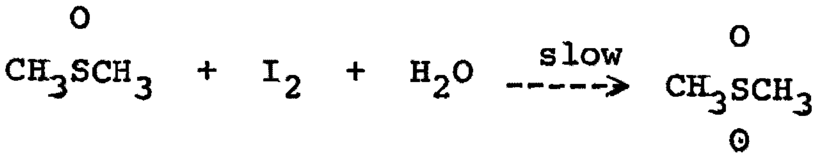
Trapping all of the DMS in the freeze-out trap proved impossible. Therefore, the DMS entered the KI solution when the ozone stream was analyzed. DMS reacts with I_2 forming DMSO and $DMSO_2$[27] thereby consuming the I_2 used for ozone concentration determination. Tests determined that adding starch solution to the KI sample while analyzing for ozone eliminated this problem since the starch complexed immediately with the I_2 on its formation, thus preventing the reaction with dimethyl sulfide. Water was placed in the sampler between KI analysis in order to maintain a constant pressure head.

$$2\,KI + O_3 + H_2O \longrightarrow I_2 + KOH + O_2$$

$$CH_3SCH_3 + I_2 \longrightarrow CH_3SCH_3 \cdot I_2$$



$$CH_3SCH_3 \cdot I_2 + H_2O \longrightarrow CH_3\overset{O}{S}CH_3 + 2HI$$



$$CH_3\overset{O}{S}CH_3 + I_2 + H_2O \xrightarrow{slow} CH_3\overset{O}{\underset{O}{S}}CH_3$$

REAGENTS

The gases used in the experiments were purchased from Liquid Air Inc.

Nitrogen

Before entering the reaction system, the nitrogen was further dried and cleaned by passing it through a column packed with a layer of Drierite and silica gel and a layer of 4 Å molecular sieves.

Oxygen

Tests were run on the purity of the oxygen by passing the gas through a Drierite-silica gel column. Extended use indicated a level of purity and dryness sufficient for this investigation.

Dimethyl Sulfide

The Baker grade sulfide was dried over anhydrous calcium sulfate and triple distilled using a 600 mm Vigreux distilling column attached to a 400 mm Claisen-Vigreaux distilling head.

Dimethyl Sulfoxide

The Baker analysed DMSO was stirred at 25°C with 5% of its weight of Darco G-60, filtered, treated with $MgCO_3$ to remove the acidic impurities, stored overnight over CaH_2, and triple distilled through a 400 mm Claisen-Vigreaux column at approximately 10 mm of Hg.

Methylene Chloride

The Mallinckrodt Spectr AR grade methylene chloride was washed with concentrated sulfuric acid followed by dilute sodium hydroxide and finally water. The washed material was allowed to stand overnight over sodium hydroxide pellets and calcium chloride and was then triple distilled using a

600 mm Vigreux column attached to a 400 mm Claisen-Vigreux distilling head.

Butyl Benzoate

The Matheson Coleman and Bell butyl benzoate was triple distilled using a 400 mm Vigreux column.

All chemicals were analyzed by gas chromatography for purity and stored under nitrogen until needed.

CALIBRATION OF EQUIPMENT

Calibration of several components of the experimental system was required before runs were made. These calibrations are as follows.

Rotometers

Both rotometers were calibrated using soap-film flow meters. Hales found that on continued use the sapphire rotometer floats picked up static electricity rendering them useless for accurate flow indicators. Therefore, the rotometers were used only as secondary indicators and soap-film flow meters were used for actual gas flow rates.

Syringe Drive

The syringe pump output was calibrated for several settings on ml/hr for a .1 ml Hamilton syringe by measuring the time required for .01 ml of material to be injected. Five settings were calibrated for dimethyl sulfide (see below).

	Setting on ml/hr	Flow Rate
DMS	9	$3.2593 \cdot 10^{-4}$ ml/min
	8	$2.131 \cdot 10^{-4}$ ml/min
	7	$1.359 \cdot 10^{-4}$ ml/min
	6	$9.147 \cdot 10^{-5}$ ml/min
	5	$6.222 \cdot 10^{-5}$ ml/min

Determination of Peak Height vs. Concentration Ratios

Gas chromatograph peak height ratios were calculated for DMSO, dimethyl sulfone, and butyl benzoate. On a mole basis these ratios came out to be:

Butyl Benzoate	1.0000
DMSO	.1359
$DMSO_2$	.1788

Evaporization Trap

A known amount of DMSO was added to 10 ml of methylene chloride and evaporated in the trap to a volume of 1 ml. Direct comparison of standard gas chromatographic peak areas with those from the trap indicated a trap efficiency of 99.0 percent.

O_3/O_2 Flow Rate

Since a normal run lasted approximately three hours, tests were run to determine the consistency of the ozone flow over this time period. Due to the slow response of the ozonator, a two hour warm-up period was allowed before samples were taken. Results indicated an average percent deviation of ± 2.41 percent. Hales[28] conducted experiments to determine the extent of ozone decay and found that at 28.5°C the decay was less than 1% during a run. Since my flow rates were much higher and my reactor diameter smaller, ozone decay should present no problems.

KI Sampler

When ozone was the limiting reagent, O_3 flow rates were measured before and during the reaction to determine the rate of decrease in ozone concentration with respect to time. Construction limitations dictated that 145 mm of 6 mm glass tubing be between the freeze-out trap exit and the actual point of analysis. Since this volume was from .7 to 1.2 times the volume of the reactor depending on the actual outside diameter (i.e. OD = 6 mm ± .3 mm) and wall thickness (1 mm ± .1 mm) of the tubing, study of the possibility of further DMS/O_3 reaction was necessary. The following tests and changes in analysis deemed the extent of further reaction as minimal.

1. Chromel-Alumel thermocouple readings determined the temperature at the actual point of analysis to be no higher than -11°C--a temperature 36° to 46°C below the reaction temperature. It is important to note that the reaction mixture warmed up to -11°C from a freeze-out trap exit temperature of -100°C.

2. Even though all of the DMS wasn't held in the freeze-out trap, some was trapped thereby decreasing the DMS concentration and the possibility of further reaction with

ozone.

3. A volume between 8.6 - 14.2 percent of the tube was immersed in water when a KI sample was taken. In order to decrease the rate of DMS/O_3 reaction in this volume, ice water was used when an ozone sample was taken.

Freeze-out Trap

Known amounts of DMSO were injected by means of the syringe pump into a nitrogen stream and passed through the freeze-out trap. Nitrogen flow rates used were the same as those encountered during experimental runs. Gas chromatography analysis indicated a trap efficiency of 99.3 percent.

CHAPTER III

RESULTS

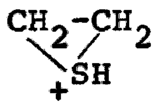
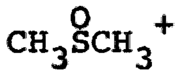
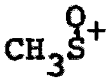
The kinetics for the gas phase reaction of dimethyl sulfide with ozone was studied at 25° and 35°C.

PRODUCTS OF THE OZONATION OF DIMETHYL SULFIDE

Coinjection g.l.c. and mass spectroscopy (see below) determined the detectable products to be dimethyl sulfoxide and dimethyl sulfone with the sulfoxide as the major product. Dimethyl sulfone constituted only 1.1 - 1.6 mole percent of the products at 25°C and 1.9 - 2.5 mole percent at 35°C.

Mass Spectrum

Dimethyl Sulfoxide

m/e*	assignment		
80	Parent + 2	61	
79	Parent + 1	48	CH_3SH^+
78	Parent  $CH_3\overset{O}{S}CH_3{}^+$	47	CH_3S^+
63	 $CH_3\overset{O}{S}{}^+$	46	$CH_2{=}S^+$
62	$CH_3SCH_3{}^+$	45	$CH{\equiv}S^+$
		15	$CH_3{}^+$

The yield of the sulfone proved too small to obtain a mass spectrum.

Coinjection Data

A 3 ml sample was injected and the peak height areas of the unknown compounds and the internal standard, butyl benzoate, were measured. Dimethyl sulfone and dimethyl sulfoxide were then added individually to the sample and two more 3 ml injections were made. The increase in peak areas determined the products to be the sulfone and sulfoxide (see below). Figure 10 shows a typical g.l.c. of the reaction products.

Compound	Unknown (Reaction Products)	Peak area
Butyl Benzoate		138956
Unknown 1		173785
Unknown 2		5578
	Second Injection (Dimethyl Sulfone added)	
Butyl Benzoate		unchanged
Unknown 1		unchanged
Unknown 2		71887
	Third Injection (Dimethyl Sulfoxide added to second sample)	
Butyl Benzoate		unchanged
Unknown 1		189285
Dimethyl Sulfone		unchanged

The products were therefore identified as dimethyl

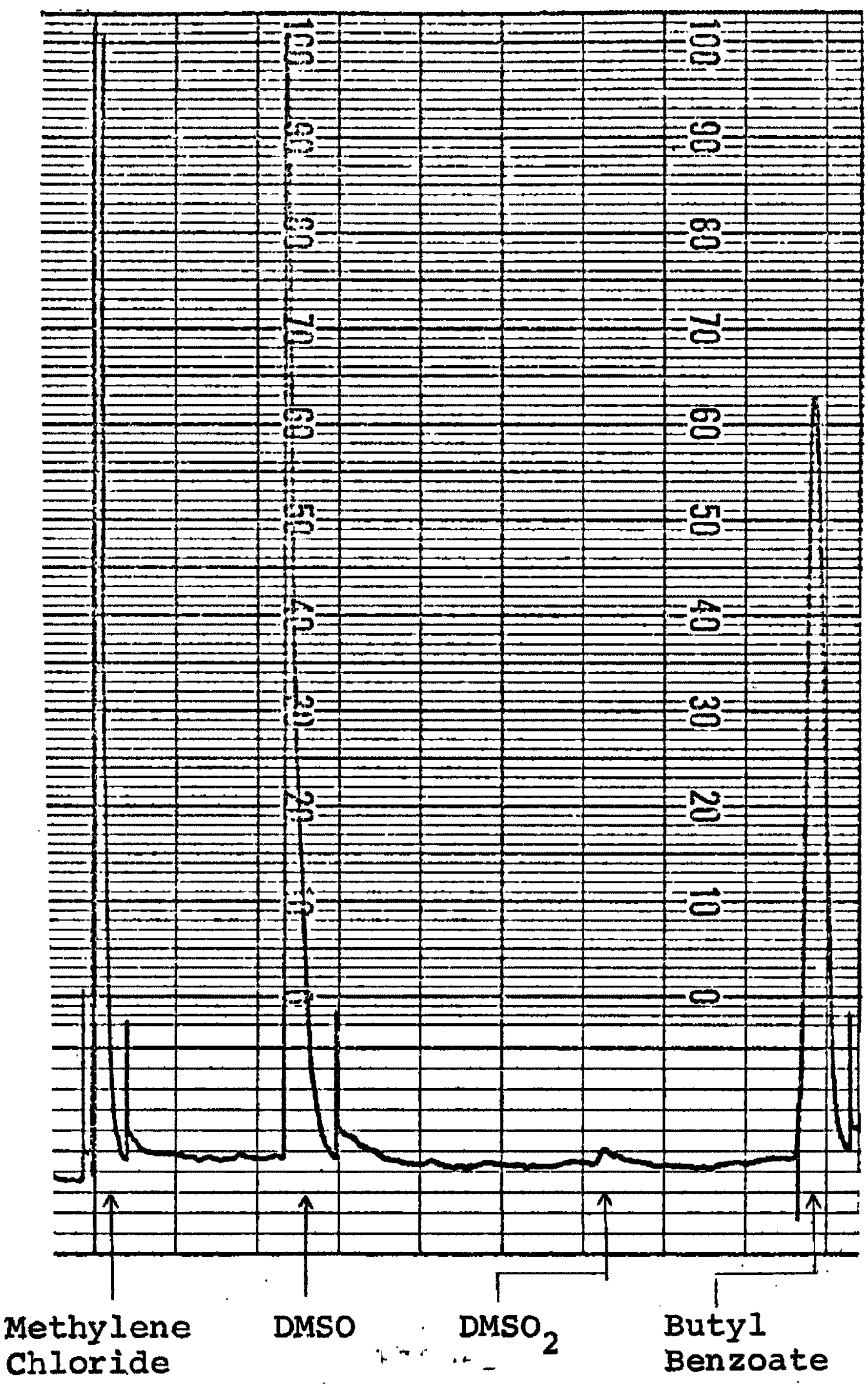


FIGURE 10

TYPICAL GAS CHROMATOGRAM OF REACTION PRODUCTS

Temperature Program = 1°/min, Initial Temperature=85°C, Final Temperature = 230°C, Injector Temperature = 230°C, Detector Temperature = 270°C, Carrier Gas=52.5 ml/min, Chart Speed = 1"/10 min

ivity was utilized to obtain the DMSO to $DMSO_2$

sulfone and dimethyl sulfoxide.

STOICHIOMETRY

Once the O_3/DMS reaction began, approximately an hour was required for stabilization to occur. During this unstable period more ozone was taken up than after stabilization resulted. In order to determine the total ozone uptake, both the unstable and stable periods were monitored. With ozone as the limiting reagent, samples from a reaction were taken at ten minute intervals and ozone uptake/min and total time for the reaction were measured thereby allowing determination of the total number of moles of ozone consumed during the reaction. Total product formation was obtained by g.l.c. using butyl benzoate as an internal standard. Comparison of the product formation and total ozone uptake yielded a stoichiometry of .613 ± .04 (see Table 4).

TABLE 4

STOICHIOMETRY FOR THE OZONE DIMETHYL SULFIDE REACTION

Moles DMS available $\times 10^4$	Moles O_3 available $\times 10^4$	Moles O_3 reacted $\times 10^4$	Moles DMSO formed $\times 10^4$	Stoichiometry Moles O_3/Mole DMS
2.76	1.44	1.22	2.08	.586
2.76	1.50	1.33	2.27	.589
2.76	2.35	1.61	2.44	.663

A value of .6 will be used for further determinations.

REACTANT ORDERS AND REACTION RATES

Results from the solution chemistry of sulfides and ozone indicate that the sulfoxide could compete with the sulfide for O_3.[29] It was initially thought, therefore, that the gas phase reaction would behave similarly and determination of two rate constants, K_1 and K_2, would be necessary.

$$\text{DMS} + O_3 \xrightarrow{K_1} \text{DMSO} + O_3 \xrightarrow{K_2} \text{DMSO}_2$$

$$d(O_3)/dt = K_1(\text{DMS})^m(O_3)^n + K_2(\text{DMSO})^x(O_3)^y$$

However, since product analysis of the gas phase reaction showed very little sulfone,[30] the equations reduce to:

$$\text{DMS} + O_3 \xrightarrow{K_1} \text{DMSO}$$

$$d(O_3)/dt = K_1(\text{DMS})^m(O_3)^n$$

It is therefore possible to determine reactant orders and reaction rates simply by knowing initial ozone and sulfide concentrations and measuring the decrease in ozone with respect to time.

Reactant Orders (Uncorrected)

Orders were determined by holding the concentration of one of the reactants constant while varying the other. This reduces the general rate equation to:

$$d(O_3)/dt = K'(O_3)^m \text{(if DMS is held constant)} \qquad (1)$$

The log of equation 1 can be written in the form y=mx + b. Plotting the log $d(O_3)/dt$ vs. log (O_3) or log (DMS) yields a straight line with a slope equal to the reactant order (see Figure 11). Tables 5, 6 and 7 give the $d(O_3)/dt$ for the corresponding initial concentrations of sulfide and ozone at 25° and 35°C. Uncorrected orders were:

$DMS_{25} = .457 \pm .03$

${O_3}_{25} = .635 \pm .02$

${O_3}_{35} = .661 \pm .02$

Reactant Orders (Corrected)

The kinetics were to be studied by initial rates, however, the reaction proved too fast to reach the desired less than 10% completion. Indeed, in certain runs, over 70% completion resulted. Initial concentrations were, therefore, not good approximations of actual reactant concentrations. Thus, the initial concentrations were changed using one of the following two equations:

$$\text{Corrected Ozone Concentration} = (O_3)_{\text{initial}} \cdot \left[1 - \left[\frac{ml._{\text{used/min}}}{ml_{\text{total/min}}} \cdot 2\right]\right]$$

where $ml_{\text{total/min}}$ = number of milliliters of $S_2O_3^{=}$ per minute needed to titrate the initial ozone concentration

$ml_{\text{used/min}}$ = difference in number of milliliters needed to titrate the initial ozone concentration and the final ozone concentration.

FIGURE 11

UNCORRECTED REACTANT ORDERS

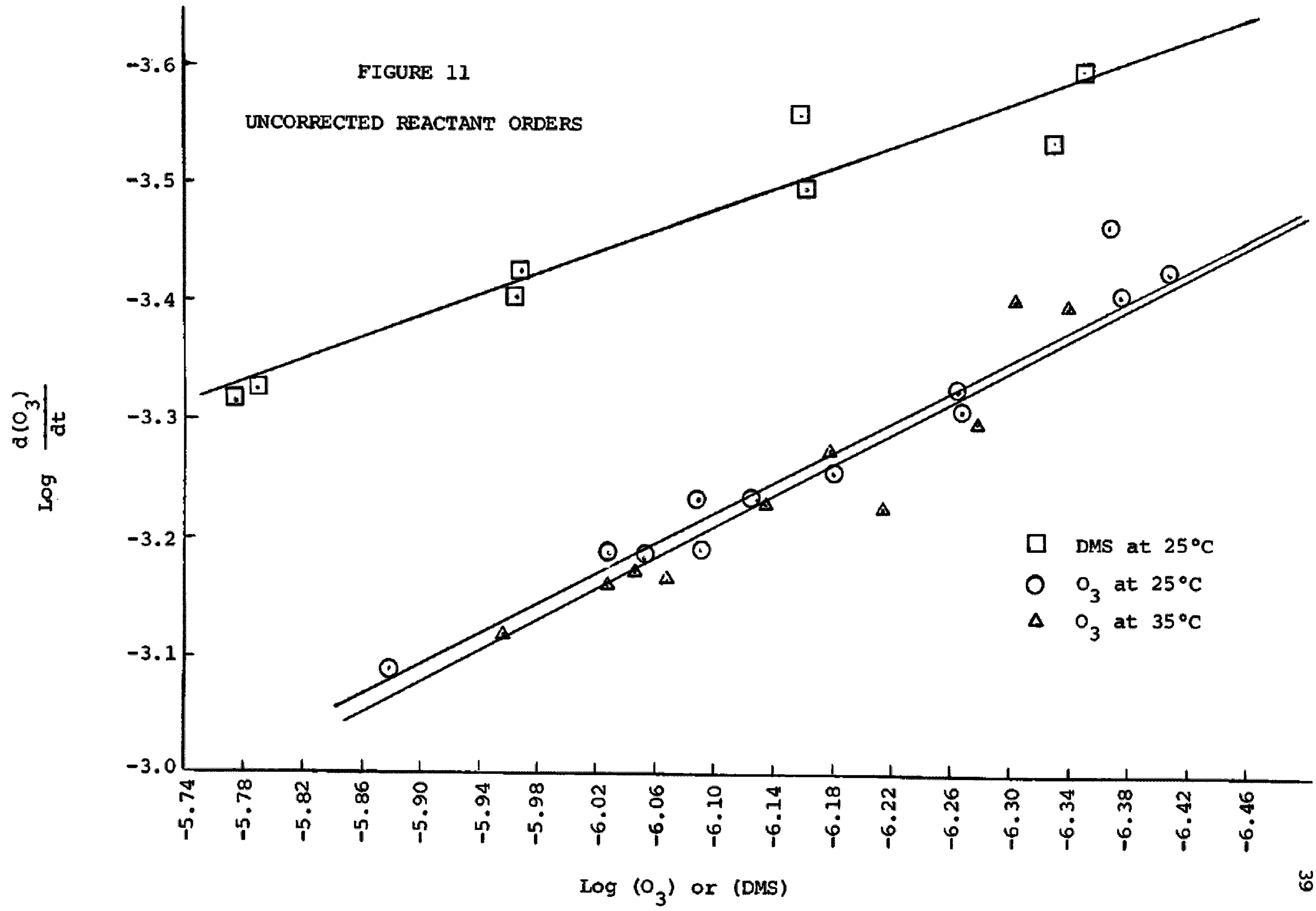


TABLE 5

UNCORRECTED DMS ORDER

25°C

Flow Rate l/min	M (DMS) x 10^7	log (DMS)	M (O_3) x 10^7	log (O_3)	M $d(O_3)/dt$ x 10^4	log $d(O_3)/dt$	Reaction Time (min) x 10^4
2.800	4.446	-6.3520	4.195	-6.3772	2.513	-3.5997	7.099
2.690	4.628	-6.3345	4.208	-6.3759	1.725	-3.7633	7.388 ***
2.695	10.77	-5.9679	3.900	-6.4089	3.738	-3.4274	7.376
2.695	6.864	-6.1634	4.167	-6.3801	3.184	-3.4970	7.375
2.673	6.921	-6.1598	4.080	-6.3893	2.748	-3.5609	7.437
2.678	10.83	-5.9652	4.220	-6.3747	3.912	-3.4076	7.423
2.665	16.64	-5.7789	4.100	-6.3872	4.805	-3.3183	7.458
2.723	16.28	-5.7883	4.194	-6.3773	4.717	-3.3263	7.299
2.662	4.677	-6.3300	4.174	-6.3794	2.902	-3.5372	7.466

*** This run was not included in any calculations since it was greater than two standard deviations from the line.

TABLE 6

UNCORRECTED O_3 ORDER

25°C

Flow Rate l/min	M (DMS) x 10^6	log (DMS)	M (O_3) x 10^7	log (O_3)	M $d(O_3)/dt$ x 10^4	log $d(O_3)/dt$	Reaction Time (min) x 10^4
2.654	1.093	-5.9613	7.376	-6.1322	5.840	-3.2336	7.490
2.691	1.078	-5.9673	4.279	-6.3686	3.418	-3.4663	7.386***
2.698	1.075	-5.9684	13.19	-5.8797	8.138	-3.0895	7.368
2.704	1.073	-5.9694	9.310	-6.0310	6.471	-3.1890	7.352
2.681	1.082	-5.9657	5.391	-6.2683	4.931	-3.3070	7.413
2.692	1.078	-5.9675	8.114	-6.0908	5.805	-3.2362	7.385
2.686	1.080	-5.9665	8.065	-6.0934	6.421	-3.1924	7.401
2.678	1.083	-5.9652	6.588	-6.1812	5.542	-3.2564	7.423
2.695	1.077	-5.9679	3.900	-6.4089	3.738	-3.4274	7.376
2.678	1.083	-5.9652	4.220	-6.3747	3.912	-3.4076	7.423
2.668	1.088	-5.9636	5.424	-6.2656	4.723	-3.3258	7.451
2.671	1.086	-5.9641	8.788	-6.0561	6.529	-3.1852	7.443

*** This run was not included in any calculations since it was greater than two standard deviations from the line.

TABLE 7

UNCORRECTED O_3 ORDER

35°C

Flow Rate l/min	M (DMS) x 10^6	log (DMS)	M (O_3) x 10^7	log (O_3)	M $d(O_3)/dt$ x 10^4	log $d(O_3)/dt$	Reaction Time (min) x 10^4
2.668	1.088	-5.9636	9.415	-6.0261	6.881	-3.1623	7.450
2.665	1.089	-5.9631	7.354	-6.1335	5.833	-3.2341	7.458
2.668	1.088	-5.9636	4.571	-6.3400	4.005	-3.3974	7.449
2.671	1.086	-5.9641	5.279	-6.2774	5.000	-3.3010	7.443
2.665	1.089	-5.9631	6.599	-6.1805	5.309	-3.2750	7.458
2.665	1.089	-5.9631	8.929	-6.0492	6.347	-3.1974	7.458
2.668	1.088	-5.9636	8.456	-6.0728	6.822	-3.1661	7.450
2.667	1.088	-5.9634	10.997	-5.9587	7.600	-3.1192	7.452
2.670	1.087	-5.9639	6.088	-6.2155	5.475	-3.2616	7.444

Since the ozone concentration and the $d(O_3)/dt$ are employed to determine the corrected concentration for the sulfide, a stoichiometric term must be incorporated into the equation before the corrected DMS concentration can be determined.

$$\text{Corrected DMS Concentration} = (\text{DMS})_{\text{initial}} \cdot (.6) \cdot \left[1 - \left[\frac{\text{ml}_{\text{used/min}}}{\text{ml}_{\text{total/min}}} \cdot 2 \right] \right]$$

Corrected orders were then found using the data from Tables 8 and 9 (see Figure 12).

$DMS_{25} = .578 \pm .04$

$O_{3_{25}} = .547 \pm .02$

$O_{3_{35}} = .566 \pm .03$

Reaction Rates at 25° and 35°C.

Using Tables 8 and 9 and assuming an order of .5 for both reactants and a stoichiometry of .6 moles of ozone per mole of DMS, the following rates were obtained.

$K_{25} = 1181 \pm 40\ \mu$ moles/l min

$K_{35} = 1217 \pm 59\ \mu$ moles/l min

ACTIVATION ENERGY AND ENTROPY

By taking the natural logarithm of the Arrhenius equation it is again possible to obtain an equation of the form $y = mx + b$ with the slope equal to $-E_a/2.303R$.[31]

$$K = se^{-E_a/RT}$$

TABLE 8

CORRECTED O_3 ORDER

25°C

M (DMS) x 10^7	log (DMS)	M (O_3) x 10^7	log (O_3)	M $d(O_3)/dt$ x 10^4	log $d(O_3)/dt$
4.613	-6.3360	5.188	-6.2849	5.840	-3.2336
4.983	-6.3025	10.192	-5.9917	8.138	-3.0895
4.792	-6.3194	6.931	-6.1592	6.471	-3.1890
4.290	-6.3675	3.563	-6.4481	4.931	-3.3070
4.759	-6.3225	5.970	-6.2240	5.805	-3.2362
4.570	-6.3400	5.689	-6.2450	6.421	-3.1924
4.469	-6.3498	4.531	-6.3438	5.542	-3.2564
4.177	-6.3791	2.521	-6.5983	3.738	-3.4274
4.262	-6.3703	2.768	-6.5578	3.912	-3.4076
4.410	-6.3556	3.664	-6.4360	4.723	-3.3258
4.714	-6.3265	6.358	-6.1966	6.529	-3.1852

CORRECTED DMS ORDER

25°C

M (DMS) x 10^7	log (DMS)	M (O_3) x 10^7	log (O_3)	M $d(O_3)/dt$ x 10^4	log $d(O_3)/dt$
2.120	-6.6736	3.334	-6.4770	2.513	-3.5997
4.178	-6.3790	2.521	-6.5983	3.738	-3.4274
2.958	-6.5290	2.993	-6.5239	3.184	-3.4970
3.112	-6.5069	3.058	-6.5146	2.748	-3.5609
4.262	-6.3703	2.768	-6.5578	3.912	-3.4076
5.621	-6.2502	2.308	-6.6367	4.805	-3.3183
5.759	-6.2396	2.472	-6.6068	4.717	-3.3263
2.077	-6.6824	3.090	-6.5100	2.902	-3.5372

TABLE 9

CORRECTED O_3 ORDER

35°C

M (DMS) x 10^7	log (DMS)	M (O_3) x 10^7	log (O_3)	M $d(O_3)/dt$ x 10^4	log $d(O_3)/dt$
4.750	-6.3232	6.852	-6.1642	6.881	-3.1623
4.601	-6.3371	5.179	-6.2858	5.833	-3.2341
4.397	-6.3568	3.079	-6.5115	4.005	-3.3974
4.219	-6.3747	3.418	-6.4662	5.000	-3.3010
4.573	-6.3397	4.619	-6.3354	5.309	-3.2750
4.801	-6.3186	6.562	-6.1830	6.347	-3.1974
4.566	-6.3404	5.915	-6.2280	6.822	-3.1661
4.846	-6.3145	8.164	-6.0881	7.600	-3.1192
4.338	-6.3626	4.050	-6.3925	5.475	-3.2616

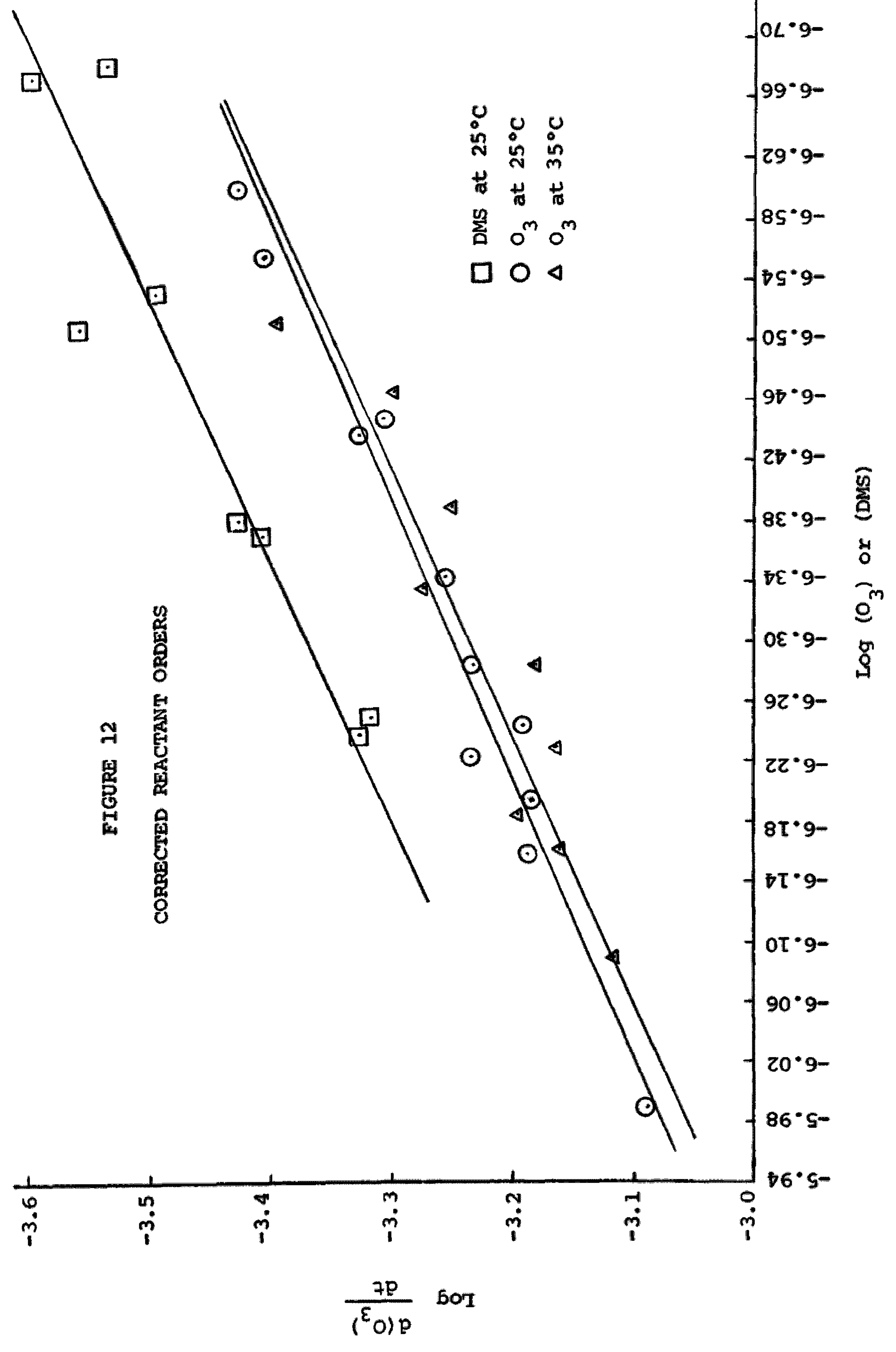


FIGURE 12

CORRECTED REACTANT ORDERS

$$\log K = -\frac{E_a}{2.303R} \cdot \frac{1}{T} + \text{constant}$$

A plot of log K vs. 1/T for 25° and 35° yields an activation energy of 549 cal/mole. This very low activation energy results in a question of the effectiveness of quenching the reaction with a freeze-out-trap. This problem will be further dealt with in the Appendix.

By extrapolation of the graph, the Arrhenius factor can be obtained and from this the entropy of the reaction determined (see Figure 13).

$$A = e^{\Delta S/R}$$

$$\Delta S = 16 \text{ cal/° mole}$$

There exist two sources of significant error in this entropy value. The first results from the assumption that reactant orders are .5. If experimentally determined orders are used, a value of 16.9 cal/° mole is obtained. While this is only a six percent error, a much greater one occurs due to the inaccuracy in measurement of the rate constants. When the extreme values for the Arrhenius factor are calculated using the high and low standard deviation values for the determined rate constants, the accuracy of the entropy term is 16 cal/° mole ± 5 cal/° mole.

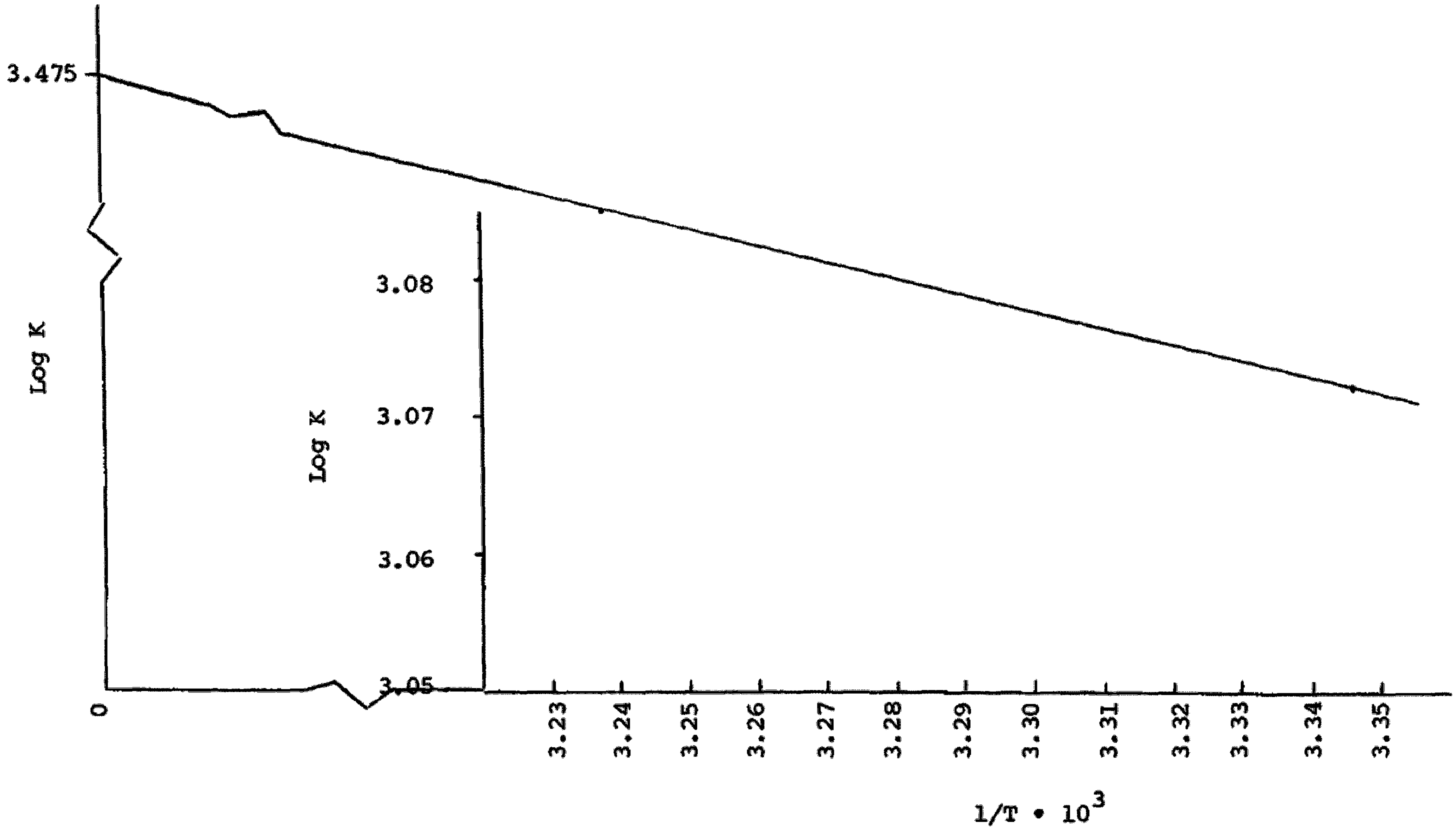


FIGURE 13

DETERMINATION OF ΔS

RATE EQUATION

Determination of the rate equation for all temperatures yielded:

$$d[O_3]/dt = -2984 \cdot e^{-549/RT} \cdot [DMS]^{.5} \cdot [O_3]^{.5} \quad \mu \text{ moles/l min}$$

EFFECT OF LIGHT ON THE REACTION

An obvious difference in the H_2S/O_3 kinetic study of Hales and that of Cadle and Ledford was that Hales conducted his reactions in the absence of light. Since considerably differing rates were found from the two studies,[33] a test was made to determine if light had any significant effect on the DMS/O_3 reaction. A run was carried out in the undarkened reaction chamber. When the run had stabilized, the chamber was painted black and further samples were taken. It was found that within experimental error no significant change in rate resulted (see Table 10).

TABLE 10

LIGHT EFFECT ON THE REACTION

	Time	Milliliters S_2O_3 = required for titration	
Chamber Undarkened	4:10	1.515	1.522 = Average
	4:30	1.525	
	4:50	1.525	
Chamber Darkened	5:20	1.450	1.527 = Average
	5:40	1.550	
	6:00	1.580	

CHAPTER IV

DISCUSSION

APPARATUS ERROR

One source of significant error exists in the measurement of the ozone concentration. While the efficiency of the gas dispersion tube was effectively 100% and the method of analysis quite accurate, the ozonator showed an ozone fluctuation of ± 2.4 percent even though a two hour warm-up period was allowed.

Several possible errors arise which could explain the point scatter for the order determinations. Since flow rates varied slightly from run to run, exact reproduction of constant concentrations was impossible. This variation was quite small for the sulfide (maximum deviation = 1.1%), however considerably larger errors resulted when ozone was held constant (maximum deviation = 5.7%) due to ozonator fluctuation and errors in setting the ozonator voltage. Changes in room current necessitated a voltage adjustment each day.

While reactant concentrations could be measured with relative certainty, at low ozone reactant concentrations the unreacted ozone over any reasonable time of sample measurement was very small and therefore susceptible to titration errors.

When the standard deviation was calculated, points which fell more than two standard deviations from the line were considered random errors and were dropped from any calculations.

The rigidity in operation routine presented the possibility of some systematic error. While no noticeable effects were observed by changing cleaning solutions or using different tanks of compressed gases, systematic error in the measurement of the volume of the reaction chamber is possible. Due to the small volume (1.988 ml) any error in measurement would have a sizable effect of the $d(O_3)/dt$ and therefore would shift the reaction rates to higher or lower values. Furthermore, Hales[34] observed that turbulance to a distance of one centimeter resulted in the reaction chamber due to gas mixing. While this was insignificant for Hale's work, this distance represents approximately 5% of the reaction chamber in this study.

Flow rates were observed to be relatively constant and therefore presented no problems, however, the error in initial flow rate measurements was ± 1.3%.

EXPERIMENTAL ERROR

Although the low activation energy seems plausible for the reaction studied, the small change in the reaction rates as well as the small temperature range studied lend doubt to its accuracy.

Changing the initial concentrations to average concentrations probably results in truer reaction orders, especially when only 10 - 30% reaction occurs. In this study, however, most runs resulted in 50 - 70% completion. This means that initial concentrations were twice as large as those at the end of the reaction. Since the change is large, the average concentration does not closely approximate either the initial or final concentrations.

SCIENTIFIC IMPLICATIONS

The gas phase reaction of ozone with dimethyl sulfide has been proven to have a stoichiometry of .6 to 1. Stoichiometries of less

$$1\ \mathrm{DMS} + .6\ O_3 \dashrightarrow 1\ \mathrm{DMSO} + \mathrm{DMSO}_2\ \text{(Trace)}$$

than 1:1 have been reported for reactions in solution,[35] however, the only previous gas phase ozone-sulfide work, that of Hales and Cadle and Ledford, reported 1:1 stoichiometries. Two possible explanations of the less than 1:1 ratio are that ozone supplies more than one oxygen per ozone molecule or that oxygen from the carrier gas enters into the reaction. The first of these explanations has considerable support. Work done by Thompson and Knowles[36] on the ozonation of triphenylphosphite with oxygen and ozone and oxygen-free ozone showed no significant difference in stoichiometry. The work, carried out in methylene chloride, indicated nearly two of the three ozone oxygens were used. At low temperatures (-70°C), a stable phosphite-ozone adduct was formed. Warming the adduct to 25°C resulted in the evolution of a mole of oxygen and formation of one mole of triphenylphosphate. Wasserman and Kaplan[37] studied the EPR spectrum of the oxygen produced on warming and found the presence of Δ^1 oxygen, an excited state of oxygen. Murray and Kaplan[38,39] also found that the phosphite-ozone adduct was able to oxidize singlet oxygen acceptors both in solution and in the gas phase. Since Thompson and Knowles[40] found that diethyl and dibutyl sulfide react with ozone in less than a 1:1 stoichiometry, and since the O_3/DMS stoichiometry is .6:1, it is conceivable for the sulfides to also form an adduct which on decomposition produces excited oxygen also capable of reaction with the sulfide.

Preliminary work carried out to determine the effect of oxygen on the DMS/O_3 reaction has proven to be inconclusive as to whether or not it enters into the reaction.

The rate of reaction in the gas phase of dimethyl sulfide with ozone appears considerably faster than that of dimethyl sulfoxide. This is based on the very little sulfone found as product even though DMSO concentrations, due to the high percent of completion of the reactions, reach approximately those of the sulfide.

ENVIRONMENTAL IMPLICATIONS

Conditions used in this study were sufficiently different from those encountered either in the atmosphere or in stack gases to warrant care in applying the results. It is however, interesting to speculate about situations utilizing the observed rates. Hales[41] proposed a model in which ozone was injected into the base of a factory stack containing H_2S (500 ppm) at a temperature of 150°C. Assuming no ozone decay and a retention time of 10 seconds, he determined that only 2% oxidation would result assuming a stoichiometric amount of ozone was supplied. If, however, the same model is applied to dimethyl sulfide and ozone, 100% oxidation results. Although this indicates that DMS and O_3 seemingly react fast enough, at least under the model conditions, to warrant further study for pollution control, other considerations, such as the possible problems in removal and disposal of the resulting oxidation products, could make the method undesirable. While product removal from the stack gas should present no forseeable problems due to good water solubility, disposal of the resulting waste water may create considerable economical and/or environmental problems. Low concentrations coupled with low market prices would preclude any attempt at product recovery. Environmental effects, resulting from drainage of settling ponds into streams and rivers, are difficult to assess. Before ozone can be considered for pollution control, the feasibility and economics of the removal of all gaseous pollutants must be determined. The gaseous ozonation of all Kraft mill effluents, with the exception of sulfur dioxide, is possible. Using Table 1 and the Welsbach Corporation's ozone production value of \$.08152/lb O_3, it is possible to determine the economic practicality of the ozonation of stack gas. Each mill was assumed to use 1,150 tons of pulp per day.

Kraft Mill A

Pollutant	lbs $S^=$/day	Moles Pollutant*	Stoichiometry	lbs O_3/day
RSR	3749	27,391	.6:1	1738
RSSR	1150	5,537	5:1	2927
RSH	5865	55,311	3:1	17,544
H_2S	15,997	212,731	1:1	22,491

Cost = \$3600/day

Kraft Mill B

Pollutant	lbs $S^=$/day	Moles Pollutant*	Stoichiometry	lbs O_3/day
RSR	2611	19,076	.6:1	1210
RSSR	2818	13,590	5:1	7184
RSH	1380	13,015	3:1	4128
H_2S	6084	80,906	1:1	8554

Cost = \$1700/day

*The Moles Pollutant was determined assuming R equals CH_3.

Since the oxidation products are all quite water soluble, as is sulfur dioxide, if the ozonation process was followed by a scrubber tower removal of all pollutants, including sulfur dioxide, should be possible. At present, the \$1700-\$3600 price is quite high. However, as requirements for pollution control become more stringent, the ozonation of stack gas may prove practical.

Although atmospheric conditions vary considerably from those studied, it seems likely that in areas of high DMS concentrations the reaction with O_3 is fast enough to enter into the photochemical smog cycle.

CHAPTER V

SUMMARY

The kinetics of the gas phase ozonation of dimethyl sulfide were studied at 25° and 35°C. Product analysis determined dimethyl sulfoxide to be the only major product at both temperatures with a 1.1 - 1.6 mole % and a 1.9 - 2.5 mole % conversion to the sulfone at 25° and 35°C respectively. The stoichiometry observed was .613 ± .04 moles of ozone per mole of DMS. The corrected orders were .578 ± .04 for dimethyl sulfide and .547 ± .02 and .566 ± .03 respectively for ozone at 25° and 35°C. The rate equation was found to be:

$$d(O_3)/dt = -2984 \cdot e^{549/RT} \cdot (DMS)^{.5} \cdot (O_3)^{.5} \quad \mu \text{ moles/l min}$$

While pollution control of dimethyl sulfide with ozone seems feasible, economic and environmental problems could preclude its use. The reaction does appear fast enough to enter into the photochemical smog cycle.

BIBLIOGRAPHY

1. E. R. Stevens, J. Air Pollut. Control Assoc., 19, 181 (1969) and references cited therein.
2. J. N. Pitts, Jr., J. Air Pollut. Control Assoc., 19, 658 (1969) and references cited therein.
3. A. Miller, "Meteorology," 2nd Ed., Charles E. Merrill Publishing Company, Columbus, Ohio, 1971, p. 5.
4. I. Akamatsu, H. Kamishima and Y. Kimura, Kami-pa Gikyoshi, 20 (10), 556-60 (1966).
5. I. Akamatsu, Kami-pa Gikyoshi, 22 (4), 200-4 (1968).
6. I. Akamatsu, H. Ueshima and H. Kimura, C. A. , 73, 14186j (1970).
7. F. Fichter and P. Sjostedt, Ber., 43, 3422 (1910).
8. K. Kisskalt, C. A., 6, 1946 (1912).
9. M. W. Franklin, C. A., 8, 2767 (1914).
10. L. Farkas, C. A., 25, 5861 (1931).
11. M. Maneck, Das Braunkohlen-Archiv, 40, 61 (1933).
12. H. Böhme and H. Fischer, Ber., 75B, 1310 (1942).
13. H. Boer and E. C. Kooyman, Anal. Chim. Acta, 5, 550 (1951).
14. L. Bateman and J. I. Cunneen, J. Chem. Soc., 1596, (1955).
15. D. Barnard, J. Chem. Soc., 4547 (1957).
16. A. Maggiolo and E. A. Blair, "Ozone Chemistry and Technology," Advances in Chemistry Series No. 21, American Chemical Society, pp. 200-01.
17. L. Horner, H. Schaefer and W. Ludwig, Ber., 91, 75 (1958).
18. L. J. Hughes, T. D. McMinn Jr. and J. C. Burleson, C. A., 60, 6751 (1964).
19. B. Moody, Unpublished work.

20. Ref. 4 and Ref. 5.

21. Ref. 6.

22. J. Hales, Doctorate Thesis, University of Michigan, pp. 69-70, 1968.

23. Ref. 22, p. 67.

24. J. H. Karchmer, "The Analytical Chemistry of Sulfur and its Compounds," Part II, Wiley Interscience, New York, 1972, p. 764.

25. R. C. Weast and others, "Handbook of Chemistry and Physics," 45th Ed., Chemical Rubber Co., Cleveland, Ohio, 1964, p. D-103.

26. J. Jose, R. Philippe and P. Clechet, Bull. Soc. Chim. France, 2860 (1971).

27. Ref. 24, p. 66.

28. Ref. 22, p. 78.

29. Ref. 11, 12 and 19.

30. Ref. 15 and 17.

31. S. L. Kittsley, "Physical Chemistry," 2nd Ed., Barnes and Noble Inc., New York, 1967, pp. 105-106.

32. Ref. 23.

33. Ref. 22, p. 118.

34. Ref. 22, p. 70.

35. Ref. 13, p. 559 and Ref. 15, p. 4543.

36. W. S. Knowles and Q. E. Thompson, Chemistry and Industry, 121 (January 24, 1959).

37. E. Wasserman, R. W. Murray, M. L. Kaplan and W. A. Yager, J. Am. Chem. Soc., 90, 4160 (1968).

38. R. W. Murray and M. L. Kaplan, J. Am. Chem. Soc., 90, 537-8 (1968).

39. R. W. Murray and M. L. Kaplan, J. Am. Chem. Soc., 90, 4161 (1968).

40. Ref. 36.

41. Ref. 22, 122.

APPENDIX

PROBLEMS IN COMPUTING RATE CONSTANTS

DUE TO THE LOW ACTIVATION ENERGY

The exceptionally small activation energy creates considerable doubt about the effectiveness of the freeze-out trap and therefore the determined rate constants. The Arrhenius equation was employed to determine the effect of the small E_a on lowering the temperature from the reaction temperature of 25°C to the maximum freeze-out temperature of -131°C.

$$\mathrm{Log}\ \frac{K_{-131}}{K_{25}} = \frac{549 \cdot (142 - 298)}{2.303 \cdot 1.987 \cdot (142 \cdot 298)}$$

$$\frac{K_{25}}{K_{-131}} = 2.8$$

This means that at -131°C the reaction proceeds approximately 1/3 as fast as it does at 25°C and that quenching of the reaction does not result. Therefore, the originally determined value of K_{25} (*i.e.* 1181 μ moles/l min) can only be considered an upper limit for the rate constant. In order to determine the lower limit, the volume of the reaction chamber, the freeze-out trap and the KI sampler must be known. Assuming a flow rate of 2683.2 ml/min (the average of all the 25°C ozone runs), and no temperature dependence it is possible to redetermine the $d(O_3)/dt$ and finally a new lower limit for K_{25}. The new volume was 90 milliliters.

$$K = \frac{12.43}{(.453)^{.5} \cdot (.5011)^{.5}} = 26.1\ \mu \text{ moles/ 1 min}$$

Further complications arise from the loss of a laminar flow system and also from the possibility of an ozone/solid DMS reaction once the reaction reaches the freeze-out trap. It is possible, therefore, to only say that the actual rate constant (K_{25}) lies somewhere between $1.18 \cdot 10^3$ and $2.61 \cdot 10^1$ μ moles/l min, probably closer to the upper limit.