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THE AQUEOUS PHASE OZONATION OF
METHANETHIOL AND DIMETHYL DISULFIDE

By

Lawrence R. Schmitz

B.S., Saint John's University, 1970

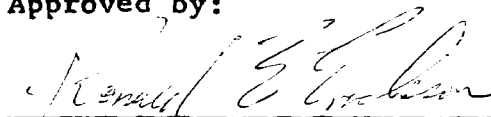
Presented in partial fulfillment of the requirements for the degree of

Master of Science

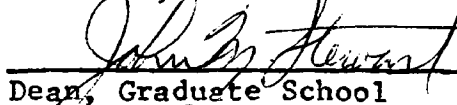
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FOR MY MOTHER

ACKNOWLEDGMENTS

I am indebted to my advisor, Ronald Erickson, for his guidance, understanding, and patience. The help of Steve Jarrard, who performed some experiments, is also gratefully acknowledged.

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CHAPTER I

INTRODUCTION AND HISTORICAL

An undesirable result of the Kraft wood pulping process is the release of large amounts of malodorous reduced sulfur compounds into the air. This thesis deals with the ozonation of two of these compounds, methanethiol (CH_3SH) and dimethyl disulfide (CH_3SSCH_3). The importance of this work is three-fold. One, ozonation may be the basis for controlling odors from Kraft pulp mills. Two, the fate of these compounds once released may involve ozone. Three, little is known concerning these reactions.

KRAFT PULP MILL EFFLUENT

Two components of the effluent of Kraft pulp mills are methanethiol and dimethyl disulfide. Both compounds are extremely malodorous and are in part responsible for the stench surrounding these mills. Methanethiol is particularly bad because it is detectable at a concentration of one part per 5×10^{10} parts of air.¹ Hydrogen sulfide is also a major component of the effluent. Effluent data for some pulp mills are given in Table I. The amount of pollutants released is a function of the pulping conditions as shown in Table II.³

TABLE I
A Pulp Mill in Italy²

Compound	Concentration In Effluent	Total Output
CH SH 3	23 mg/l	60 kg/day
H S 2	25 mg/l	70 kg/day

³
*Two Mills in Japan

Source	SO 2	H S 2	RSH	RSR	RSSR	Total lb/ton	% of Total
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 Nonconden- sable	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	3.00		100.00

* lb S--/ton airdried pulp

Source	*Form of Gas Emission					Total lb/ton	% of Total
	SO 2	H S 2	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 Acidifica- tion	----	0.27	0.01	0.00	0.01	0.29	2.30
Neutrali- zation	----	<u>1.01</u>	<u>0.02</u>	<u>0.00</u>	<u>0.00</u>	<u>1.03</u>	<u>8.20</u>
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

*1b S--/ton airdried pulp

TABLE II

Organosulfer Compounds Released in Kraft Pulping

Wood Type	Pulping Condition	CH ₃ SH, mg/g. wood Sulfidity %			CH ₃ SCH ₃ , mg/g. wood Sulfidity %			CH ₃ SSCH ₃ , mg/g. wood Sulfidity %		
		14.7	22.2	30.5	14.7	22.2	30.5	14.7	22.2	30.5
Pine	180° C., 1 hr	0.21	----	0.70	0.18	----	0.30	0.10	----	0.20
Spruce	180° C., 1 hr	0.20	0.41	0.65	0.12	0.21	0.31	0.02	0.02	0.04
Maple	180° C., 2 hrs	0.63	0.91	1.37	0.92	0.82	1.36	0.04	0.06	0.06
Pine	170° C., 2 hrs	0.21	0.49	0.73	0.17	0.23	0.33	0.01	0.02	0.02
Pine	180° C., 2 hrs	0.55	0.68	0.90	0.46	0.57	0.74	0.01	0.02	0.05
Spruce	180° C., 3 hrs	0.69	0.98	1.20	0.75	1.00	1.27	0.04	0.05	0.09
Spruce	180° C., 4 hrs	0.68	0.78	1.34	1.07	1.25	1.77	0.04	0.03	0.08
Maple	180° C., 4 hrs	0.72	0.96	1.45	1.62	2.01	2.84	0.06	0.10	0.10

OZONE

Ozone is a major component of the photochemical smog that is often found in the atmosphere of large cities. Ozone is a strong oxidant and has been shown to be responsible for most of the oxidizing power of the smog. In contrast to its role as a pollutant, ozone is very beneficial to man in a number of ways. It is an important component of the upper atmosphere and has been employed as an antipollution agent, e.g. in odor control and water purification.

Ozone in Photochemical Smog

On the earth's surface the natural ozone concentration is very low, approximately 0.02 to 0.03 ppm.⁴ However, the air in large cities often contains several tenths of a part per million ozone. The existence of this phenomenon has been particularly well documented based on studies of the Los Angeles atmosphere. It has been found that the reactions producing ozone involve nitrogen oxides, oxygen, hydrocarbons⁵⁻¹⁷ and light.¹⁶ The following mechanism is essentially that of Stephens. Upon photolysis, nitrogen dioxide forms nitric oxide and atomic oxygen.



In a three-center reaction, atomic and molecular oxygen combine to form ozone.



M is the third center. However, these two reactions can be reversed as follows:



Therefore, the following equilibrium is set up in a short period:



The equilibrium, however, lies far to the left and will not produce enough ozone to account for the amount found in the atmosphere. This is where the hydrocarbons enter the cycle. The hydrocarbons allow the build up of ozone by slowly converting nitric oxide to nitrogen dioxide without a net decomposition of ozone. Olefins are one of the most reactive types of hydrocarbons. Stephens¹⁶ proposes this mechanism:



This mechanism is still open to question, but it does explain the ozone build up. Note that a potential ozone molecule is lost in equation (5) (as O). Two potential ozone molecules are gained though (as NO₂), one each in equations (6) and (8).

Atmospheric Ozone

At an altitude of approximately 25 km to 30 km the natural concentration of ozone reaches a maximum, about 6×10^{12} molecules/cc.

The vertical distribution of ozone is given in Figure I.

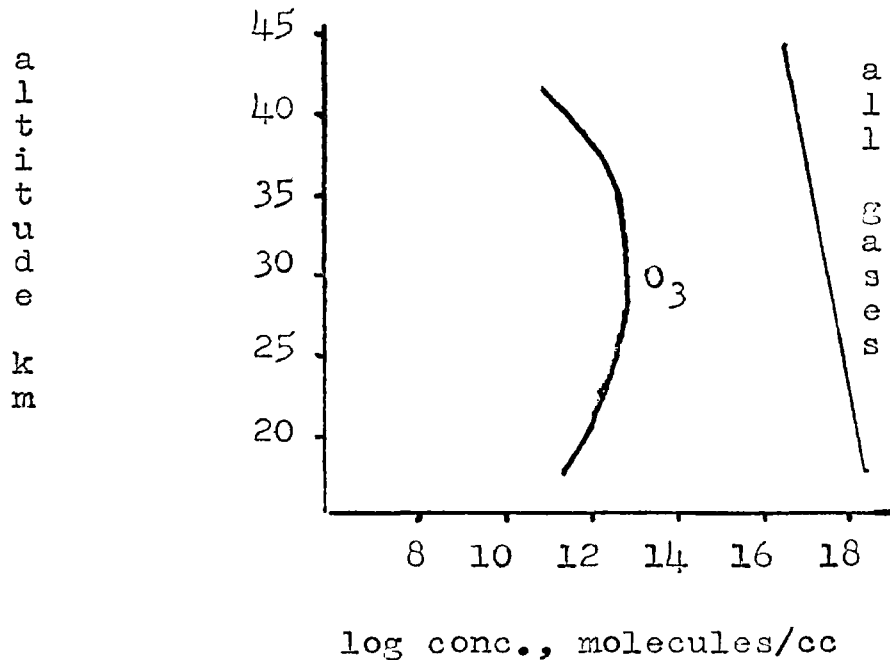


FIGURE I

Ozone Concentration as a Function of Altitude

Although the concentration of ozone is low (6×10^{12} molecules/cc $\times 10^6$ air molecules/ 10^3 molecules), it serves an important function.

Due to its strong absorption of ultraviolet light ozone removes rays that would otherwise be lethal. In the upper atmosphere ozone is formed when molecular oxygen is cleaved by light.



Atomic and molecular oxygen then combine according to equation (2) to form ozone.

Ozone as an Antipollution Agent

Being a strong oxidant, ozone will oxidize many malodorous compounds often producing mildly odorous or odorless products. For this reason ozone has found many uses as an odor control agent. Applications include odor control for restaurants, sewage plants, morgues, rubber plants, fish processing plants, rendering plants, and paper mills.

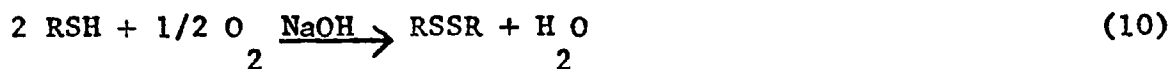
OXIDATIONS OF THIOLS AND DISULFIDES

Bivalent sulfur can be oxidized by many compounds. Both thiols and disulfides can be converted to sulfonic acids by strong oxidants. Under mild oxidizing conditions, thiols give disulfides. The oxidation of disulfides can also stop at lower oxidation states; thiolsulfonates (RSOSR) or thiolsulfonates (RSO SR) are the common products.

2

Oxidations Using Oxygen

The autoxidation of thiolate anions is a well-known reaction. In 1941 Xan and coworkers²⁰ noted that more oxygen is absorbed by basic aqueous solutions of thiols than could be accounted for according to equation (10).



They suspected further oxidation to the sulfonic acid, but did not show that it occurred.

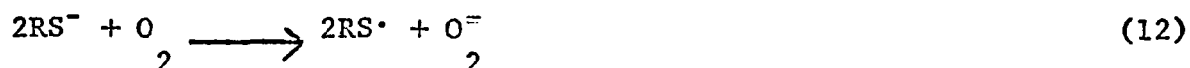
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Wallace and Schriesheim²¹ found that the stoichiometry given in equation (10) is followed for at least the first 50% of the reaction.

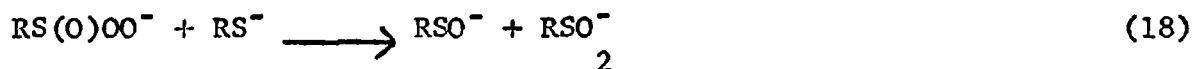
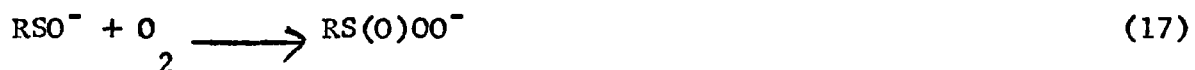
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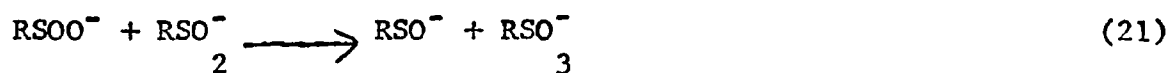
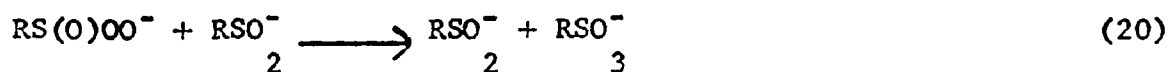
Several years later, they^{22,23} confirmed the suspicions of Xan et al when they found that letting the reaction go to completion resulted

in the formation of sulfonic acids. Because disulfides were converted to sulfonic acids under the reaction conditions, it was assumed that the sulfonic acids were formed from the disulfides. However, these studies were run in nonaqueous solvents. Protic solvents were found to inhibit the formation of sulfonic acids; in water the final product was the disulfide. The following mechanism was proposed for the formation of the disulfide.²¹ B⁻ is the base.



In 1962 Berger²⁴ obtained mainly sulfinic acids and lesser amounts of sulfonic acids and disulfides when thiols were oxygenated in excess base (K⁺t - OBu in t - HOBu). In the cases in which the thiol was in excess, the disulfide was the major product. Thiyl radicals were shown not to be involved in the reactions yielding the disulfides of the sulfur acids. It was also determined that the sulfenate anion was an important intermediate in the formation of the acids. The following mechanism was proposed:





Two mechanisms for the formation of the disulfide were presented, but Berger felt that neither explained all the data. He did feel, however, that the mechanism of disulfide formation involved the undissociated thiol.

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Harkness and Murray finally explained the absorption of excess oxygen in the aqueous systems. Studying the reaction of methanethiol and oxygen, they found that the products were dimethyl disulfide and hydrogen peroxide. They also demonstrated that the disulfide was not oxidized further under the conditions of the reaction.

The autoxidation of thiols in the absence of base is a very slow reaction.

Oxidations Using Ozone

The first ozone oxidation of a thiol was reported in 1933 by Martin Maneck.²⁶ He ozonized ethanethiol and obtained ethanesulfonic acid. The conversion of thiols to sulfonic acids has also been observed by several other authors.²⁷⁻²⁹ Asinger and coworkers used ozonation of thiol to prepare a number of long chain aliphatic sulfonic acids in yields from 70 to 100%.³⁰ Barnard reported quantitative conversion of thiophenol to benzenesulfonic acid. The conversion of isobutanethiol to isobutanesulfonic was accomplished with a 90% yield³¹ by Erickson.

Both Barnard and Erickson have determined the stoichiometry³⁰ involved. Barnard found that 1.6 moles of ozone per mole of thiophenol were absorbed when the reaction was carried out by adding

ozonized oxygen to a CCl_4 solution of the thiol maintained at -20°C . Working in methanol at -78°C Erickson³¹ found a stoichiometry of 1.6 :1 when an ozone-oxygen stream was used and a stoichiometry of 3.3 :1 when an ozone-nitrogen stream was used for the conversion of isobutane-thiol to the corresponding sulfonic acid.

Disulfides and thiolsulfonates have been reported as minor products of the reaction. Maneck²⁶ found both. In Erickson's³¹ work the disulfide was formed, but the thiolsulfonate was not identified. However, all the minor products were not identified. Erickson also found methyl isobutanesulfonate, a product that must have arisen through a reaction with the solvent (CH_3OH). An ozonation of thiophenol²⁶ performed by Maneck³ yielded no sulfonic acid. The only products were the corresponding disulfide, thiolsulfonate and α -disulfone. Maneck also noted that continued ozonation of either ethanethiol or thiophenol resulted in an attack of the carbon-sulfur bonds and the formation of sulfuric acid.

The mechanism of the ozone-thiol reaction has hardly been considered. Maneck²⁶ offered the following, but he gave no proof for it.



At that time thiolsulfonates were believed to have a disulfoxide structure and the thiolsulfonate was reported as a disulfoxide.

Two studies of the ozone-thiol reaction in the gas phase have been carried out. The use of ozone to control Kraft pulp mill odors has been considered by Akamatsu.³ He found that methanethiol was converted to an odorless, water-soluble compound.

A kinetic study of the ozone-ethanethiol reaction in the gas phase was performed by Kirchner, Kastenhuber and Biering.³² Concentrations were in the parts per million range and under those conditions the reaction proceeded with carbon-sulfur bond cleavage. The kinetics were determined by competitive reactions with hexene and isobutene. At 30° C. a rate constant of $2.4 \pm 0.8 \times 10^3$ l/mole sec was found.

A series of disulfides has been ozonized by Barnard.³⁰ The reactions were carried out in carbon tetrachloride at -25° C. Sulfonic anhydrides and thiol-sulfonates were the major products. Disulfones were also formed in small quantities. His results are summarized in Table III. Dimethyl and dibenzyl disulfide were atypical. Dibenzyl disulfide reacted by giving carbon-sulfur bond cleavage. Dimethyl disulfide gave abnormal product ratios. He proposed that the reaction proceeds according to the following scheme:

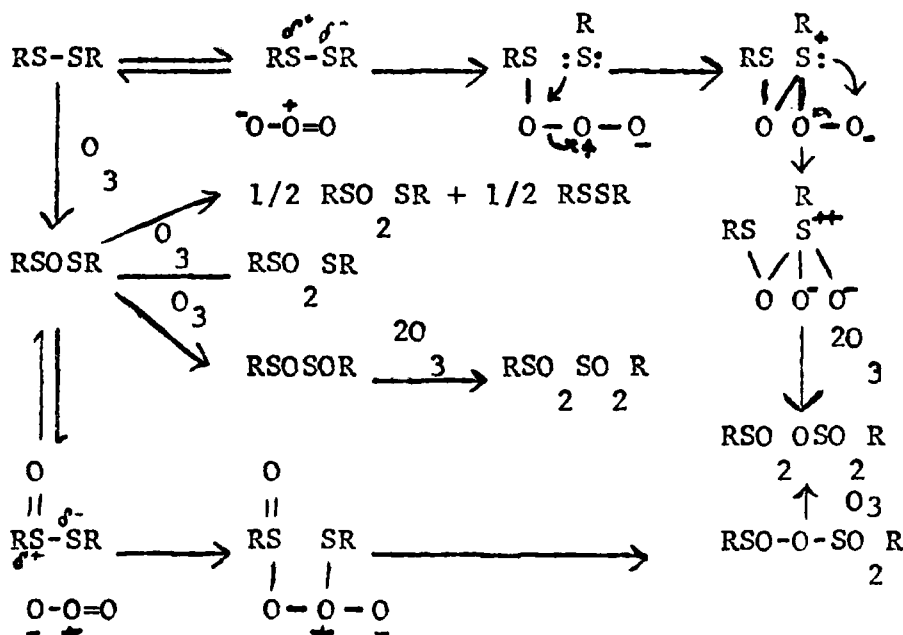


TABLE III
Products of Ozonolysis of Disulfides 30

R	O ₃ Absorbed (moles)	Sulfonic Anhydride (%)	Thiol- sulfonate (%)
Ph	2.6	90	6
p-Cl·C ₆ H ₄	2.9	84	10
n-Bu	2.6	80	10
Me	2.0	39	50
CH ₂ Ph	5	--	--

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Horner et al have ozonized some of the same disulfides as Barnard. The reactions were done in ethyl chloride and they obtained different results. Horner obtained an 82% yield of benzyl phenylmethanethiolsulfonate from dibenzyl disulfide. Diphenyl disulfide also gave its thiolsulfonate, but only in 23% yield. The product from ozonation of di-n-butyl disulfide decomposed and was not identified.

OBJECTIVE OF THIS RESEARCH PROJECT

In light of the preceding discussion, it can be seen that the reactions of ozone with methanethiol and dimethyl disulfide are environmentally important. These reactions may be involved in the fate of these organics in the air and may be the basis for odor control

of Kraft pulp mills. Previous work has shown that ozonation of thiols and disulfides does occur, but differing results have been obtained under different reaction conditions. Except for the work of Kirchner,³² Kastenhuber and Biering³² the earlier studies were done under conditions dissimilar to those of the environment. In the natural environment, oxidation can take place in the gas phase or in water droplets. The work of Akamatsu³ on odor control in Kraft pulp mills is not complete. Ozone can be added to either the stack gases or the black liquor, a very basic aqueous solution.

The objective of this research project was to investigate the reactions of ozone with methanethiol and dimethyl disulfide in aqueous solution. The reaction products, yields and stoichiometry were to be determined. Long range plans include kinetic studies in aqueous solution and chemical and kinetic studies in the gas phase.

CHAPTER II

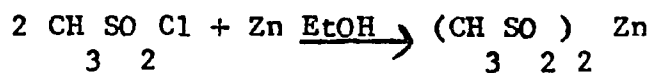
EXPERIMENTAL

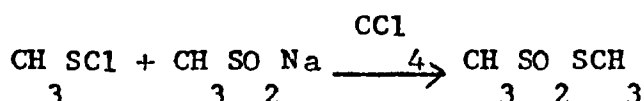
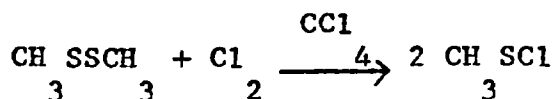
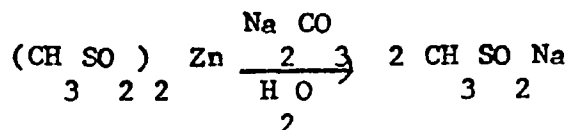
CHEMICALS

Chemically pure methanethiol was obtained from Air Products and Chemicals Incorporated. It was shown to be pure by gas liquid chromatography and was used without further purification. The dimethyl disulfide was supplied by Eastman Organic Chemicals. It was purified by swirling with Darco G - 60 activated carbon, filtering and distilling from P O through a 40 cm Vigreux column. Gas chromatographic^{2 5} analysis indicated that the disulfide was pure. Practical grade methanesulfonic acid was purchased from J. T. Baker Chemical Company and distilled twice before use. The methanesulfonyl chloride used in the identification of the methanesulfonic acid was Baker grade from the J. T. Baker Chemical Company. Methylene chloride which was used to extract some of the reaction products from the reaction mixtures, was purchased from three companies: Matheson Coleman and Bell (reagent grade), Mallinckrodt (SpectrAR), and J. T. Baker (Baker Analyzed Reagent Spectrophotometric Grade). The oxygen and nitrogen used were purchased from Liquid Air Incorporated. Two of the minor products were synthesized to aid in their identification.

Methyl Methanethiolsulfonate

This compound was prepared according to the following scheme.

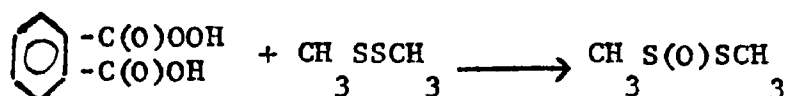




To an ethanol solution of methanesulfonyl chloride an equal molar portion of zinc dust was added slowly. The mixture was refluxed for one hour. The excess zinc was filtered off and the ethanol was evaporated. The zinc salt was stirred in an aqueous sodium carbonate solution and the resulting zinc carbonate was filtered off. Evaporating the water gave the sodium methanesulfinate. Methanesulfonyl chloride was prepared by adding dimethyl disulfide to a CCl_4 solution of chlorine at 0°C . A CCl_4 solution of sodium methanesulfinate was added to the CCl_4 solution of methanesulfonyl chloride and refluxed for six hours to yield the product. The product was isolated by vacuum distillation. The infrared spectrum of the product (see Table VI) was the same as spectrum given in the Sadtler Standard Spectra.

Methyl Methanethiolsulfinate

This compound was prepared by peracid oxidation of dimethyl disulfide.



The perphthalic acid was prepared by hydrogen peroxide oxidation of phthalic anhydride as described in Reagents for Organic Synthesis.

To 3.4 ml (0.038 mole) of dimethyl disulfide in 1000 ml of ether was added 100 ml of 0.369 M perphthalic acid in ether. After standing one

hour at room temperature, the ether solution was washed twice with 250 ml of 1% Na₂CO₃ and once with 150 ml of water. The ether was evaporated and the product was dissolved in 15 ml of petroleum ether (30 - 60°). It was then extracted six times, each with 200 ml of water. The combined aqueous extracts were extracted four times, each with 50 ml of methylene chloride. The methylene chloride was stripped off and the product was distilled under reduced pressure. The yield was only one drop. The infrared spectrum of the product (see Table VI) was consistent with the expected structure.

INSTRUMENTATION

Gas liquid chromatography was done on two instruments: a Varian Aerograph model 90-P with a thermal conductivity detector and a Varian Aerograph series 1400 with a flame ionization detector. A 10' X 1/4" 5% G.C. SE-30 on Chromosorb G column was employed with the model 90-P. A 5" X 1/8" 3% G.C. SE-30 on Varoport-30, and a 6' X 1/8" 2% OV-1 on Gas Chrom Q column were used with the series 1400 chromatograph.

All mass spectra were obtained from a Varian Mat G.C./M.S. System Mat 111. All samples were introduced into the mass spectrometer through the gas chromatograph which contained a 10' X 1/8" 5% G.C. SE-30 on AW DMCS Chromosorb W column.

A Varian HA-60 Analytical NMR Spectrometer was used to obtain all the nuclear magnetic resonance spectra. All spectra were obtained in methylene chloride and the solvent was used for the lock signal.

All infrared spectra were obtained on a Beckman IR-33 spectrophotometer. The spectra were all of neat samples and were obtained

using thin films between sodium chloride plates.

Potentiometric titrations of acids were performed using a Beckman Century SS pH meter. Calibration to a pH of 4.00 was done using a 1.00% solution of potassium hydrogen phthalate.

Ozone was generated from an oxygen feed by a Welsback T-408 electric discharge ozonator. Ozone-nitrogen streams were obtained by absorbing the ozone on a silica gel column cooled to -78° C. and later blowing off the ozone by removing the column from the cold bath and passing nitrogen through it.

Qualitative observations of reaction rates were made using an Aminco-Morrow Stopped Flow apparatus.

ANALYTICAL METHODS

Ozone

The standard iodide-thiosulfate method was used to determine ozone concentrations. Although there recently has been some debate concerning the stoichiometry of the ozone-iodide reaction,³⁶⁻³⁸ the following is generally accepted.



The iodine was determined by titration with sodium thiosulfate as shown.



A 100.0 ml aliquot of an aqueous ozone solution was pipetted into a potassium iodide solution. The solution was acidified with 5 ml of 6M HCl and titrated with 0.005 M sodium thiosulfate. Just before the end point, 3 ml of a 0.3% starch solution was added and the titration

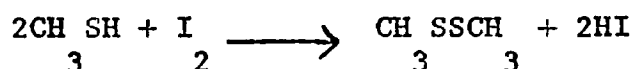
was continued to the starch end point.

The potassium iodide used was Baker Analyzed and Millinckrodt AR; both contained less than 0.0003% iodate. Baker Analyzed sodium thiosulfate pentahydrate was used. The crystals were used as a primary standard after determining that the values obtained based on the weight of the crystals agreed within 1.5% of those based on standardization against potassium dichromate.

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Methanethiol

Solutions of methanethiol were made by passing the thiol into water and then cooling to the reaction temperature (0° C). An accurately measured aliquot of the thiol solution was transferred to a glass stoppered flask containing 25.00 ml of a known concentration (approximately 0.15M) iodine solution. After forty minutes, the solution was acidified with 5 ml of 6M HCl and the remaining iodine was titrated with a standard 0.1M thiosulfate solution to a starch end point. This method is based on the following reaction.



Methanesulfonic Acid

Potentiometric titrations using standard base solutions as titrant were used to determine methanesulfonic acid. The base solutions were standardized against potassium hydrogen phthalate. Ozone was found to interfere with the determination and was removed by bubbling out with nitrogen before the titration.

The methanesulfonic acid was identified by converting it to methanesulfonyl chloride using thionyl chloride. About 2 ml of the

suspected sulfonic acid was isolated from the reaction mixture by evaporating the water and refluxed with 20 ml of thionyl chloride for four and a half hours. The thionyl chloride was distilled and the reaction product was identified by coinjection gas chromatography and its mass spectrum (see Table VI).

Sulfuric Acid

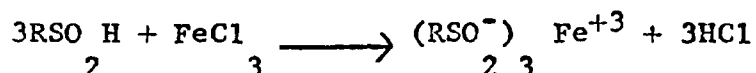
The precipitation of barium sulfate from aqueous solutions is the basis for a number of qualitative and quantitative techniques for sulfate. Qualitative tests for sulfuric acid were performed using three techniques. One, a small portion of the solution to be tested was added to a barium chloride solution; the formation of a white precipitate indicates sulfate and the absence of the precipitate indicates the absence of sulfate. For very dilute solutions the formation of a precipitate can better be detected using a spectrophotometer. Two, a small portion of the solution to be tested was used to adjust a Spectronic 20 U.V. - visible spectrophotometer to 100% transmittance and then a few crystals of barium chloride were added. A decrease in the transmittance indicates precipitation. Three, a drop of a saturated potassium permanganate solution and three drops of the solution to be tested were mixed. One drop of the mixture was placed on a filter paper which had been impregnated with barium chloride and heated at 70° -80° C. for seven to eight minutes. The filter paper was then washed with water and 1N oxalic acid. If sulfate was present, the precipitated barium sulfate would trap potassium permanganate in its crystal structure. The trapped potassium permanganated would not be washed away; a pink or purple spot indicates sulfate.

40

Methanesulfinic Acid

41

Ferric ions precipitate sulfinic acids as shown.



Qualitative tests for sulfinic acids were carried out by adding 1 ml of 15% $\underset{3}{\text{FeCl}}$ to 2 ml of the solution to be tested.

OZONATION OF METHANETHIOL AND DIMETHYL DISULFIDE

Ozone-Gas Streams

An ozone-oxygen stream was passed into a 0° C methanethiol solution in a gas washing bottle equipped with a glass frit. It was found that large quantities of the thiol were removed with the exit gases. Cold traps cooled to -78° C and precipitation as its silver mercaptide were used to trap the escaping thiol. The exit gases from the reaction vessel were passed through an aqueous potassium iodide solution. When ozone passed through the solution as indicated by the formation of iodine, the reaction was stopped and the aqueous solution was extracted with several portions of methylene chloride. The extracts were concentrated by evaporation of the solvent and analyzed by g.l.c. and NMR. The aqueous layer was analyzed for sulfuric, sulfinic and methanesulfonic acids.

Dimethyl disulfide was ozonized by a similar method. Because the disulfide is not very soluble in water, some of the reactions were run on suspensions of the disulfide in water. Methylene chloride extracts of the resulting solutions were analyzed by g.l.c. Evaporation of the methylene chloride yielded a compound that was distilled under reduced pressure. The compound was characterized by NMR and IR spectra. The

aqueous portion was analyzed for sulfuric, sulfinic and methanesulfonic acids.

Ozone Solutions

During the ozonations using gas streams to introduce ozone, it was found that large quantities of methanethiol or dimethyl disulfide were lost in the gas streams. Therefore, quantitative results were obtained by adding solutions of the thiol or disulfide to an ozone solution.

About 4000 g of water were weighed, cooled to 0° C, and used to make an ozone solution. Both ozone-oxygen and ozone-nitrogen streams were used to make the solution. Methanethiol solutions prepared as previously described were made while the ozone solution was being prepared. Because of the instability of the solutions, the following procedure was carried out as rapidly as possible. An aliquot of the methanethiol solution was added to an iodine solution for analysis of the thiol. The initial ozone determination was started by adding an aliquot of the ozone solution to a dilute potassium iodide solution. Then an aliquot of the thiol was added to the ozone solution and stirred slowly for approximately a minute to insure complete reaction and mixing. Two aliquots of the reaction mixture were then added to potassium iodide solutions for determination of the final ozone concentration. In the initial experiments an aliquot of the reaction mixture was then used to determine the methanesulfonic acid. For reasons described later, it was necessary to remove the residual ozone before titrating. The ozone was removed by bubbling with nitrogen until a small sample of the reaction mixture would give no

color when added to a potassium iodide-starch solution. The quantitative work on dimethyl disulfide was done using the same procedure. The disulfide was used as a primary standard in making up solutions and was not analyzed.

CHAPTER III

RESULTS

The reactions of ozone with methanethiol and dimethyl disulfide were studied by two methods. Ozone-gas streams were added to aqueous solutions of the thiol or disulfide to obtain qualitative data. Quantitative data was obtained by addition of solutions of the organics to ozone solutions.

METHANETHIOL

When an ozone oxygen stream was passed into a 0° C aqueous solution of methanethiol, a rapid reaction occurred. Quantitative analysis was not possible using this system because large amounts of methanethiol were carried away in the oxygen stream. Cold traps were not effective in trapping all of the escaping thiol, but silver ions were found to precipitate all of it. Since the determination of the amount of thiol precipitated was not practical, an indirect method of analysis was attempted. A known amount of silver nitrate was used to trap the escaping thiol and the excess silver was titrated with potassium thiocyanate. Unfortunately, absorption of silver ions on the precipitated mercaptide obscured the end point. Therefore, the reaction was usually stopped when the thiol concentration was so low that some of the ozone passed through the solution without reacting.

A strongly acidic solution resulted from the reaction; however, qualitative tests for sulfuric and methanesulfinic acids were negative.

before it was titrated, a single inflection point having a value equal to that of the second inflection in the original solution was obtained. It was found that if the excess ozone was removed before titrating, only one inflection point was obtained and it corresponded to near quantitative conversion of the thiol to sulfonic acid. For reasons given in Chapter IV the yield of sulfonic acid was taken at the first inflection point or from a titration in which the excess ozone had been removed. The yields obtained are given in Table IV.

TABLE IV

Run	Moles of O ₃ Consumed	Moles of CH ₃ SH Added	O ₃ / CH ₃ SH	Moles of CH ₃ SO ₃ H Produced	% Yield
1	1.24 X 10 ⁻³	6.30 X 10 ⁻⁴	1.97	6.86 X 10 ⁻⁴	101
2	1.18 X 10 ⁻³	6.84 X 10 ⁻⁴	1.75	6.87 X 10 ⁻⁴	100
3	#9.7 X 10 ⁻⁴	5.58 X 10 ⁻⁴	1.74	5.54 X 10 ⁻⁴	99.3
4	#4.3 X 10 ⁻⁴	2.38 X 10 ⁻⁴	1.80	2.74 X 10 ⁻⁴	115
5	1.03 X 10 ⁻³	5.97 X 10 ⁻⁴	1.73	7.40 X 10 ⁻⁴	124
6	9.6 X 10 ⁻⁴	5.73 X 10 ⁻⁴	1.68	-----	---
7	#-----	1.65 X 10 ⁻⁴	----	1.71 X 10 ⁻⁴	*103
8	#1.82 X 10 ⁻³	1.03 X 10 ⁻³	1.76	1.02 X 10 ⁻³ 1.09 X 10 ⁻³	98.5 *106

- Solution made with ozone-nitrogen stream.

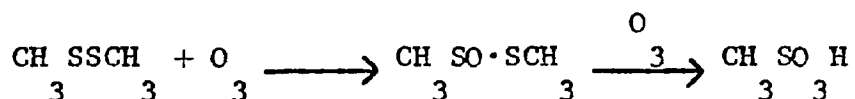
* - Yield determined after removal of excess ozone.

The rate of the reaction appeared to be very fast. Observation of the decrease in ozone was followed spectrophotometrically at 285 nm using the stopped flow apparatus. At initial thiol concentrations of 7×10^{-5} M and ozone concentrations of 3×10^{-4} M the reaction was

over in about 0.1 seconds.

DIMETHYL DISULFIDE

When an aqueous solution of dimethyl disulfide was ozonized by passing an ozone-oxygen stream into the solution, the major product formed was methanesulfonic acid. The acid was identified by converting it to methanesulfonyl chloride and identified as the sulfonyl chloride by coinjection gas chromatography and its mass spectrum (see Table VI). Methyl methanethiolsulfinate was observed to form in high yield during the beginning of the reaction. In one experiment 0.0056 moles of ozone was added to 0.011 moles of dimethyl disulfide dissolved in two liters of water. The only product detected by NMR spectra of a methylene chloride extract was methyl methanethiolsulfinate. The final pH of the reaction mixture was 5.3. In some runs a small amount of methyl methanethiolsulfonate was also formed. No sulfinic acids were detected. This is summarized below.



The stoichiometry and yields found for the disulfide reaction are given in Table V. All titrations of the sulfonic acids were performed after the removal of excess ozone from the solution.

The rate of this reaction appeared to be slower than that of the thiol. At initial concentrations of $1 \times 10^{-4} \text{ M}$ $\begin{array}{c} \text{CH SSCH} \\ 3 \quad 3 \end{array}$ and $6 \times 10^{-4} \text{ M}$ $\begin{array}{c} \text{O} \\ 3 \end{array}$ the reaction was observed to be complete in about one half minute.

Some of the qualitative experiments described in this section were performed by Steve Jarrard.

TABLE V

Run	Moles of O ₃ Consumed	Moles of CH ₃ SSCH ₃ Added	O ₃ / CH ₃ SSCH ₃	Moles of CH ₃ SOH ₃ Produced	% Yield
1	*2.24 X 10 ⁻³	5.63 X 10 ⁻⁴	3.97	1.16 X 10 ⁻³	103
2	*2.17 X 10 ⁻³	5.63 X 10 ⁻⁴	3.84	1.13 X 10 ⁻³	100
3	2.68 X 10 ⁻³	5.63 X 10 ⁻⁴	4.77	1.10 X 10 ⁻³	98.1
4	2.15 X 10 ⁻³	5.63 X 10 ⁻⁴	3.82	1.04 X 10 ⁻³	92.2
5	2.21 X 10 ⁻³	5.63 X 10 ⁻⁴	3.92	9.37 X 10 ⁻⁴	83.2
6	1.90 X 10 ⁻³	5.63 X 10 ⁻⁴	3.38	1.04 X 10 ⁻³	92.2

* - solution made with an ozone-oxygen stream.

TABLE VI

Spectra of Some Organic Sulfur Compounds

Methanesulfonyl Chloride

Mass Spectrum

m/e ⁻	assignment
116	parent + 2
114	parent CH ₃ SOCl ⁺
99	SOCl ⁺
79	CH ₂ SO ⁺
64	SO ⁺
48	CH ₃ SH ⁺
47	CH ₃ S ⁺
46	CH ₂ =S ⁺
45	CH=S ⁺
15	CH ₃ ⁺

Dimethyl Disulfide

Mass Spectrum

m/e ⁻	assignment
98	parent + 4
96	parent + 2
94	parent CH ₃ SSCH ₃ ⁺
79	CH ₃ SS ⁺
48	CH ₃ SH ⁺
47	CH ₃ S ⁺
46	CH ₂ =S ⁺
45	CH=S ⁺
15	CH ₃ ⁺

NMR

Singlet 2.25δ

Methyl Methanethiolsulfonate

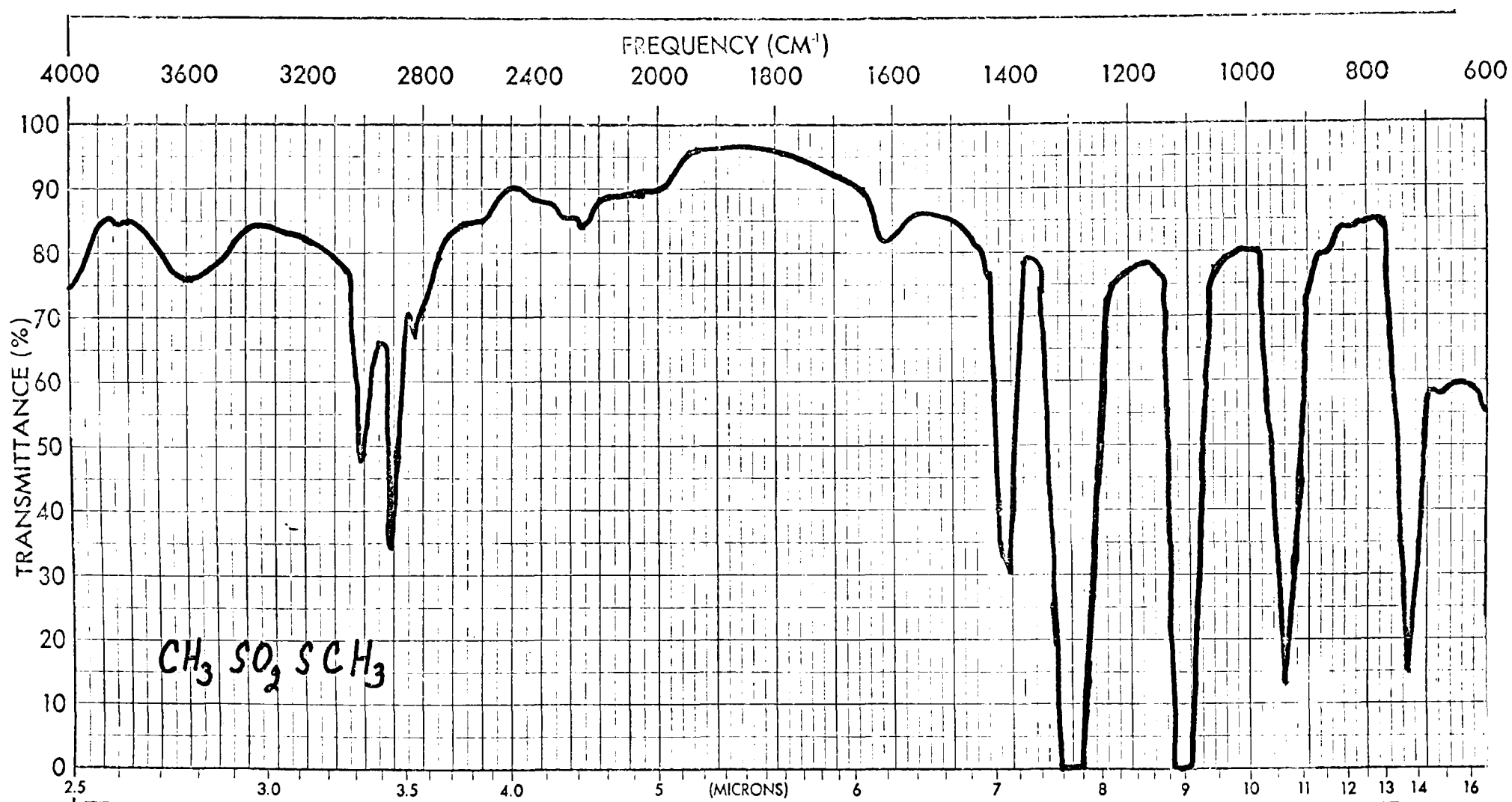
Mass Spectrum

m/e ⁻	assignment
128	parent + 2
126	parent CH SO SCH + 3 2 3
94	CH S O ⁺ 2 2
81	
79	CH SO + 3 2
64	SO + 2
63	CH S=O ⁺ 3
62	CH =S-O ⁺ 2
48	CH SH ⁺ 3
47	CH S ⁺ 3
46	CH =S ⁺ 2
45	CH=S ⁺
15	CH + 3

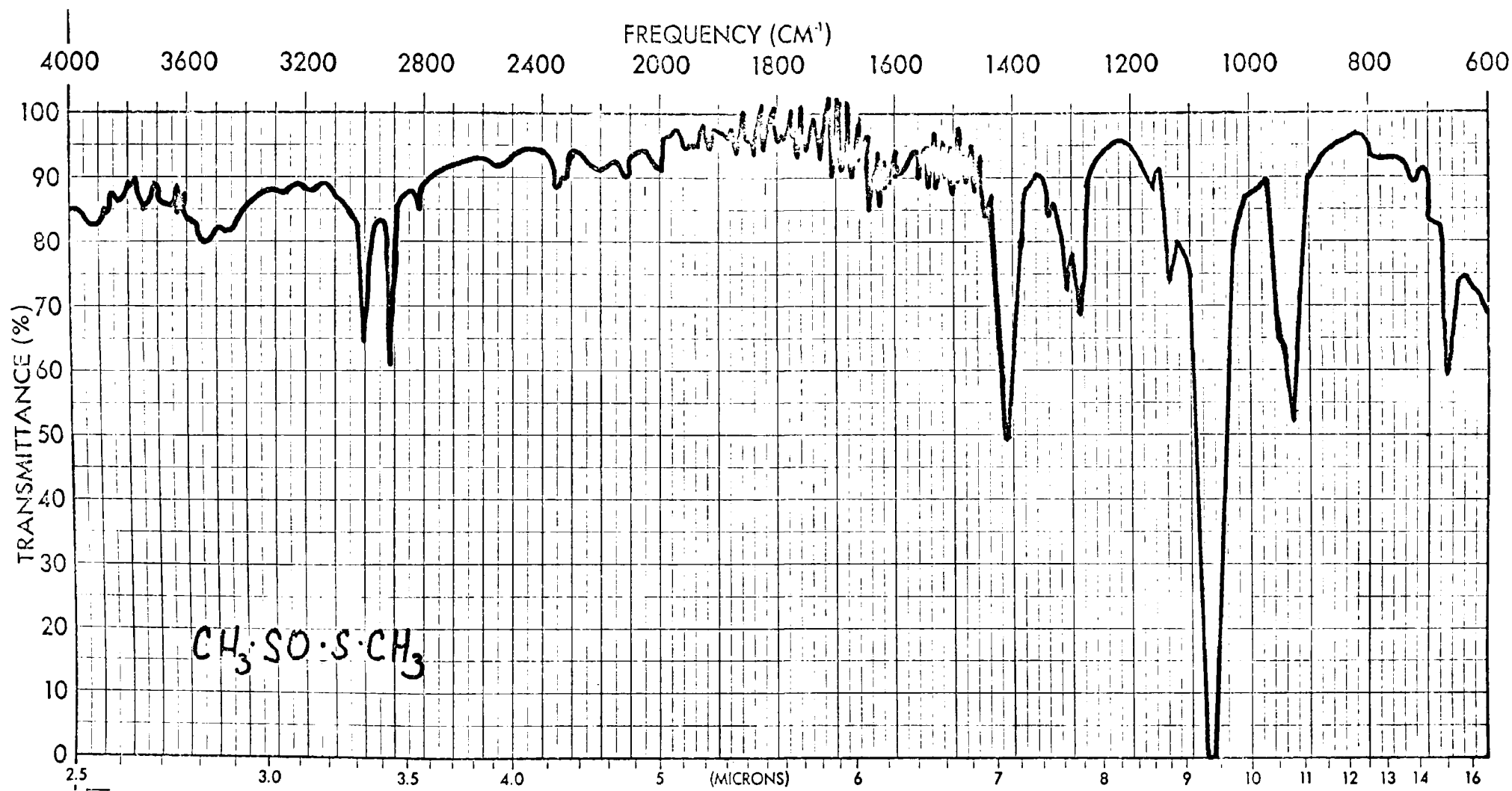
NMRSinglet 2.5 δ Singlet 3.1 δ

Methyl Methanethiolsulfinate

NMRSinglet 2.4 δ Singlet 2.7 δ



SPECTRUM NO. 1



CHAPTER IV

DISCUSSION

METHANETHIOL

Errors

Any quantitative measurement is subject to some error. The results given in Table IV exhibit some random error. The stoichiometry from run #1 and the yield from run #5 are more than two standard deviations from the mean and, therefore, have been dropped from the respective calculations. Doing this one obtains a stoichiometry of 1.74 ± 0.04 and a yield of $103\% \pm 6\%$. The limits of error given are one standard deviation.

This treatment of random errors does not include any systematic errors. Although efforts were made to reduce any error of this type, several sources of possible error exist. The solutions used in this study were all unstable with respect to loss of the solute into the air. In order to minimize this type of error, initial concentrations were measured, the reaction was carried out and final concentrations were measured as rapidly as possible. Ozone is also known to undergo thermal decomposition, but this is a slow reaction compared to the time between samplings (about one minute).

Because of the limited solubility of ozone in water, the solutions used were very dilute. Final ozone concentrations were as low as 3×10^{-5} M, but generally were an order of magnitude larger. Initial ozone concentrations were as high as 1×10^{-3} M. The sulfonic acid

concentrations ranged from 5×10^{-5} to 3×10^{-4} M. At these concentrations, end points were not extremely sharp. This was particularly a problem in the sulfonic acid determinations. The steep portion of the titration curve generally occurred in 1/4 to 1/2 milliliter. In titrations of about four milliliters, an end point error of 1/2 milliliter is very significant. However, the end point can be estimated much more accurately than 1/2 milliliter from the titration curve.

Scientific Implications

The reaction of ozone with methanthiol has been shown to produce methanesulfonic acid and eventually sulfuric acid. The conversion of the sulfonic acid to sulfuric acid is very slow and, for practical purposes, the reaction stops at the sulfonic acid. When insufficient ozone was added directly to a solution of the thiol, dimethyl disulfide, methyl methanethiolsulfinate and methyl methanethiolsulfonate were also detected. The quantitative results seem to indicate that these products were not formed in the reactions carried out by mixing solutions. This is reasonable because, in the presence of excess ozone, any disulfide and thiolsulfinate would have been oxidized further. However, Barnard³⁰ has reported that thiolsulfonates are resistant to ozonation. No minor products were detected from these reactions; but at such low concentrations, they may have escaped detection.

These results are not surprising and are similar to the results reported for other thiols. A thiolsulfinate, however, has not previously been reported as a minor product or intermediate in the ozonation of a thiol. The reason for this probably involved a difference in the mechanism of disulfide ozonations in aqueous and organic solvents.

Previous workers using organic solvents have not found thiolsulfinates to be products or long-lived intermediates in the ozone-disulfide reaction. This evidence, although it seems to indicate that the thiolsulfinate is formed from the disulfide, is not sufficient for proof.

Because thiols are readily converted to disulfides, it might be expected that the ozonation of thiols proceeds via disulfides. This does not appear to be the case for methanethiol. If the reaction involved the disulfide, the overall rate would be controlled by the rate of ozonation of the disulfide or the rate of conversion of the thiol to the disulfide, whichever is slower. But methanethiol was observed to react faster than dimethyl disulfide. Therefore, it must be concluded that disulfide production is only a minor side reaction.

The stoichiometry found is similar to those obtained by Barnard³⁰ (1.6 O₃ :SH) and Erickson³¹ (1.6 O₃ :iso-BuSH) when the ozone-oxygen streams were passed into the thiol solutions. Using an ozone-nitrogen stream, Erickson found a stoichiometry of 3.3:1. This behavior was not observed using the experimental technique employed in this study. This may have been due to the experimental technique, rather than a difference in reaction mechanisms between the two thiols. The solubility of oxygen in water at 0° C is about 0.04925 cc/cc (2.2 X 10⁻³ M); enough to significantly affect the stoichiometry if it reacts. Why then do the two nitrogen systems give different results? It seems likely that in the isobutanethiol/ozone-nitrogen system the nitrogen stream will purge the system of any oxygen formed in the reaction. In the methanethiol/ozone-nitrogen system there is no gas stream to purge the reaction mixture of oxygen.

The titration curves in Figure II show the double hump pattern obtained when an aliquot of the reaction mixture is titrated in the presence of ozone and the pattern which is obtained if the ozone is removed.

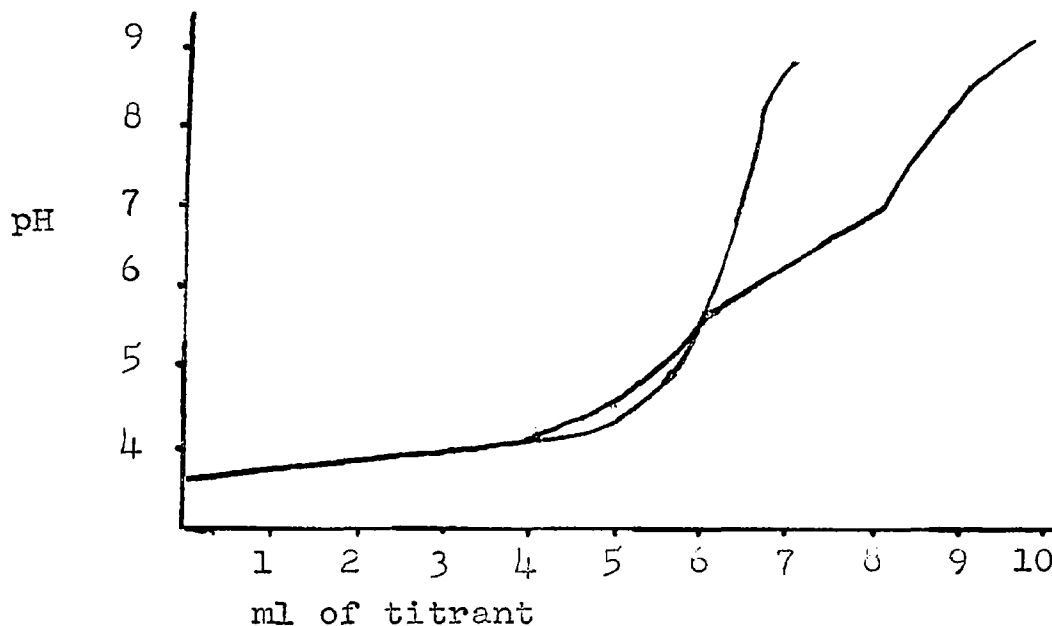


FIGURE II

Titration Curves

This pattern, although puzzling at first, proved to have a simple cause. In basic solutions, ozone will react with methane sulfonic acid to produce sulfuric acid much faster than in acidic solutions. In acidic solutions, the reaction proceeds very slowly. That is why letting the solution stand for several days results in a single hump pattern corresponding to the second hump in a titration with ozone present. As the equivalence point is reached during titrations with ozone present, the pH rises allowing sulfuric acid to be produced at a reasonable rate. The pH then remains relatively constant until the ozone has all reacted. Tests with methanesulfonic acid showed the same behavior as the reaction mixtures. Other tests demonstrated that sulfate was formed when ozone was added to basic solutions of

methanesulfonic acid.

Environmental Implications

The reaction product ($\text{CH}_3\text{SO}_3\text{H}$) from the ozone-methanethiol reaction is odorless, nonvolatile, and water soluble. These are all positive attributes that could be taken advantage of in designing pollution control equipment for Kraft pulp mills. Although the rate data obtained are in no way complete, it appears that the reaction is fast enough to not cause any major technological difficulties in equipment design. There are some difficulties in using aqueous phase ozonations for pollution control, however. A likely place to add ozone to a thiol-containing solution is in the black liquor. Unfortunately, the black liquor also contains many other compounds that would compete with thiols and other pollutants for ozone. Use of ozonized water in the water scrubbers for stack gases might be possible. Gas phase ozonations would also be possible, but this is outside the scope of this thesis.

The importance of this reaction in the atmosphere is hard to judge. In regions where ozone and thiols are present in the atmosphere together, some reaction no doubt takes place. However, these reactions are probably occurring in the gas phase for the most part. In plumes from pulp mills, where suspended water droplets are in high concentration, some aqueous phase reaction may occur.

The situation in the upper atmosphere is similar; if thiols and ozone are both present, some reaction probably occurs, but in the gas phase. Two things should be kept in mind when dealing with the upper atmosphere: 1) it has not been shown that thiols are present in the upper atmosphere, and 2) other pathways involving the high

energy species found there would compete for any thiol present.

DIMETHYL DISULFIDE

Errors

The mean stoichiometry and yield found were 3.95 ± 0.45 and $94.8\% \pm 7.1\%$. Eliminating runs more than two standard deviations away from the mean gives 3.89 ± 0.07 and $95.6\% \pm 4.0\%$.

This reaction was carried out using the same procedure as the thiol reaction, and the limitations of the method are the same. One additional problem was encountered, however. The time necessary for completion of the reaction was not considerably less than the time allowed for reacting. Although enough time for complete reaction was generally allowed, it is remotely possible that some reactions were stopped before completion. Longer reaction times were avoided because of the instability of the solution.

Scientific Implications

There appears to be a difference in yield of sulfonic acid between reactions run with solutions made from ozone-oxygen and ozone-nitrogen streams. Considering the limited amount of data and the large degree of scatter, it is possible that this apparent difference is not real. It is probably best to conclude that ozone will convert dimethyl disulfide to methanesulfonic acid in high yield.

Sulfonic acids have not previously been reported as the products from the reactions of disulfides with ozone, but the formation of sulfonic anhydrides was observed in nonaqueous solvents by Barnard.³⁰ Although water must be involved at some point in the reaction sequence,

the reaction does not necessarily follow the mechanism proposed by Barnard with the addition of a hydrolysis step at the end. In fact, the results of the investigation indicate that a different mechanism is in operation. In trying to elucidate the mechanism of the reaction, Barnard³⁰ conducted experiments in which insufficient ozone for complete conversion was used. Only the normal products of complete ozonation were found. In this study, however, high yields of methyl methanethiol-sulfinate were isolated when insufficient quantities of ozone were used. Apparently in water, the first step of the conversion to sulfonic acid is the oxidation of the disulfide to the thiolsulfinate. Although no sulfonic acid was formed early in the reaction, quantitative data is needed to show that another reaction pathway going through an undetected intermediate was not in operation. The small amounts of thiolsulfonate that were detected in some runs probably arose through minor side reactions. Known reactions that could possibly be the source are: 1) the disproportionation of thiolsulfinate to disulfide and thiolsulfonate, and 2) the autoxidation of thiolsulfinate. It is also possible that the thiolsulfonate is a direct ozonation product.

Environmental Implications

Because methanesulfonic acid is the major product of this reaction as well as from methanethiol, the same advantages (odorless, nonvolatile, and water soluble) in designing pollution control equipment are gained. The slower reaction rate would make removal of the disulfide more difficult.

The opportunity for reactions in the atmosphere are the same as those for the thiol.

CHAPTER V

SUMMARY

The aqueous phase ozonations of methanethiol and dimethyl disulfide were studied. Both compounds were converted in high yields to methanesulfonic acid. The stoichiometries observed were 1.74 ± 0.04 moles of O_3 / mole of CH_3SH and 3.89 ± 0.07 moles of O_3 / mole CH_3SSCH_3 .

The thiol oxidation was shown not to proceed by way of a disulfide intermediate. It was also determined that the slower disulfide reaction proceeds at least in part through methyl methanethiolsulfinate.

It appears technologically feasible that ozonation could be used for odor control from Kraft pulp mills. The importance of these ozonations in the lower and upper atmosphere remains speculative.

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