

**Comparison of Chlorine Dioxide and Ozone as Oxidants for the
Degradation of Volatile Organic Compounds**

by

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ABSTRACT

The presence of hazardous volatile organic compounds (VOCs) in both indoor and outdoor air is a grave issue in environmental pollution. The exposure of these compounds may cause chronic disease or adverse effects in humans. The major sources of these toxic compounds are due to improper waste disposal by chemical manufacturers, waste stream from food processing, industrial sources, and decay of living cells. Therefore, the reduction of VOCs by oxidative reactions is the primary goal of this thesis project. Both chlorine dioxide and ozone are used to evaluate the degradation characteristics of dimethyl trisulfide, isoprene, 1-bromopropane, 2,3-butanedione, and 1,1,2-trichloroethane. Gas chromatography coupled to mass spectroscopy (GC-MS) and Fourier Transform infrared spectrometry (FTIR) were used to characterize the gas phase reaction products of these compounds.

The results show that dimethyl trisulfide and isoprene were substantially degraded into other by-products, including methane sulfonyl chloride and sulfur dioxide, during oxidation by chlorine dioxide and ozone, respectively. In contrast, 1-bromopropane, 2,3-butanedione and 1,1,2-trichloroethane have slow reaction kinetics and did not break down completely. Degradation of dimethyl trisulfide by chlorine dioxide and ozone follows the second order kinetics with half-lives of 2.2 min and 24 min, respectively. On the other hand, isoprene follows the first order reaction kinetics with rate constants of 0.4051 min^{-1} and 0.02244 min^{-1} and half-lives of 1.73 min and 32 min for degradation using ozone and chlorine dioxide, respectively.

The oxidative degradation of 1-bromopropane, dimethyl trisulfide, and 2,3-butanedione by chlorine dioxide were more efficient than their reactions with ozone. However, the degradation of isoprene and 1,1,2-trichloroethane showed a greater reactivity toward ozone compared to chlorine dioxide. Most of the reaction products of oxidative degradation such as acetone, ethanol, formic acid, and dimethyl ether are chemically benign. But there are also by-products such as methane sulfonyl chloride, sulfur dioxide, chloroform, and cyanogen bromide that require further toxicological study.

TABLE OF CONTENTS

	Page
1 INTRODUCTION.....	1
1.1 Environmental pollution.....	1
1.2 Air pollution.....	1
1.3 Selected harmful or malodorous compounds.....	3
1.3.1 1-Bromopropane.....	4
1.3.2 Dimethyl trisulfide.....	5
1.3.3 2,3-Butanedione.....	6
1.3.4 Isoprene.....	6
1.3.5 1,1,2-Trichloroethane.....	7
1.4 Ozone overview.....	7
1.4.1 Properties of ozone.....	7
1.4.2 Ozone generation method.....	7
1.4.3 Application of ozone.....	9
1.4.4 Formation of ozone by-products.....	10
1.5 Chlorine dioxide overview.....	11
1.5.1 Properties of chlorine dioxide.....	11
1.5.2 Chlorine dioxide generation method.....	11
1.5.3 The application of chlorine dioxide.....	12
1.5.4 Chlorine dioxide disinfectant by-products (DBPs).....	13
1.6 Thesis proposal.....	13

2	MATERIALS AND METHODS	15
2.1	Materials and chemical reagents	15
2.2	Production of ozone	15
2.3	Generation of chlorine dioxide gas	16
2.4	Canister cleaning system.....	18
2.5	Methods for analytical measurements.....	19
2.5.1	Sample preparation for GC-MS and FTIR analysis.....	19
2.5.2	GC-MS measurements	20
2.5.3	FTIR analysis	21
3	RESULTS AND DISCUSSIONS	23
3.1	GC-MS and FTIR analysis of air pollutants by ozone.....	23
3.1.1	Degradation of dimethyl trisulfide with chlorine dioxide.....	23
3.1.2	Degradation of dimethyl trisulfide by ozone	27
3.1.3	Degradation of 1-bromopropane with chlorine dioxide.....	31
3.1.4	Degradation of 1-bromopropane with ozone	35
3.1.5	Degradation of isoprene with chlorine dioxide.....	39
3.1.6	Degradation of isoprene with ozone	42
3.1.7	Degradation of 2,3-butanedione with chlorine dioxide	45
3.1.8	Degradation of 2,3-butanedione with ozone.....	48
3.1.9	Degradation of 1,1,2-trichloroethane with chlorine dioxide.....	51
3.1.10	Degradation of 1,1,2-trichloroethane with ozone	53
3.1.11	Degradation kinetics study of selected compounds with chlorine dioxide by FTIR analysis	56

CONCLUSION.....	60
REFERENCES	62
APPENDIX	65

LISTS OF FIGURES

	Page
Figure 1: Setup for the production of ozone from pure oxygen	16
Figure 2: Generation of chlorine dioxide gas using precursors	18
Figures 3: Comparison of FTIR spectra of treated dimethyl trisulfide by chlorine dioxide at different time interval	24
Figure 4: FTIR spectral changes of chlorine dioxide after treatment of dimethyl trisulfide samples.....	24
Figure 5: Plots showing decreasing concentration of dimethyl trisulfide and chlorine dioxide as a function of their reaction time at room temperature	25
Figure 6: GC-MS overlay chromatograms of treated and untreated dimethyl trisulfide.	27
Figure 7: Comparison of FTIR spectra of dimethyl trisulfide oxidized by ozone as a function of different reaction periods	28
Figure 8: FTIR spectral comparison of ozone peak intensity in ozone-treated dimethyl trisulfide samples	29
Figure 9: Plots showing decreasing concentration of dimethyl trisulfide and ozone as a function of their reaction time at room temperature	29
Figure 10: Overlaid GC-MS chromatograms of treated and untreated dimethyl trisulfide samples.....	31
Figure 11: Comparison of FTIR spectra of treated 1-bromopropane by chlorine dioxide gas at different time intervals.....	32
Figure 12: FTIR spectral changes of chlorine dioxide after treatment of 1-bromopropane samples.....	33

Figure 13: Plots showing decreaseing concentration of 1-bromopropane and chlorine dioxide as a function of their reaction time at room temperature.	33
Figure 14: GC-MS chromatograms of treated and untreated 1-bromopropane.	35
Figure 15: Comparison of FTIR spectra of treated 1-bromopropane by ozone at different time intervals.....	36
Figure 16: FTIR spectral comparison of ozone peak intensity in ozone-treated 1-bromopropane samples	37
Figure 17: Plots showing decreaseing concentration of 1-bromopropane and ozone as a function of their reaction time at room temperature	37
Figure 18: GC-MS overlay chromatograms of treated and untreated 1-bromopropane..	39
Figure 19: Comparison of FTIR spectra of treated isoprene by chlorine dioxide at different time intervals.....	40
Figure 20: Plots showing decreaseing concentration of isoprene and chlorine dioxide as a function of their reaction time at room temperature.	40
Figure 21: GC-MS overlay chromatograms of treated and untreated isoprene..	41
Figure 22: Comparison of FTIR spectra of isoprene oxidized by ozone at different treatment periods.....	42
Figure 23: Plots showing decreasing concentrations of isoprene and ozone as a function of their reaction time at room temperature	43
Figure 24: GC-MS overlay chromatograms of treated and untreated isoprene.	44
Figure 25: Comparison of FTIR spectra of 2,3-butanedione reacting with chlorine dioxide after different treatment periods.....	46

Figure 26: Plots showing decreasing concentration of 2,3-butanedione and chlorine dioxide as a function of their reaction time at room temperature	46
Figure 27: GC-MS overlay chromatograms of treated and untreated of 2,3-butanedione samples.....	47
Figure 28: Comparison of FTIR spectra of 2,3-butanedione reacting with ozone after different treatment periods	49
Figure 29: Plots showing decreasing concentrations of 2,3-butanedione and ozone as a function of their reaction time at room temperature	49
Figure 30: GC-MS overlay chromatograms of treated and untreated 2,3-butanedione...	50
Figure 31: Comparison of FTIR spectra of 1,1,2-trichloroethane with chlorine dioxide after different treatment periods	51
Figure 32: Plots showing decreasing concentration of 1,1,2-trichloroethane and chlorine dioxide as a function of their reaction time at room temperature	52
Figure 33: GC-MS overly chromatograms of treated and untreated 1,1,2-trichloroethane samples.....	53
Figure 34: Comparison of FTIR spectra of 1,1,2-trichloroethane oxidized by ozone after different treatment periods	54
Figure 35: Plots showing decreasing concentration of 1,1,2-trichloroethane and ozone as a function of their reaction time at room temperature.	55
Figure 36: GC-MS overlay chromatograms of treated and untreated 1,1,2-trichloroethane.	56
Figure 37: Plot of $\ln[A]/[A^\circ]$ vs Reaction Time (min) at time-dependent reaction concentration of the compounds at room temperature.....	58

Figure 38: Plot of $\ln[A]/[A^\circ]$ vs Reaction Time (min) at time-dependent reaction concentration of the compounds at room temperature..... 58

Figure 39: Plot of $1/[A]$ vs Reaction Time at time-dependent concentration of compounds at room temperature..... 59

Figure 40: The plot of $1/[A]$ vs Reaction Time (min) in time-dependent concentration of compounds at room temperature..... 59

LISTS OF TABLES

	Page
Table 1: Toxic industrial air pollution in the U.S. 2011.....	3
Table 2: Instrumental conditions of HP5890 GC/5970MSD.....	21

LISTS OF ABBREVIATIONS

VOCs- Volatile Organic Compounds

EPA- Environmental Protection Agency

NRDC- Natural Resources Defense Council

OSHA- Occupational Safety and Health Administration

NIOSH- National Institute for Occupational Safety and Health

PEL- Permissible Exposure Limit

TLV- Threshold Limit Value

AIHA- American Industrial Hygiene Association

FDA- Food and Drug Administration

UHP- Ultra High Purity

GC-MS- Gas Chromatography-Mass Spectroscopy

FTIR- Fourier Transform Infrared Spectroscopy

NIST- National Institute of Science and Technology

MCT- Mercury Cadmium Telluride

PNNL-Pacific Northwest National Library

ISTD- Internal Standard

REL- Recommended Exposure Limit

ACGIH- American Conference of Governmental Industrial Hygienists

IARC- International Agency for Research on Cancer

CHAPTER 1

1 INTRODUCTION

1.1 Environmental pollution

The presence of hazardous compounds in aquatic systems, soil, and air is a very serious issue in environmental pollution. Accumulation of chemical and pharmaceutical ingredients is often associated with inadequate environmental management in various industrial sectors. There are many harmful chemicals which have adverse effects on human health. Major sources of these chemicals are due to improper waste disposal by drug manufacturers¹, decay of living cells², and waste streams from food processing. In many cases, occurrence of these chemicals in the atmosphere and in water bodies has not been regulated yet. So, it is important to conduct research on these chemicals in the environment and provide the scientific data to government agencies to determine the need for possible regulatory actions.

1.2 Air pollution

Harmful or excessive quantities of chemical compounds such as volatile organic compounds (VOCs), particulate matters, and biological molecules are responsible for air pollution. The major classes of VOCs are alkanes, alkenes, and oxygenated compounds that are released from different sources such as industrial facilities, solvent usage, degreasers, food flavoring agents, vehicles, and biogenic emissions.³ Toxicity of these kinds of air pollutants are very acute and can cause health hazards for humans as well as the ecosystem. To control the organic vapor pollutants in the air, the United States

Environmental Protection Agency (USEPA) for ambient air quality standard proposed the concentration of nonmethane hydrocarbons content is $1.6 \times 10^{-4} \text{ kg/m}^3$ (0.24 ppm) for maximum three hours length which cannot be exceeded for more than a year.⁴ It is very important to destroy such hazardous chemicals completely from the air to ensure quality air for the living systems. There are many techniques to control air pollution such as oxidation, bio-filtration, adsorption, and absorption. The absorption method for air pollution control could be using large interfacial contact area, providing a mixture of liquid and gas phases or allowing adequate contact time between the phases.

The health of millions of Americans is affected by air pollution in everyday life. The probable health threats due to exposure to air pollution include asthma, heart disease, emphysema, and chronic obstructive pulmonary diseases (COPD). According to the statistical report from the Natural Resources Defense Council (NRDC), half of air pollution is from electricity generation. The sources of these toxic air pollutants are commonly related to electricity generation, chemical manufacturing, paper products, food and beverages, primary metals, and others (Table 1).⁵

Table 1: Toxic industrial air pollution in the U.S. 2011

Sector	Toxic Air Pollution (pounds/ year)	% of National Air Pollution
Electricity generation	381,740,601	49%
Chemicals	112,870,057	15%
Paper products	103,249,010	13%
Food and beverages	26,908,977	3%
Primary metals	24,923,246	3%
Other	121,888,815	16%
Total	771,580,707	100%

1.3 Selected harmful or malodorous compounds

There are many toxic volatile organic compounds with or without unpleasant smells which contribute to air pollution. The presence of these compounds in the air may cause chronic disease in humans, as well as discomfort in their olfactory senses.

Dimethyl trisulfide, dimethyl disulfide, diamines, carbonyl compounds, thiols, and mercaptans are examples of some odor-causing compounds in air. Quality of air and health of the residents living near these sources can be affected by the presence of these odorous compounds.⁶ Emission sources of these malodorous compounds in the atmosphere include intensive livestock production, waste disposal from chemical

industries, water treatment plants, food production, storage and transport of chemicals from industries. Intensive porcine farming is a source of many odorous compounds, such as aldehydes, ketones, phenols, amines, and volatile reduced sulfur compounds.⁷ Based on the literature review, we have chosen odorous compounds including 2,3-butanedione, 1-bromopropane, 1,1,2-trichloroethane, dimethyl trisulfide, and isoprene. The use of 2,3-butanedione as food flavoring additives is common in popcorn manufacturing and the production of e-liquids for electronic cigarettes. Both 1-bromopropane and 1,1,2-trichloroethane are used as solvents in cleaning products and degreasing agents in many automotive products. Dimethyl trisulfide is produced as a by-product of the decomposition of organic waste, animal carcasses, and waste food products. Isoprene has been selected for the analysis because of its widespread emission from biogenic sources in many areas.

1.3.1 1-Bromopropane

1-Bromopropane is an organo-bromine compound with a characteristic hydrocarbon odor. It was first introduced as a solvent for fats and waxes, but was later used in dry cleaning, degreasing, and manufacture of adhesive and aerosol solvents. Workers exposed to 1-bromopropane showed some clinical signs and symptoms such as reduced perception abilities, decreased sensation of vibration, paresthesia in the lower extremities, stumbling, difficulty of walking, headache, neurobehavioral abnormalities, and memory dysfunctions.⁸ In the European Union, it has been reported as a reproductive toxicant and was reasonably anticipated as a human carcinogen in 2013.⁹

1-Bromopropane has been listed as a toxic chemical under Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986, and in

Section 6607 of the Pollution Prevention Act (PPA) of 1990 by the Environmental Protection Agency.¹⁰ The amount of 1-bromopropane in ambient air is not routinely monitored because it is not required to be reported (EPA 2005). Permissible Exposure Limit (PEL) for 1-bromopropane has not been specified by Occupational Safety and Health Administration (OSHA), but the time-weighted average (TWA) limit of 1-bromopropane is 25 ppm for 8 hours according to the EPA.¹¹

1.3.2 Dimethyl trisulfide

Dimethyl trisulfide (DMTS) is an odor-causing volatile organic compound used in different food products, such as whiskey, beer, wine, and cognac as a flavor enhancer.¹² It is also found in volatiles emitted from cooked onions, leeks, and other *allium* species, like broccoli and cabbage, as well as from Limburger cheese. It is a decomposition product from bacterial decomposition, which is encountered in the early stages of decomposition of human cadavers or animal carcasses. The use of dimethyl disulfide in the presence of catalysts also synthesizes DMTS.¹³

DMTS has been reported as a major taste and odor-causing compound in China. It is generated mainly by *Microcystis* and *Oscillatoria* and other decaying organisms. The decaying process influences the pungent odor of water.¹⁴ DMTS is responsible for the malodor from the fungating lesions of cancer wounds that form by breakage of cancer cells, which grow under the skin.²⁶ Removal of DMTS from drinking water can be achieved using potassium permanganate as an oxidizing agent.¹⁴ .

1.3.3 2,3-Butanedione

2,3-Butanedione or diacetyl is a yellowish-green organic compound with a buttery flavor which occurs naturally as well as in manufactured food additives. It is used in different food products such as butter flavored microwave popcorn, candy, baked goods, and cake mixes. OSHA suggests this as a hazardous compound because of its health effects. Exposure to 2,3-butanedione may cause lung disease and bronchitis¹⁰. The Centers for Disease Control's National Institute for Occupational Safety and Health (NIOSH) has set up workplace exposure limit at 10 microwave popcorn plants, as well as animal studies to investigate the effects of 2,3-butanedione. The recommended exposure limits (RELs) and ACGIH threshold limit value of this compound are 0.005 ppm and 0.01 ppm respectively. Health effects such as irritation of eyes, nose, throat, skin, and the respiratory system have been reported for this compound.

1.3.4 Isoprene

Isoprene is a colorless volatile liquid emitted from trees, including oaks, poplars, eucalyptus, and some legumes. Reaction of isoprene with hydroxyl radicals in the atmosphere increases the formation of ozone, which affects the quality of air.¹⁵ Isoprene is also capable of causing aerosol formation in the air which affects visibility.¹⁶ Exposure to this compound may have harmful effects such as irritation of the eyes, the skin, and the respiratory tract. The substance may have effects on the central nervous system, resulting in respiratory depression. Workers are exposed to isoprene in the manufacturing of various elastomers. Isoprene has no Permissible Exposure Limit (PEL) or Threshold Limit Value (TLV). It does have an American Industrial Hygiene Association (AIHA) workplace environmental exposure level of 50

ppm.¹⁷ The International Agency for Research on Cancer (IARC) has classified the isoprene as a 2b human carcinogen.¹⁶

1.3.5 1,1,2-Trichloroethane

1,1,2-Trichloroethane is a colorless, sweet-smelling organochlorine compound. It is a non-flammable organic solvent and is insoluble in water. It is widely distributed in ground water because of its improper disposal and accidental release. Very low levels of 1,1,2-trichloroethane have been detected in ambient air at the levels of around 0.01 to 0.05 parts per billion (ppb) due to its widespread use as chemical intermediates, degreasing agents, and paint removers. It has been classified as a possible human carcinogen and has adverse effects on the kidney, the liver, and the nervous and immune systems.¹⁸ An animal study reported liver tumors and adrenal tumors in mice, but no tumors in rats, exposed to 1,1,2-trichloroethane by gavage (experimentally placing the chemical in the stomach).¹⁹

1.4 Ozone overview

1.4.1 Properties of ozone

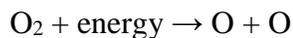
Ozone is a colorless gas with a distinctively pungent smell. It can be converted back to oxygen because of its short atmospheric life time. The solubility of ozone is 109 mg/l at 25°C, which is 13 times greater than oxygen. It has high reactivity in both the gas and liquid phases.

1.4.2 Ozone generation method

There are many ways to produce ozone (O₃) in laboratories or commercially. The common ozone generation techniques are:

- (i) Electrical discharge or corona discharge
- (ii) Electrolysis of an acid
- (iii) Photochemical reaction of oxygen via UV irradiation, and
- (iv) Radiochemical production. Certain isotopes such as ^{137}Cs , ^{60}Co or ^{90}Sr are used for the excitation of circulating air in a water-cooled closed system, but this procedure is rarely used because of radioactive contamination.²⁰

Corona discharge is the safest, most effective, economical, and dependable controlled method for the generation of ozone. Applying a high voltage across electrodes splits the oxygen molecules into oxygen atoms, which then combine with diatomic oxygen to form ozone.



Corona discharge is an enclosed ozone generation method in a controlled environment. The concentration of ozone depends on power input and flow rate of oxygen. Increasing the power input will increase the concentration of ozone, whereas increasing the flow rate of oxygen will lower the concentration.²¹

The advantages and disadvantage of corona discharge method:

- (i) Corona discharge method can produce higher concentrations of ozone than other methods like ultraviolet radiation and electrolysis.
- (ii) This method is less expensive for long-term operation compared to electrolytic and radiochemical process.
- (iii) It is easy to maintain

Disadvantage of Corona Discharge Method:

- (i) This method requires pure oxygen gas whereas other methods can use oxygen in the air for generation of ozone.
- (ii) It produces heat during operation.
- (iii) The cost of primary investment is high.

1.4.3 Application of ozone

Ozone is a very powerful oxidizing agent in breaking down large organic pollutants by oxidation reaction. The application of ozone was first discovered in 1840 (Schonbein), for utilization as a disinfectant agent in the production of portable water in France in early 1900.²² It can be used to remove odor, change color and taste in a short reaction time. The National Secondary Regulation recommended that ozone can be effective for the treatment of water for taste and odor problems, especially when the water is free from radical scavengers.²³ The application of ozone in food processing is increasing rapidly because of its anti-microbial properties. The Food and Drug Administration (FDA) approved ozone use in food processing, food storage, and for the sterilization of bottled water. This FDA approval enhanced the application of ozone in applications ranging from washing to recycling of poultry wash water to seafood sterilization. Ozone has a relatively short half-life and can be easily neutralized by reacting with oxygen. The use of ozone is more effective than other disinfectants because of its application in both gas and liquid phases for killing a large number of microorganisms in food, with no residue left.²⁴ Though there are restrictions for workplace ozone exposure by OSHA, the proliferation of ozone application in the destruction of undesirable chemical vapors has continued because of its degradation efficiency and the relative ease of ozone conversion into diatomic oxygen. The reaction

rate of ozone as an oxidant is very high with few harmful reaction by-products and the oxidation of ozone produces oxygen at the end of the reaction.²⁵ Some of the specific applications of ozone are:

- Control of taste and odor in foods and beverages
- Wastewater treatment
- Killing germs
- Elimination of synthetic organic compounds
- BOD and COD enhancer
- Fungicides, pesticides, and algicides
- Decolorizing agents
- Miscellaneous uses, such as detoxifier, flocculant aid, precursors reduction.

1.4.4 Formation of ozone by-products

The advantage of using ozone is its ability to avoid formation of harmful by-products like chlorinated organic compounds. Chlorine can produce trihalomethanes (THMs) in wastewater treatment, which has carcinogenic effects on human health. Oxidation of organic compounds by ozone usually forms carbon dioxide, aldehydes, ketones, and carboxylic acids, which are less harmful than halogenated compounds. The main concern in wastewater treatment by ozone is the formation of bromate for bromide-containing water.²⁶ Iodate is the main by-product during ozonating of iodide-containing water, which is considered less problematic because of its transformation capacity to iodide endogenically.²⁶

1.5 Chlorine dioxide overview

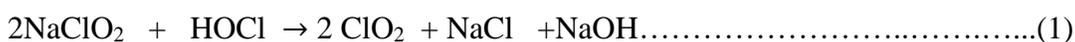
1.5.1 Properties of chlorine dioxide

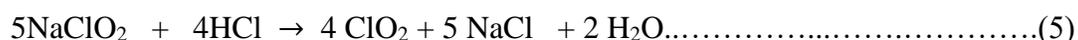
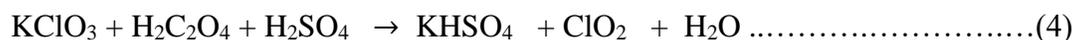
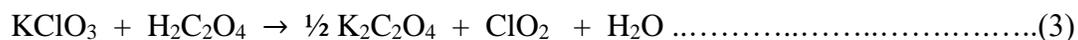
Chlorine dioxide is a yellowish-green volatile compound. It is a neutral chlorine compound with an acrid odor. The selective oxidative function of chlorine dioxide has unique one electron transfer ability to form chlorite ions upon reduction.² The solubility of chlorine dioxide is 8 g/L, which is 10 times greater than chlorine. Chlorine dioxide remains dissolved in water instead of undergoing hydrolysis.²⁷ The reactivity of chlorine dioxide is tremendous even in diluted solutions.

1.5.2 Chlorine dioxide generation method

Chlorine dioxide (ClO₂) is a highly volatile oxidative agent and potentially explosive at high concentrations. As ClO₂ is highly reactive and potentially explosive, and it is difficult to transport ClO₂ at high concentrations and to store it for extended periods. So, it is more desirable to prepare ClO₂ on-site when it is needed.

Generation of chlorine dioxide can be done in laboratory or commercially using one of the following schemes: (1) the reaction of sodium chlorite and hypochlorous acid (HOCl), (2) the reaction of sodium chlorite and gaseous chlorine (Cl₂), (3) the reaction of potassium chlorate with oxalic acid, (4) the reaction of potassium chlorate with oxalic acid and sulfuric acid, and (5) the reaction of sodium chlorite and hydrochloric acid (HCl).²⁸ Over 95% chlorine dioxide produced in the world is made from sodium or potassium chlorate by using reducing agents such as methanol, sulfuric acid, and hydrogen peroxide.





1.5.3 The application of chlorine dioxide

Chlorine dioxide is a strong oxidative agent with multiple applications, such as wastewater treatment, textile bleaching, food processing, and anti-microbial activity. The use of chlorine dioxide as a disinfectant instead of chlorine is because of its lesser tendency to yield harmful by-products. It is very reactive compared to other oxidative reagents like chlorine and ozone, even at very low concentration. The useful applications of chlorine dioxide are:

- i) Distillation of wastewater in water treatment facilities. It is a unique water treatment disinfectant with no harmful by-products (chlorine, chloramine and ozone).²⁹
- ii) Removal of odor by oxidation reaction of odor-causing compounds like dimethyl disulfide, dimethyl trisulfide, aldehydes, various amines, and ketones.
- iii) Bleaching reagent in paper and textile industry.
- iv) Anti-fungal activity for sanitizing food. It kills microorganism by oxidation reaction in a very short time period.
- v) Miscellaneous uses, like cleaning agent, stabilization of latex and vinyl enamels, and oxidants in the preparation of vaccines.³⁰

1.5.4 Chlorine dioxide disinfectant by-products (DBPs)

The formation of by-products through oxidation process is very crucial before an oxidant is chosen for particular process applications. In recent years, chlorine dioxide is used as an alternative disinfectant to chlorine for water treatment. Both of these chemicals yield by-products, but the by-products generated by chlorine dioxide are less harmful than by-products produced by chlorine.^{29,31} For example, in the water treatment process, toxic by-products classified as trihalomethanes can be produced by chlorine, which are classified as carcinogenic. Chlorine dioxide produces different by-products, such as chlorate and chlorite, rather than trihalomethanes as end-products.

1.6 Thesis proposal

VOCs including dimethyl trisulfide, isoprene, 2,3-butanedione, 1-bromopropane and 1,1,2-trichloroethane are chosen for evaluating the degradation efficiencies of chlorine dioxide and ozone because they have different oxidative reaction pathways and various harmful or undesirable effects on health and environment. The goal of this project is to study the feasibility of reducing human inhalation exposure to these compounds by using the two oxidants that have been successfully used for water treatment. The use of 2,3-butandione as food flavoring additives is common in popcorn manufacturing and the production of e-liquids for electronic cigarettes. Exposure of workers to 2,3-butandione in these industries has been investigated by Occupational Safety and Health Administration and workplace monitoring of 2,3-butandione is required. Both 1-bromopropane and 1,1,2-trichloroethane are used as solvents in cleaning products and degreasing agents in many automotive products. They represent a wide range of

halogenated compounds that may have adverse human health effects. Dimethyl trisulfide is produced as a by-product of the decomposition of organic waste, animal carcasses, and waste food products. Its odor is objectionable and therefore its elimination or reduction in indoor or ambient air is desirable. Isoprene has been selected for the analysis because of its widespread emission from biogenic sources in many areas. It is very important to degrade such kind of odorous and harmful VOCs into harmless compounds to prevent toxicity on human health as well as in the ecosystem. Chlorine dioxide and ozone were chosen as oxidizing agents for applications in water treatment, disinfection of surface contaminated by pathogenic microbes, removal of odorous compound and as a bleaching agent in paper and pulp industry. Chlorine dioxide is a selective gaseous oxidant and highly soluble in water. It does not produce toxic trihalomethanes (THM) by-products like chloroform and carbon tetrachloride. On the other hand, ozone, also a highly powerful oxidant, produces less harmful by-product during oxidation. Both oxidants are producible in laboratory and cost efficient. This project is aimed at characterizing the by-products of the reactions between each of the five VOCs and chlorine dioxide or ozone and to determine the reaction rate constants and half-lives of their degradation.

CHAPTER 2

2 MATERIALS AND METHODS

2.1 Materials and chemical reagents

The chemicals used in this project including dimethyltrisulfide ($\geq 98\%$), 1-bromopropane (99%), isoprene ($\geq 99\%$), 1,1,2-trichloroethane ($\geq 96.40\%$) which were purchased from Sigma Aldrich (St. Louis, MO, USA). Diacetyl or 2,3-butanedione ($\geq 98\%$) was purchased from TCI America, (Portland, OR, USA). Fast release chlorine dioxide was provided by ICA Trinova (Newman, GA, USA). Scotty Analyzed Gases (SAG) was purchased from RESTEK (Bellefonte, PA, USA).

2.2 Production of ozone

Ozone was produced from UHP pure oxygen gas by using an ozone generator which was made by Ozone Forever (Nevada, USA). There are many methods for producing ozone including the use of UV radiation and corona discharge. We chose to use the principles of corona discharge for the purpose of this experiment. The advantages of ozone production via corona discharge are its high production capacity and its cost effectiveness. As shown in Figure 1, the ozone generator was enclosed in a transparent Plexiglass box with an inlet connected to a UHP oxygen cylinder and was purged with oxygen for five minutes to remove the nitrogen gas that depletes ozone via the formation of nitric oxide. Then ozone generator was connected to the power supply to produce ozone, which was collected by a cleaned and evacuated six-liter SilcoCan® canister (RESTEK, Bellefonte, PA) connected to the outlet of the Plexiglass box containing the

ozone generator. The produced ozone was then transferred into the canister and pressurized to 30 psig by using UHP argon gas for the dilution.

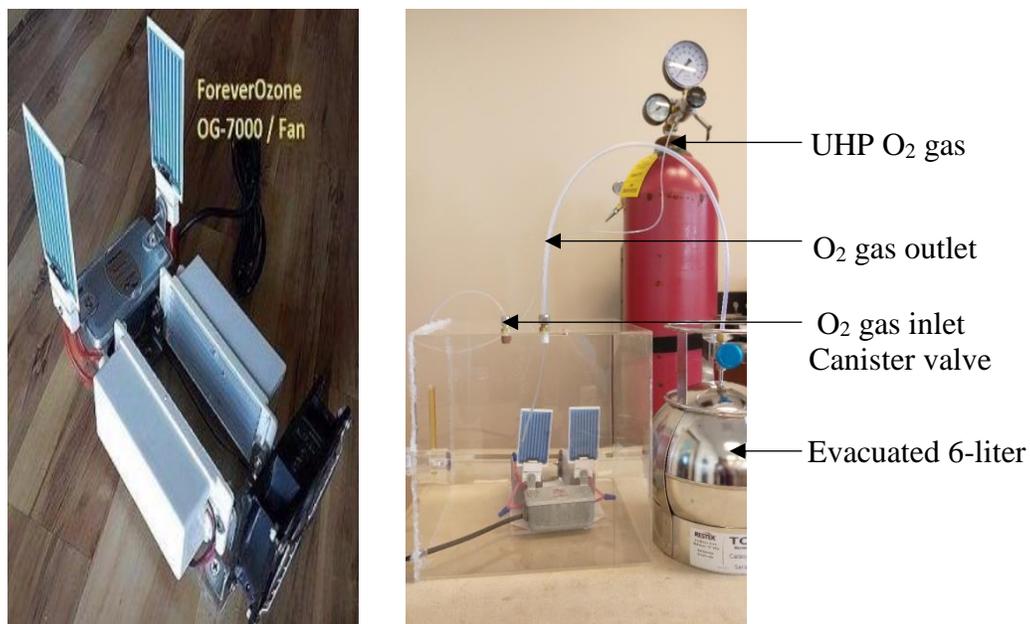


Figure 1: Setup for the production of ozone from pure oxygen. ForeverOzone generator was used to produce ozone and transferred into a cleaned evacuated canister

2.3 Generation of chlorine dioxide gas

Generation of chlorine dioxide was based on the reaction between two precursors, such as precursor A and precursor B, in equivalent proportions. The chemical formula of precursor A is $\text{NaClO}_2 + \text{Ca}_3(\text{Na, K})_2 \text{Al}_8\text{Si}_{28}\text{O}_{72} \cdot 24\text{H}_2\text{O}$ and precursor B is $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{Ca}_3(\text{Na, K})_2 \text{Al}_8 \text{Si}_{28}\text{O}_{72} \cdot 24\text{H}_2\text{O}$.

The chlorine dioxide gas was collected in a cleaned and evacuated, six-liter silcoCan® canister (RESTEK, Bellefonte, PA, USA), by a 30-cm long stainless steel tube which was connected with a Tedlar® sampling bag (SKC Inc. Eighty Four, PA, USA) filled with UHP nitrogen (Figure 2). The 100 mg of each precursor was mixed thoroughly and quickly transferred into a 30-cm long stainless steel tube for producing the desirable concentration (30 ± 5 ppm) of chlorine dioxide gas for this research. The lower part of the the stainless steel tube was closed with cotton so that canister valve does not clogged in by precursors particles. The duration of the reacton for generation of chlorine dioxide gas was 1 hour. The produced chlorine dioxide gas was tranferred into the canister. Chlorine dioxide concentration concentration was proportional to the reaction time. The nitrogen gas from Tedlar® sampling bag was used to push the produced chlorine dioxide gas from the precursors in the tube into the evacuated canister. The collected gas from the Tedlar® sampling bag into the canister was then diluted with UHP nitrogen to 30 psig pressure for the degradation reactions.

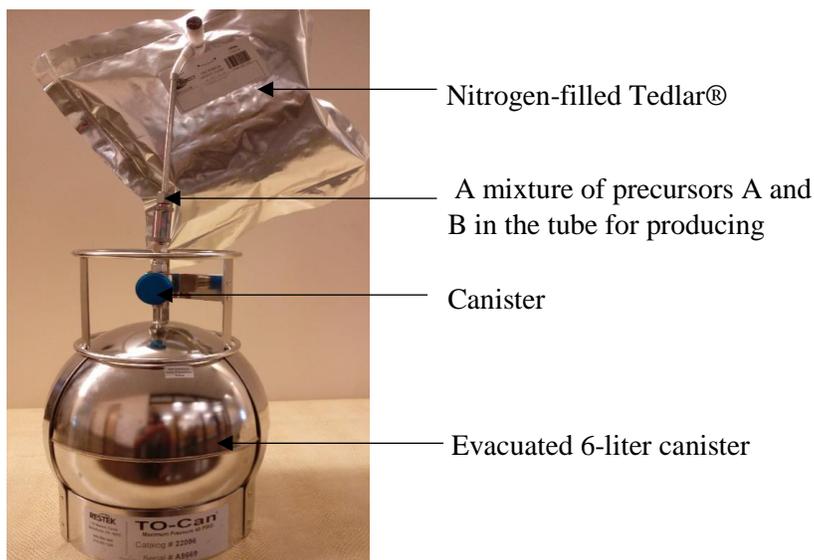


Figure 2: Generation of chlorine dioxide gas using precursors. A Tedlar® bag with full of nitrogen gas is used to push the chlorine dioxide produced in the tube into the canister

2.4 Canister cleaning system

It is very essential to clean each canister before using it to prepare standards and samples for gas phase analysis. The chemical compounds adsorbed on the internal surface of the canister have to be removed during cleaning to prevent cross contamination. Before preparing a new sample, a canister was cleaned by using a Nutech canister cleaner was used to clean canister by filling the canister with UHP nitrogen followed by evacuation to -30 in Hg pressure with repeated steps. In this process, four canisters were placed into four separate heating jackets by setting 150°C temperature for better removal of waste compounds from the canister. During the cleaning process, the canister valves remained open and the same time UHP nitrogen cylinder valve was also

opened before starting the the cleaning process. Power was turned on and “Auto” operation was selected in order to complete the cleaning. It took about 80 minutes time for completing three cycles to achieve the final pressure of 1.5×10^1 m Torr. The canister valve was closed after the cleaning was completed and the canister pressure gauge was measured and varified to be between -29.50 to -30.00 in Hg to ensure proper cleaning.

2.5 Methods for analytical measurements

2.5.1 Sample preparation for GC-MS and FTIR analysis

A six-liter capacity canister and a 10 μ L glass syringe (Hamilton, Reno, NV, USA) were used for gas samples. A canister was cleaned and pre-evacuated by measuring the pressure upto <-29.0 in Hg to makesure the cleanliness of the canister. Then, after opening the canister valve, 1 μ L each of dimethyltrisulfide, 1-bromopropane, 2,3-butanedione, isoprene and 1,1,2-trichloroethane liquid sample was measured to be analyzed was injected into an evacuated canister by using a clean glass syringe through a compression fitting with a rubber septum. The liquid sample was converted to gas phase inside the evacuated canister that was subsequently pressurized to 30 psig with UHP nitrogen for the study of the reaction between the target compound and ozone or chlorine dioxide gas. The sample was prepared first according to the procedure mentioned above prior to being mixed with ozone produced by the method mentioned in Section 2.2 or with chlorine dioxide prepared by the procedure described in Section 2.3. For the kinetics study based on GC-MS analysis, the canister with the reaction mixture was connected to the GC-MS via the preconcentrator. For the analysis of ozone, chlorine

dioxide, and other highly volatile by-products of the studied compounds, the gaseous reaction mixture was transferred into to a cleaned and evacuated 10-m gas cell for the analysis using FTIR.

2.5.2 GC-MS measurements

Hewlett Packard 5890 Series II gas chromatograph interfaced with a single-quadrupole Hewlett Packard 5970 MSD were used for the analysis of gas phase sample. Low molecular weight compounds such as H₂O and CO₂ were removed by a Nutech 8900DS preconcentrator which was connected to the HP5890 gas chromatograph. The preconcentrator analyte enrichment steps and conditions are shown in Table 1 and Table 2, respectively, in the Appendix Section A. Each sample was injected manually at 250°C and the GC separation was carried out through a Phenomenex ZB-624 column having dimensions of 60 m length, 0.25mm internal diameter, and of 1.40 µm thickness (Torrance, CA, USA). GC oven temperature program is as follows: initial oven temperature 30°C and hold time 3 minutes, ramp 100°C at 8°C/min; hold time 1 minute, ramp 150°C at 12°C/min; hold time 1 minute and ramp 220°C at 20°C/min; hold time 7 minutes. The duration of each complete run was about 28.42 minutes. The full scan mode with mass range of 35-350 amu were setup for the mass spectrometer operation with 2 scans/sec, and hydrogen was used as a carrier gas. Other important GC-MS conditions are summarized in Table 2.

Table 2: Instrumental conditions of HP5890 GC/5970MSD

Parameters	Conditions
Initial oven temperature	30 °C
Initial temperature	250 °C
Injection mode	Splitless
pressure	10.2 psi
Flow	1.25 mL/min
Velocity	40.6 cm/sec
Start time	3.00 min
End time	28.42 min
MS interface temperature	250 °C
MS scan range	35-350 amu

The obtained data was analyzed by using ChemStation, TargetView, and AMDIS software. National Institute of Science and Technology (NIST) mass spectral library was used to match the sample spectra for identifying degradation by-products. The tentatively identified compounds were also confirmed by plotting their retention time against their retention indices along with a set of chemical standards. All compounds reported in this study have reverse match indices of greater than 800 for mass spectral matching and a correlation coefficient (r^2) value of greater than 0.94 for the linear regression plot of the retention index versus retention time values.

2.5.3 FTIR analysis

Varian 7000 FTIR spectrometer was used for analyzing gas samples for spectral changes in the region between 400 to 4000 cm^{-1} . A Mercury Cadmium Telluride (MCT) detector was used for measurement. For collecting data, 32 scans were used with resolution 4 cm^{-1} and gain 1 sensitivity to get the high signal IR spectra without noise. As

degradation of dimethyl trisulfide by chlorine dioxide was very quick, 16 cm^{-1} resolution was used for faster scanning. The spectra collected using the Resolution Pro software were exported for analysis with OMNIC 7.3 software. The OMNIC integration tool was used for determining the peak areas of different spectral regions for quantifying the concentrations of the oxidants, target compounds, and their reaction by-products. REF5 reference spectra were used for quantification of DMTS, isoprene, 1,1,2-trichloroethane, and Ozone. Both 2,3-butanedione and 1-bromopropane sample spectra were compared with NIST and standard reference spectra respectively for identification and determination of concentration. In addition, QAS5 reference spectra of chlorine dioxide was used for the quantitative analysis. Beer-Lambert's law was used to calculate the concentration with the help of subtraction factor. Though the spectral features of the compounds had different resolutions than reference spectra, the concentrations were identical.

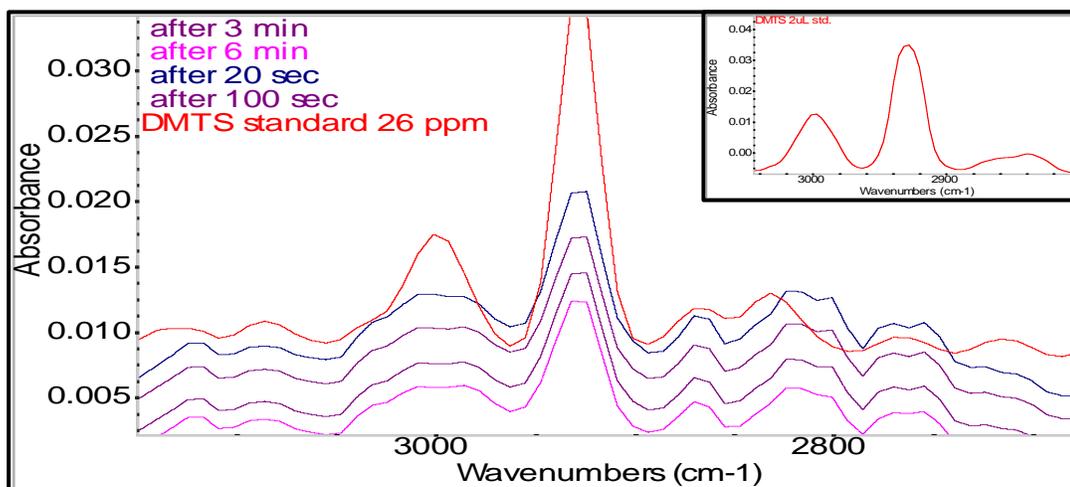
CHAPTER 3

3 RESULTS AND DISCUSSIONS

3.1 GC-MS and FTIR analysis of air pollutants by ozone

3.1.1 Degradation of dimethyl trisulfide with chlorine dioxide

Dimethyl trisulfide of 26 ppm was prepared and treated with 10.3 ppm of chlorine dioxide. The peak in the region of 2850-3050 cm^{-1} (Figure 3) the dimethyl trisulfide peak and chlorine dioxide peak is located at 1050-1150 cm^{-1} (Figure 4). After 6 minutes of treatment by chlorine dioxide, the concentration of dimethyl trisulfide was reduced to 9.48 ± 0.16 ppm while the concentration of chlorine dioxide decreased to 0.97 ± 0.14 ppm. The spectral signals of dimethyl trisulfide were changing with the increase of reaction time (Figure 3). The chlorine dioxide peak height also reduced immediately after it was exposed to DMTS. Therefore, it can be concluded that the chlorine dioxide is very reactive to DMTS. For a more detailed study of reaction byproducts, the GC-MS technique was used.



Figures 3: Comparison of FTIR spectra of treated dimethyl trisulfide by chlorine dioxide at different time interval. The peak in the range of $2850\text{-}3050\text{ cm}^{-1}$ indicates dimethyl trisulfide compound. A 26 ppm of dimethyl trisulfide gas sample was exposed to 10.28 ppm chlorine dioxide. The concentration of dimethyl trisulfide was reduced to 9.49 ± 0.16 ppm after 60 minutes of treatment.

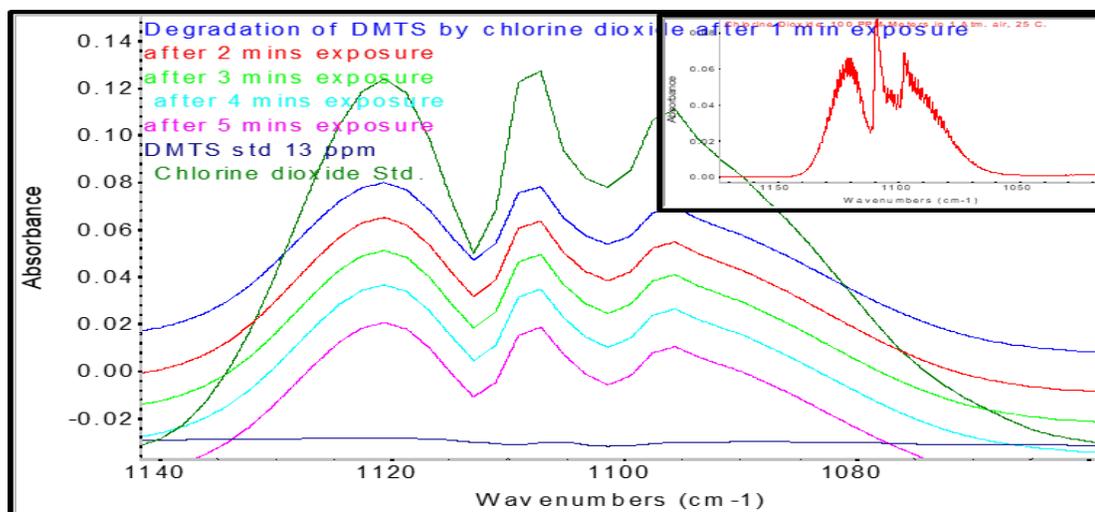


Figure 4: FTIR spectral changes of chlorine dioxide after treatment of dimethyl trisulfide samples. A Peak in the range of $1050\text{-}1150\text{ cm}^{-1}$ represent the chlorine dioxide. After 6 min minutes treatment of dimethyl trisulfide the chlorine dioxide concentration was reduced to 0.97 ± 0.14 ppm. FTIR spectra of chlorine dioxide in different time of exposure with dimethyl trisulfide

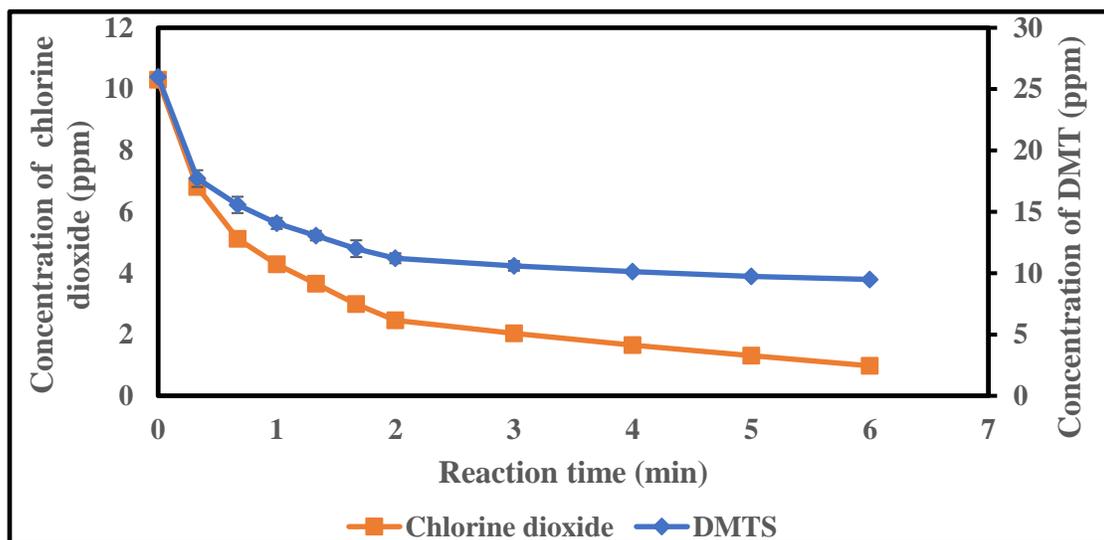


Figure 5: Plots showing decreasing concentration of dimethyl trisulfide and chlorine dioxide as a function of their reaction time at room temperature. The initial reaction mixture was 26 ppm of dimethyl trisulfide gas treated with 10.3 ppm of chlorine dioxide. The left and right Y-axes denote the concentrations of chlorine dioxide and DMTS, respectively

The reaction by-products of dimethyl trisulfide with chlorine dioxide were studied by gas chromatography coupled with mass spectrometry. A gas sample of 13 ppm dimethyl trisulfide was prepared and treated with 25 ± 5 ppm of chlorine dioxide for the degradation study. The reaction was continued for about 120 minutes and there was no sign of dimethyl trisulfide after 60 min of reaction with chlorine dioxide. Figure 6 shows the overlay of chromatograms of untreated and treated dimethyl trisulfide at different time points. All of these chromatograms, such as formic acid, chloromethane, methylene chloride, and methyl sulfonyl chloride, showed same peaks at 4.83, 5.58, 8.87, and 19.03 minutes retention time respectively. So, those compounds are tentatively identified as by-products of treated dimethyl trisulfide which are observed after both 60 min and 120 min

reaction time. The by-products produced during the degradation of dimethyl trisulfide were confirmed by NIST mass spectra library search and also using the retention time versus the retention index linearity graph (Figure 23) which are showed in the appendix. The dimethyl trisulfide compound was observed in retention time 11.35 min from untreated sample analysis. The peak in the retention time 6.11 min is chlorine dioxide which was used as oxidant for the degradation reaction. Methane sulfonyl chloride one of the by-products from dimethyl trisulfide degradation by chlorine dioxide which has adverse health effects such as corrosive to skin, also respiratory tract and also indicated as a potential genotoxic impurity in Itraconazole drug substance.³² This compound also identified in the workplace of hardwood bleaching plants.³³ Though NIOSH has no established TLV for this compound but International Conference on Harmonization Guidelines from European Medical Agency has set an exposure limit up to 1.5 $\mu\text{g}/\text{day}$.

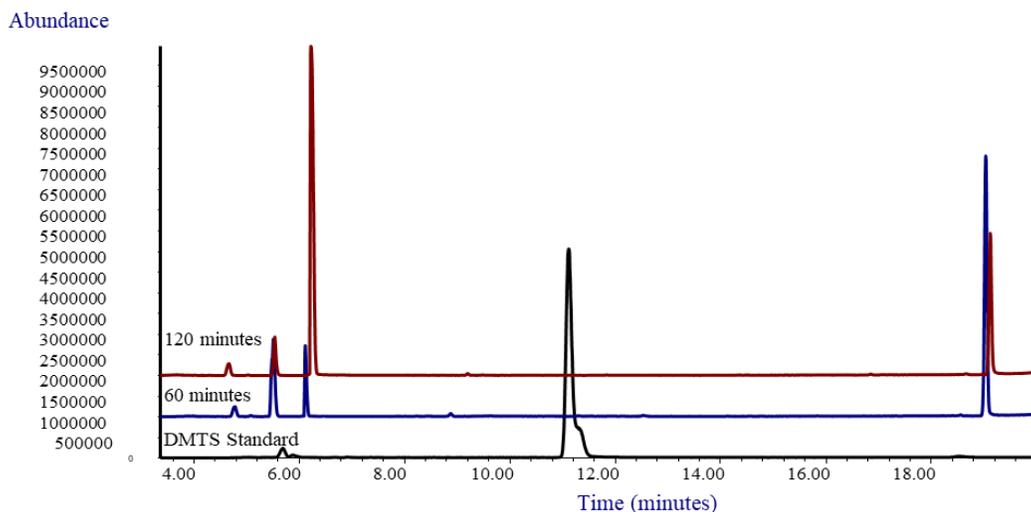


Figure 6: GC-MS overlay chromatograms of treated and untreated dimethyl trisulfide. A 13ppm sample of dimethyl trisulfide gas was treated with 30 ppm of Chlorine dioxide. The peak at retention time 11.65 min is dimethyl trisulfide and peaks at the retention times of 4.83 min, 5.58 min, 8.87 min and 19.03 are formic acid, chloromethane, methylene chloride and methane sulfonyl chloride respectively.

3.1.2 Degradation of dimethyl trisulfide by ozone

A gas phase standard of 13 ppm of dimethyl trisulfide was prepared and exposed to 28.02 ppm of ozone. After 60 minutes of treatment, the shape of the sample spectra was completely changed (Figure 7). The peak for dimethyl trisulfide appeared in the region of $2880\text{-}2980\text{ cm}^{-1}$, and ozone spectra are located in the range of $960\text{-}1080\text{ cm}^{-1}$ (Figure 8). In the beginning, concentration of dimethyl trisulfide was 13 ppm and after 5 minutes of treatment to ozone, it reduced to 10.06 ± 0.04 ppm (Figure 9). Similarly, the concentration of ozone also started to reduce and, after 5 minutes' reaction with dimethyl trisulfide, it reduced to 21.6570 ± 1.44 ppm. As the treatment periods increased, the peak of both dimethyl trisulfide and ozone disappeared. After 60 minutes of treatment, the concentration

of dimethyl trisulfide reduced to 5.10 ± 0.13 ppm and the peak of dimethyl trisulfide almost disappeared. So, it can be understood that ozone is very reactive with dimethyl trisulfide. The concentration of ozone also reduced to 3.96 ± 1.01 ppm after 60 minutes of treatment. To remove dimethyl trisulfide from different environmental sources, there are different methods, for example: granular activated carbon adsorption is one of the processes to remove dimethyl trisulfide from water bodies,³⁴ oxidation, and filtration. GC-MS analysis was performed to study all the by-products produced in degradation with ozone.

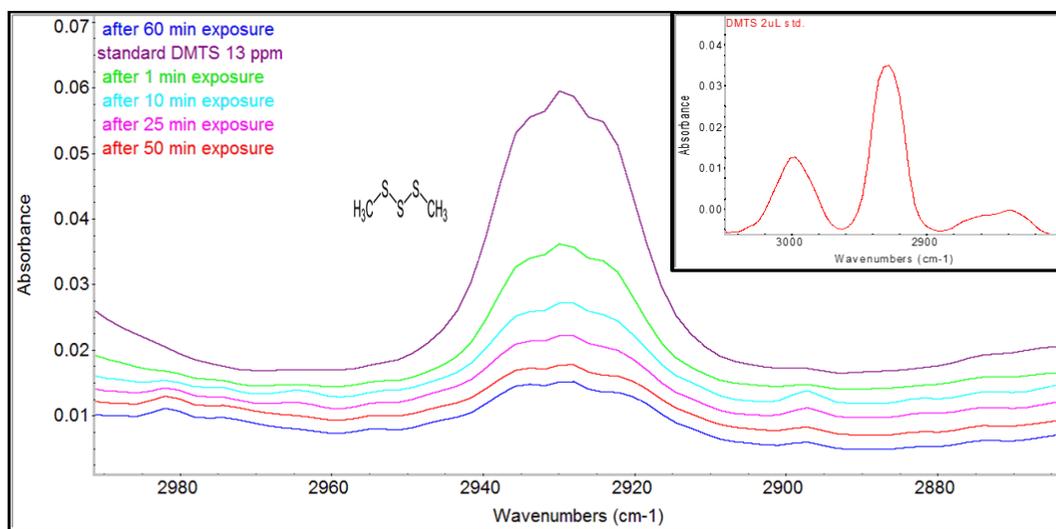


Figure 7: Comparison of FTIR spectra of dimethyl trisulfide oxidized by ozone as a function of different reaction periods. The peak in the range of $2880\text{-}2980\text{ cm}^{-1}$ represents the dimethyl trisulfide compound. 13 ppm of dimethyl trisulfide gas sample was exposed with 30 ppm of ozone gas for different periods of time. The concentration of dimethyl trisulfide reduced to 3.2 ± 0.03 ppm after 60 minutes reaction. The REF5 standard spectra of dimethyl trisulfide is shown above in the right corner of the figure.

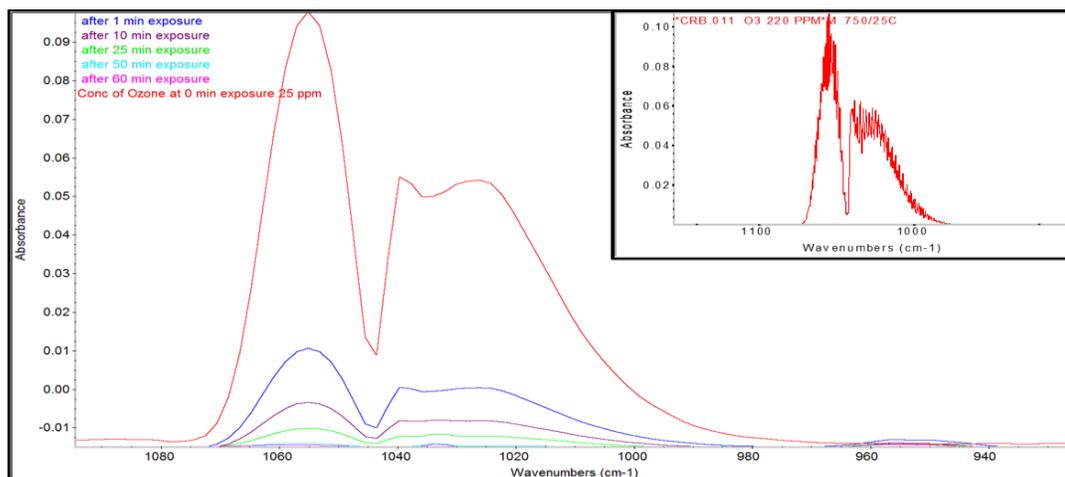


Figure 8: FTIR spectral comparison of ozone peak intensity in ozone-treated dimethyl trisulfide samples. The peak in the region of $980\text{--}1080\text{ cm}^{-1}$ shows the presence of ozone. The concentration of ozone reduced to 8.6 ± 0.5 ppm after 60 minutes of treatment period. The Ref5 standard spectra of ozone is shown above in the right corner of the figure.

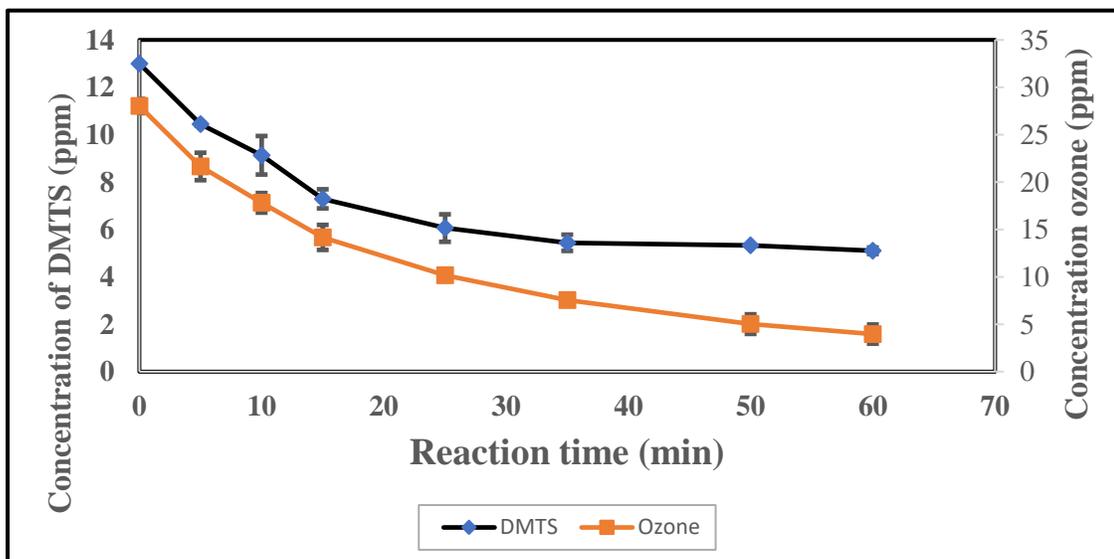


Figure 9: Plots showing decreasing concentration of dimethyl trisulfide and ozone as a function of their reaction time at room temperature. The initial reaction mixture was 13 ppm of dimethyl trisulfide treated with 28.02 ppm of ozone. treated with 28.02 ppm of ozone. The left and right Y-axes denote the concentrations of DMTS and ozone, respectively.

For the reaction of dimethyl trisulfide and ozone, 13 ppm of dimethyl trisulfide was treated with 25 ± 5 ppm of ozone and then analyzed by GC-MS after 80 minute and 180 minutes to identify the reaction products. The dimethyl trisulfide compound was completely degraded into different by-products. Figure 10 shows the overlay of chromatograms of dimethyl trisulfide untreated and treated with ozone. GC-MS spectra of both 80 min and 180 min shows similar peak at 3.50 min, 5.33 min, 6.80 min, 6.42 min, 8.53 min, and 9.7 min. By using the Agilent ChemStation search, dimethyl ether, sulfur dioxide, methyl formate, dimethyl peroxide, acetone, and methyl nitrate were primarily identified as by-products at 3.50, 5.33, 6.80, 6.42, 8.53, and 9.7 min retention time, respectively. The peak in retention time, 12.89 min, was identified as benzene, which might be contamination from other samples used by the same canister. Though the ozonation of organic pollutants, such as dimethyl trisulfide, form aldehyde, the higher dosage of ozone treatment can degrade the pollutants completely.³⁵ Dimethyl trisulfide is oxidized by most of the oxidants, such as ozone, chlorine dioxide, hydrogen peroxide, and a combination of ozone and hydrogen peroxide.³⁵ Sulfur dioxide is a volatile gas produced as a by-product from the ozonation of dimethyl trisulfide which may cause nose, throat and also breathing problems. NIOSH has set a threshold limit up to 2 ppm as TWA.

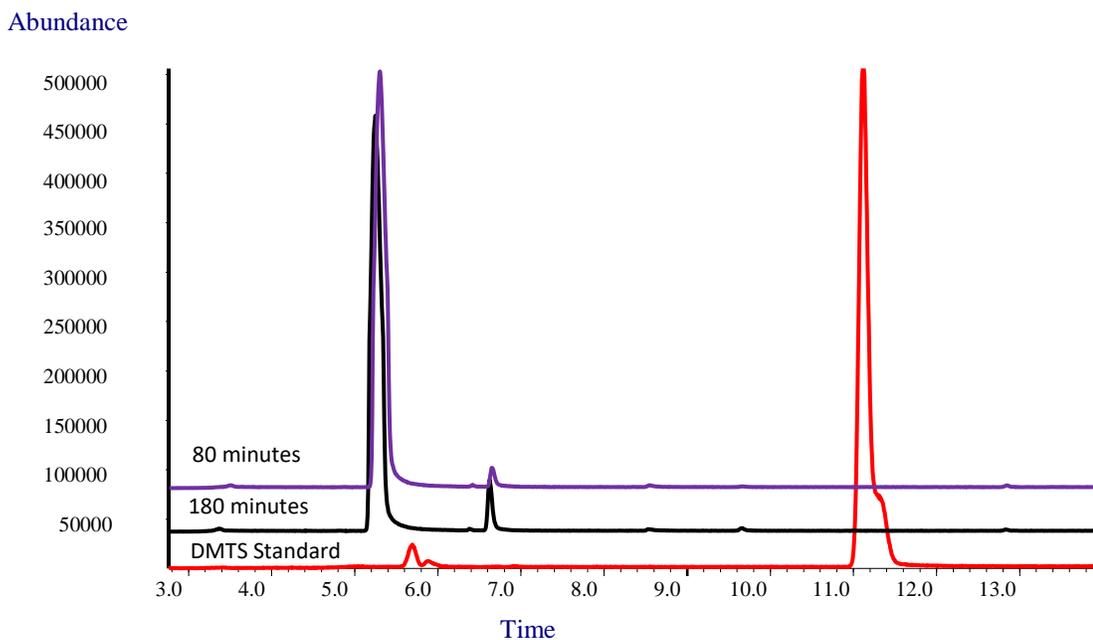


Figure 10: Overlaid GC-MS chromatograms of treated and untreated dimethyl trisulfide samples. A 13 ppm of dimethyl trisulfide gas sample was treated with 30 ppm of ozone. The peak at retention time 11.2 is dimethyl trisulfide and peaks at the retention times of 3.50 min, 5.33 min, 6.41 min, 6.87 min, 8.58 min and 9.7 min are sulfur dioxide, dimethyl peroxide, methyl format, acetone and methyl nitrate respectively.

3.1.3 Degradation of 1-bromopopane with chlorine dioxide

For FTIR analysis of 1-bromopopane, 14.5 ppm of 1-bromopopane gas sample was prepared and exposed to 30.7 ppm of chlorine dioxide. Comparison of different FTIR spectra in variable time points are shown in Figure 11 and Figure 12 for 1-bromopopane and chlorine dioxide respectively. A region of 2800-3050 cm^{-1} (Figure 11) indicates the presence of 1-bromopopane and a region of 1050-1150 cm^{-1} (Figure 12) indicates the presence of chlorine dioxide. The reaction between chlorine dioxide and 1-bromopopane was carried out up to 100 minutes, and samples were analyzed at different

time points. Concentration of 1-bromopropane was decreased as the reaction time increased. After 100 minutes of reaction, the concentration of 1-bromopropane reduced to 7.4 ± 0.5 ppm, and in the same way, concentration of chlorine dioxide also reduced to 12.0 ± 0.3 ppm.

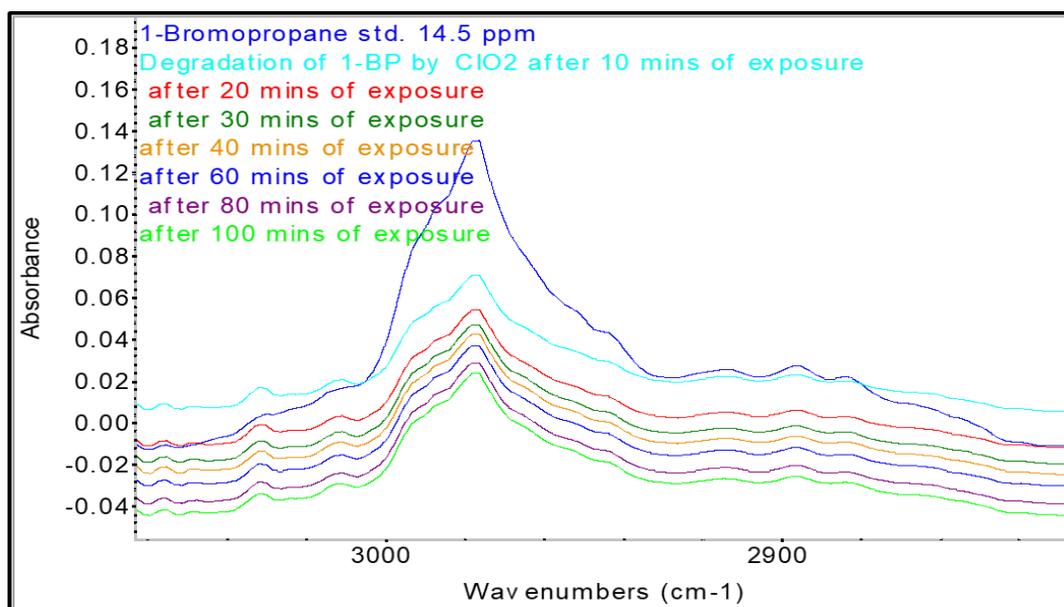


Figure 11: Comparison of FTIR spectra of treated 1-bromopropane by chlorine dioxide gas at different time intervals. The peak in the range of $2850\text{-}3050\text{ cm}^{-1}$ represents the 1-bromopropane. A 14.5 ppm of 1-bromopropane gas sample was treated with 30.1 ppm of chlorine dioxide gas. The concentration of 1-bromopropane reduced to 7.40 ± 0.5 ppm after 100 minutes of treatment.

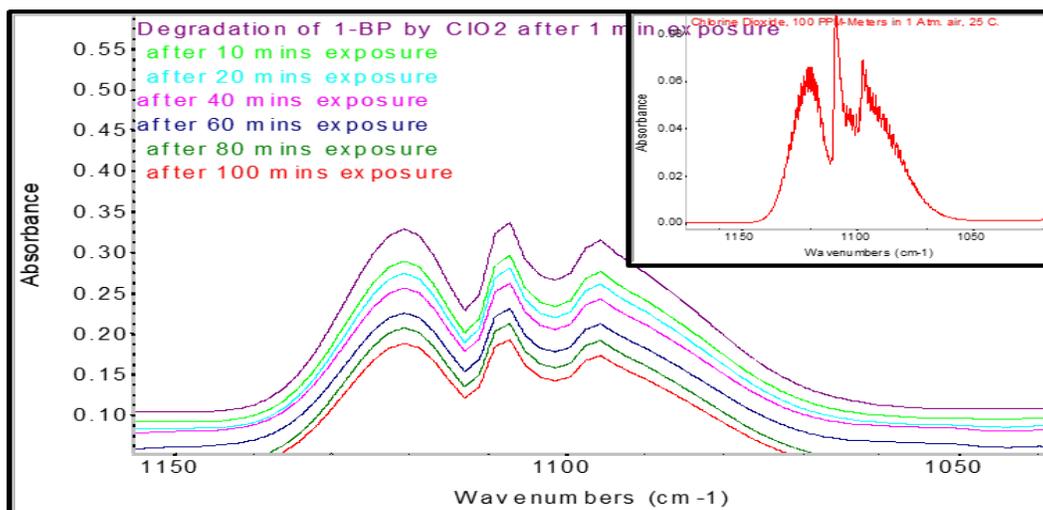


Figure 12: FTIR spectral changes of chlorine dioxide after treatment of 1-bromopropane samples. A peak in the region of 1050-1150 cm^{-1} indicates the presence chlorine dioxide. The chlorine dioxide concentration was reduced to 12.0 ± 0.3 ppm after 100 min of reaction with 1-bromopropane.

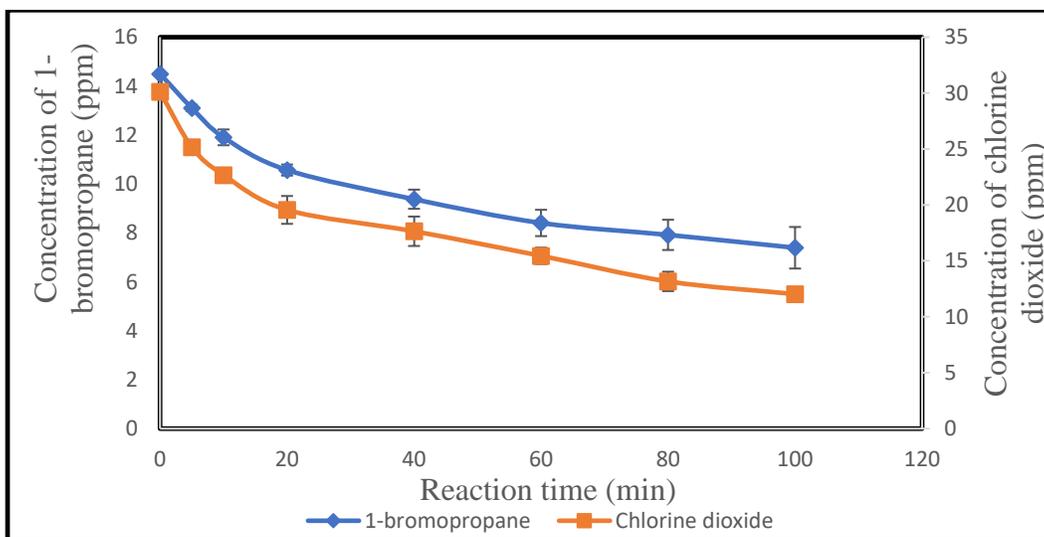


Figure 13: Plots showing decreasing concentration of 1-bromopropane and chlorine dioxide as a function of their reaction time at room temperature. An initial concentration of 14.5 ppm 1-bromopropane gas sample was treated with 30.1 ppm of chlorine dioxide. The left and right Y-axes denote the concentrations of 1-bromopropane and chlorine dioxide, respectively.

A 14.5 ppm of 1-bromopropane gas sample was prepared and treated with 25 ± 5 ppm of chlorine dioxide for GCMS analysis to study the byproducts formed during the reaction. The reaction was carried out for 4 hours to observe the reaction products with chlorine dioxide at various time intervals. The total ion chromatograms at four hours interval indicated the 22% degradation of 1-bromopropane compound. The comparison of the spectra is shown in Figure 14 at different time points. Analyzing the data from both three hours and four hours reaction time, dimethyl ether and formic acid were primarily detected as by-products at 3.73 min and 4.55 min retention time, respectively. As 1-bromopropane was not so much reactive with chlorine dioxide, there are few by-products formed during this reaction. The target compound eluted at the retention time of 11.62 minutes in both treated and untreated sample spectra. There are few by-products formed after four hours of reaction. The peak at the retention time 6.05 min is chlorine dioxide, which is an oxidant used for degradation of 1-bromopropane.

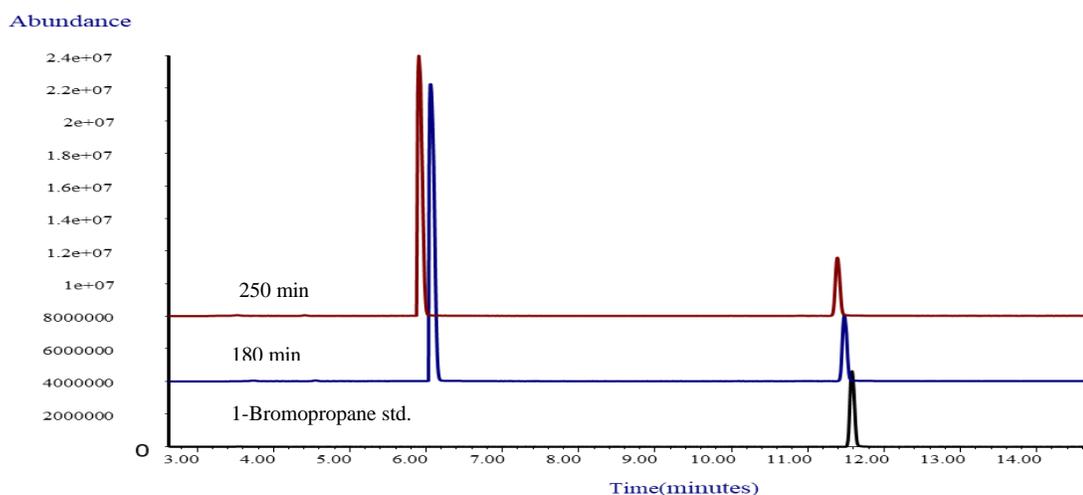


Figure 14: GC-MS chromatograms of treated and untreated 1-bromopropane. A 14.5 ppm sample of 1-bromopropane gas was exposed with 30 ppm of chlorine dioxide. The peak at retention time 11.75 min is 1-bromopropane and peaks at retention times of 3.73 min, 4.55 min and 6.2 min are dimethyl ether, formic acid chlorine dioxide respectively.

3.1.4 Degradation of 1-bromopropane with ozone

Since 1-bromopropane is traditionally used as an alternative ozone depleting solvent in the manufacturing industry,^{36,37} we are trying to observe the reaction efficiency of ozone with 1-bromopropane and the byproducts formed during the reaction. The beginning concentration of 1-bromopropane was 14.5 ppm which was treated with 30 ppm of ozone for studying the degradation rate. Comparison of spectral change in treated ozone was plotted to show the reduction of 1-bromopropane concentration and ozone.

The peak of 1-bromopropane appeared in the region of 2800-3050 cm^{-1} (Figure 15) and a region of 980-1080 cm wavelength (Figure 16) indicates the presence of ozone. The reaction continued for up to 60 minutes and analyzed at different time points. With

the increase of reaction time, the concentration of 1-bromopropane and ozone decreased as ozone was moderately reactive with 1-bromopropane and various by-products were produced. The concentration of 1-bromopropane was reduced to 10.0 ± 0.06 ppm after 100 minutes of treatment with ozone. At the same time, the concentration of ozone also reduced to 18.8 ± 1.1 ppm after 100 minutes of treatment.

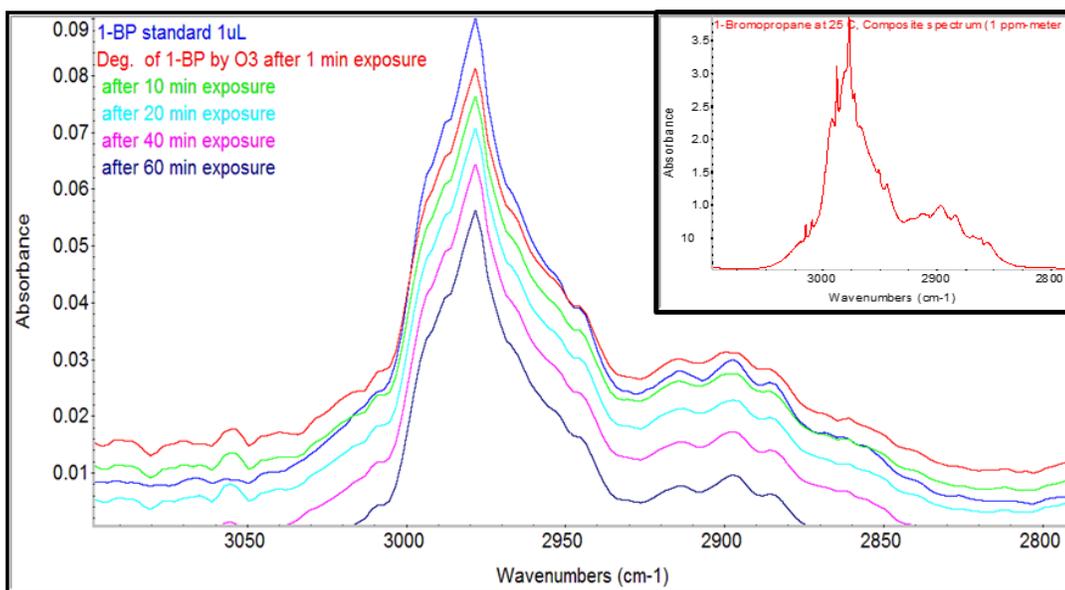


Figure 15: Comparison of FTIR spectra of treated 1-bromopropane by ozone at different time intervals. The peak in the range of $2800\text{-}3050\text{ cm}^{-1}$ represents the 1-bromopropane. A 14.5 ppm of 1-bromopropane gas sample was treated with 30 ppm of ozone gas. The concentration of 1-bromopropane reduced to $10.0 \pm 0.6\text{ ppm}$ after 100 minutes of treatment. A standard spectrum of 1-bromopropane has shown above in the right corner of the Figure 15.

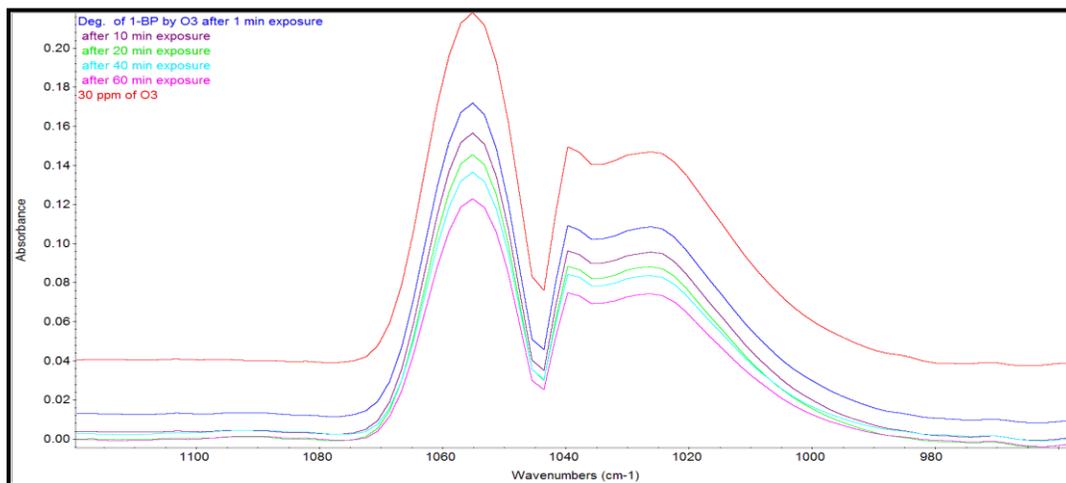


Figure 16: FTIR spectral comparison of ozone peak intensity in ozone-treated 1-bromopropane samples. A peak in the region of 980-1080 cm^{-1} indicates the presence of ozone. The concentration of ozone reduced to 18.8 ± 1.1 ppm after 100 min of reaction with 1-bromopropane.

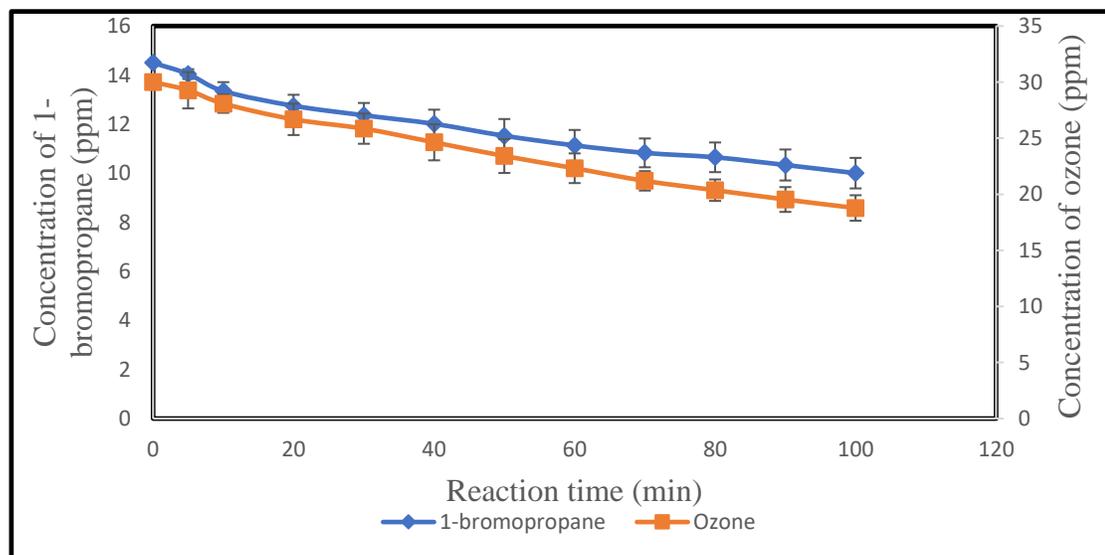


Figure 17: Plots showing decreasing concentration of 1-bromopropane and ozone as a function of their reaction time at room temperature. The initial reaction mixture was 14.5 ppm of 1-bromopropane gas treated with 30 ppm of ozone. The left and right Y-axes denote the concentrations of 1-bromopropane and ozone, respectively.

To observe the reaction by-products of 1-bromopropane treated by ozone, a GC-MS analysis was performed. A gas sample of 14.5 ppm of 1-bromopropane was prepared and exposed with 26.51 ppm of ozone, and the reaction was continued up to 120 minutes. A 14% of 1-bromopropane was breakdown after 120 min oxidation reaction by ozone. Ethanol, bromomethane, acetone, and cyanogen bromide were tentatively identified as reaction by-products at 6.57 min, 8.64 min, 10.47 min, and 11.61 min, respectively. The peak at 7.54 was identified as chloromethane, which is likely due to contamination from a previous sample. The peak at 11.61 min was identified as cyanogen bromide which has severe health effects on human as well as animals. OSHA has set a PEL value of 5 mg/m³ on average of eight hours work shift. This compound also reported as LD50 orally with 25-50 mg/kg for rate. Degradation of brominated contaminants forms a bromate ion (BrO₃⁻) during ozonation which is classified as genotoxic human carcinogen.³⁸ Since bromate ion or other harmful by-products were not produced during the degradation of 1-bromopropane by ozone, it can be a useful method for the minimization of 1-bromopropane.

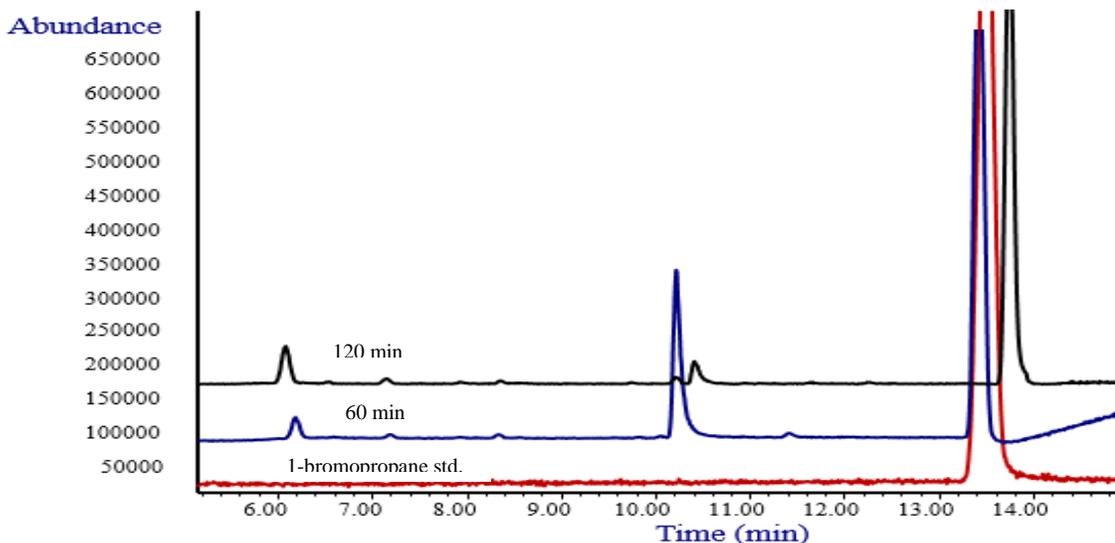


Figure 18: GC-MS overlay chromatograms of treated and untreated 1-bromopropane. A 14.5 ppm sample of 1-bromopropane gas was exposed with 30 ppm of ozone. The peak at retention time 13.85 min is 1-bromopropane and peaks at the retention times 6.57 min, 8.64 min, 10.47 min, and 11.61 min are ethanol, chloromethane, bromomethane, acetone and cyanogen bromide respectively.

3.1.5 Degradation of isoprene with chlorine dioxide

To understand the oxidative efficiency of chlorine dioxide, 13.5 ppm of isoprene were prepared and exposed with 30 ppm chlorine dioxide. With the progress of reaction, the concentration of isoprene was decreasing and similarly the concentration of chlorine dioxide also reduced to a great extent. It means the chlorine dioxide was also a very reactive oxidant like ozone for degradation of isoprene. The range 800-1000 cm^{-1} wavenumber indicates the isoprene molecule in the IR spectra (Figure 19) and 1050-1150 cm^{-1} represents the chlorine dioxide molecule. A sample of 13.5 ppm isoprene was reduced to 3.2 ± 0.3 ppm after 130 minutes of treatment and 29.11 ppm of chlorine dioxide also reduced to 6.5 ± 0.6 ppm (Figure 20)

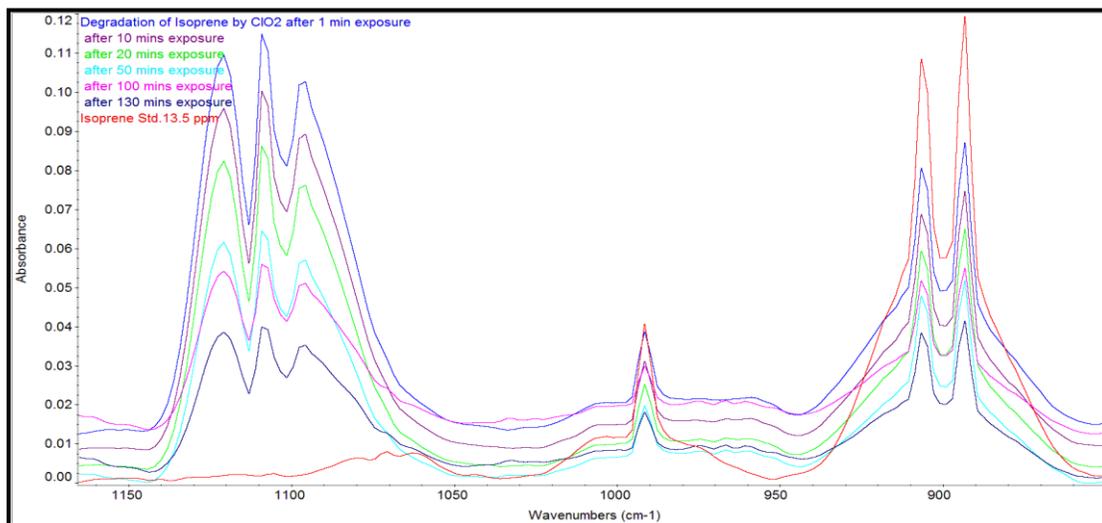


Figure 19: Comparison of FTIR spectra of treated isoprene by chlorine dioxide at different time interval. The peak in the range of $800\text{-}1050\text{ cm}^{-1}$ represent the isoprene and $1050\text{-}1150\text{ cm}^{-1}$. A 13.5 ppm of isoprene gas sample was treated with 29.1 ppm of chlorine dioxide gas. The concentration of isoprene and chlorine dioxide reduced to $3.2\pm 0.3\text{ ppm}$ and 6.5 ± 0.6 after 130 minutes of treatment, respectively.

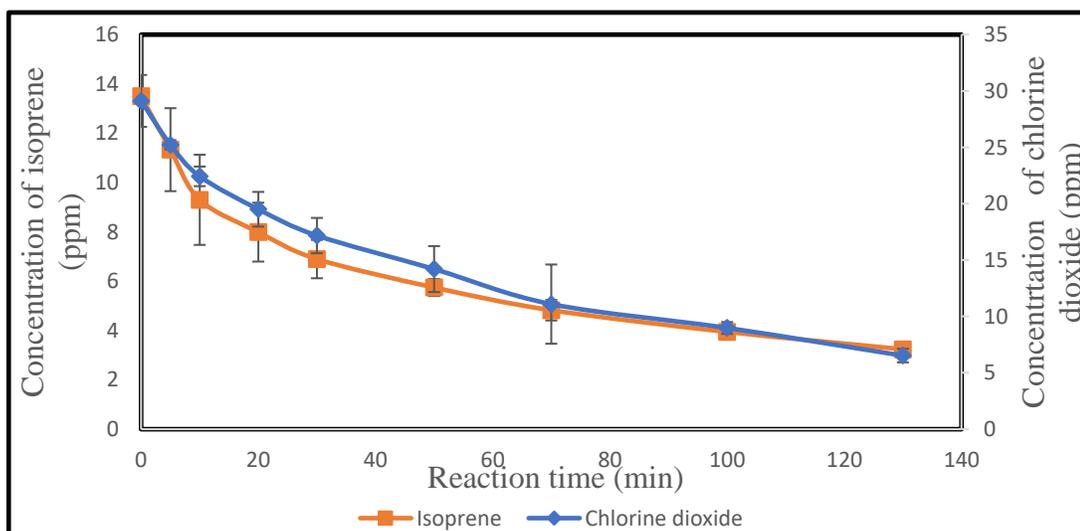


Figure 20: Plots showing decreasing concentration of isoprene and chlorine dioxide as a function of their reaction time at room temperature. The initial reaction mixture was 13.5 ppm of isoprene gas treated with 29.1 ppm of chlorine dioxide. The left and right Y-axes denote the concentrations of isoprene and chlorine dioxide, respectively.

Formation of by-products during reaction between isoprene and chlorine dioxide were studied by GC-MS analysis. 13.5 ppm of isoprene was exposed with 25 ± 5 ppm of chlorine dioxide to determine the degradation by-products. The reaction was continued up to 100 minutes. According to total ion chromatogram, 96% of isoprene was degraded by chlorine dioxide at 100 minutes of reaction. The tentatively identified reaction by-products are carbamic acid and 2-methyl butene at the retention times 8.95 min and 17.85 min respectively. The target compound isoprene was identified at retention time 13.8 min chlorine dioxide was observed at 11.6 min. NIST library search by using the Agilent Chem-Station and retention time vs retention index linearity relation were studied to confirm the reaction by-products which is shown in appendix (Figure 23). All the mass spectra also compared and has showed in the appendix to assure the by-products produced for the degradation of isoprene by chlorine dioxide.

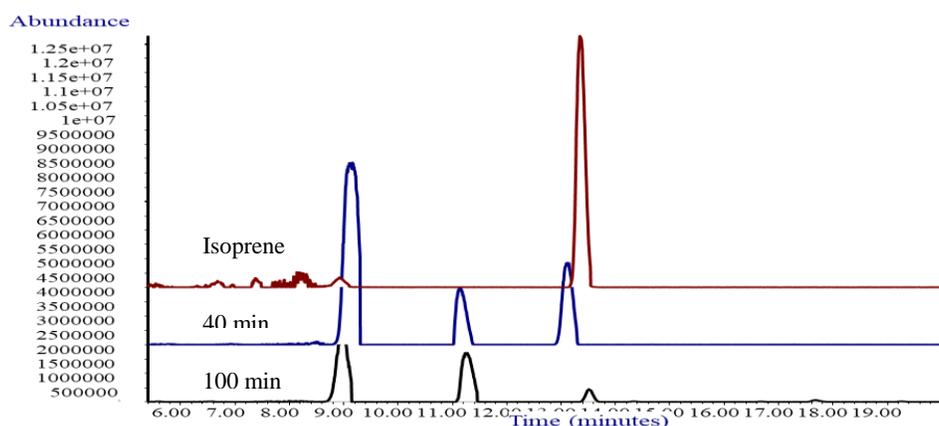


Figure 21: GC-MS overlay chromatograms of treated and untreated isoprene. A 13.5 ppm of isoprene gas sample was exposed with 30 ppm of chlorine dioxide. The peak at retention time 13.80 min is isoprene and peaks at the retention times 8.95 min, 11.6 min, and 17.85 min are carbamic acid, chlorine dioxide and 2-methyl butene respectively.

3.1.6 Degradation of isoprene with ozone

An isoprene gas sample of 13.5 ppm was prepared and treated with 26.4 ppm of ozone to observe the degradation of isoprene with ozone. After 1 minute of treatment with ozone, the concentration of isoprene was reduced to about 9.26 ± 0.06 ppm, which indicates that the ozone was very reactive with isoprene. In the same time, the concentration of ozone reduced to 23.9 ± 2.5 ppm after 1 minute of reaction time. The reaction was continued to 15 minutes and at the end of 15 minutes, the concentration of isoprene was near to zero, which is about 0.04 ± 0.06 ppm. The peak in the region of $850\text{-}950\text{ cm}^{-1}$ indicates the isoprene compound, and ozone appeared in the region of $980\text{-}1080\text{ cm}^{-1}$. GC-MS analysis was performed to study the reaction by-products of isoprene with ozone.

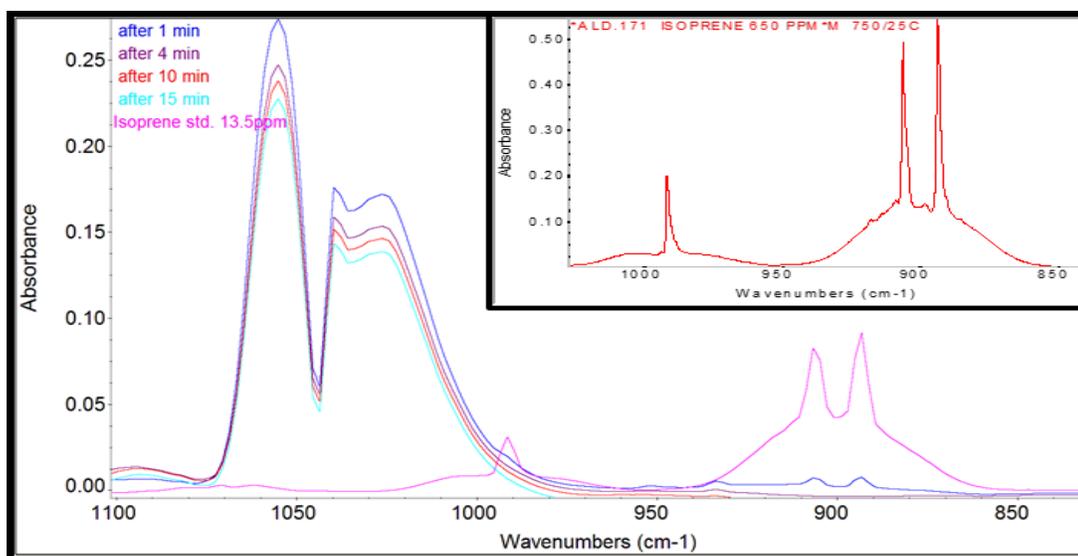


Figure 22: Comparison of FTIR spectra of isoprene oxidized by ozone at different treatment periods. A peak in the range of $850\text{-}950\text{ cm}^{-1}$ represent the isoprene compound and $980\text{-}1080\text{ cm}^{-1}$ indicates the ozone. The concentration of isoprene and ozone reduced to 0.05 ± 0.06 ppm and 13.7 ± 1.5 ppm after 15 minutes of reaction, respectively. The REF5 standard spectra of isoprene is shown above the right corner of the Figure 22.

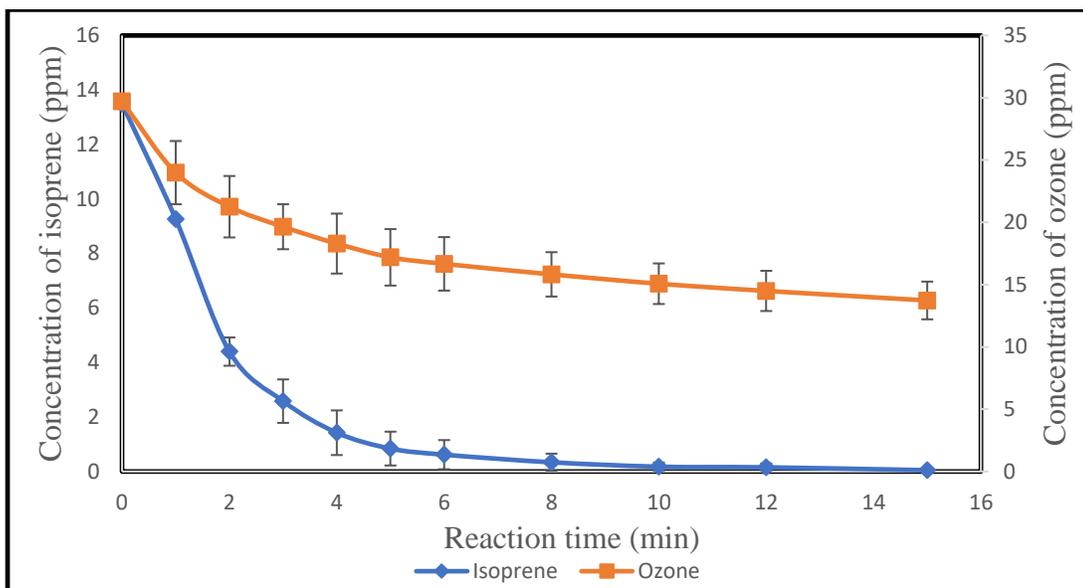


Figure 23: Plots showing decreasing concentrations of isoprene and ozone as a function of their reaction time at room temperature. The initial reaction mixture was 13.5 ppm of isoprene gas sample treated with 29.7 ppm of ozone. The left and right Y-axes denote the concentrations of isoprene and ozone, respectively.

GC-MS analysis of treated isoprene with ozone explored details about by-products produced during reaction. A gas sample of 13.5 ppm isoprene was exposed with 25 ± 5 ppm of ozone to study the degradation by-products. The reaction was continued up to 60 minutes and 100% isoprene was degraded into other by-products after this exposure time. collected chromatograms at 60 minutes and 120 minutes. Both showed the same kinds of by-products during the reaction. The overlay chromatograms of different spectra are shown below (Figure 24) at various time points. Ozone was very reactive with isoprene and produced many by-products which are primarily identified as ethanol, 1,3-pentadien, acetone, 2-butenal, and methyl vinyl ketone at retention times 6.63 min, 9.93 min, 10.48 min, and

13.03 min, respectively. The target compound isoprene was identified in retention time 6.48 min. The peak in retention time, 7.6 min, was detected as chloromethane which could be contamination from chlorine dioxide analysis. Multifunctional organic compounds produced by successive oxidation steps of isoprene may form secondary organic aerosols having climate and public health effects.³⁹ Methyl vinyl ketone was detected as a byproduct of isoprene from atmospheric oxidation by ozone determined by HPLC-MS method¹⁵.

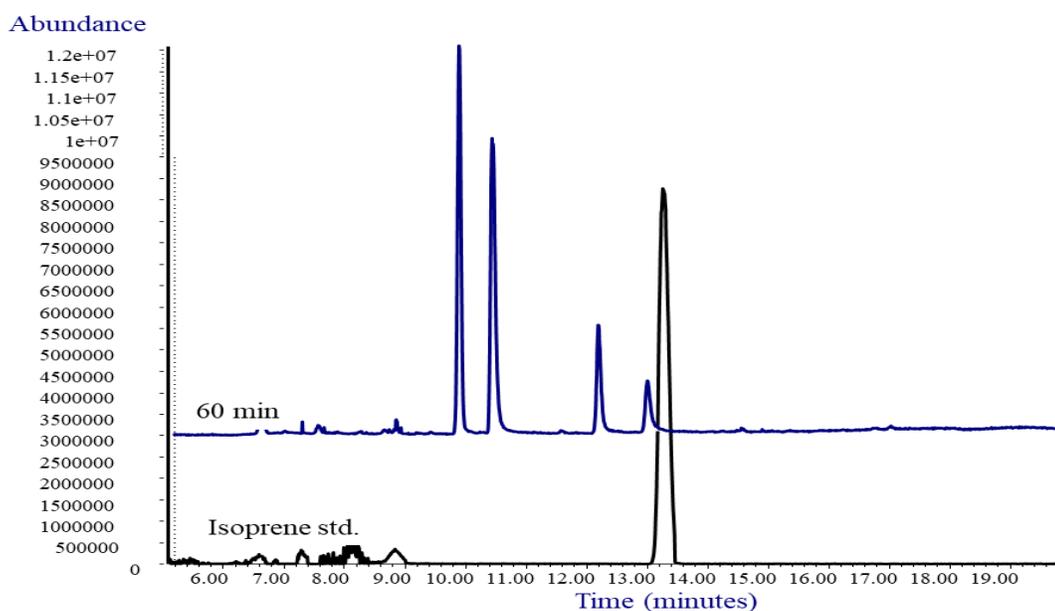


Figure 24: GC-MS overlay chromatograms of treated and untreated isoprene. A 13.5 ppm of isoprene gas sample was treated with 28 ppm of ozone. The peak at retention time 13.25 min is isoprene and peaks at the retention times 6.65 min, 9.92 min, 10.48 min, 12.22 min and 13.03 min are ethanol, 1,4-pentadiene, acetone, 2-butenal and methyl vinyl ketone respectively.

3.1.7 Degradation of 2,3-butanedione with chlorine dioxide

Degradation of 2,3-butanedione by ozone was studied by FTIR analysis which helps to understand the degradation rate and the reaction efficiency of chlorine dioxide with 2,3-butanedione. 15.5 ppm of 2,3-butanedione gas sample was prepared and treated with 30 ppm of chlorine dioxide. Figure 9a shows the degradation of 2,3-butanedione by Chlorine dioxide where the range of 1060-1140 cm^{-1} indicates the 2,3-butanedione spectra and the range of 1050-1150 cm^{-1} indicates the chlorine dioxide spectra. The total reaction time was about 60 mins. The concentration of 2,3-butanedione was reduced to 10.5 ± 0.3 ppm after 120 minutes of treatment with chlorine dioxide and in the same time concentration of chlorine also reduced where the concentration of ozone was reduced to 17.1 ± 0.6 ppm after 120 minutes of reaction.

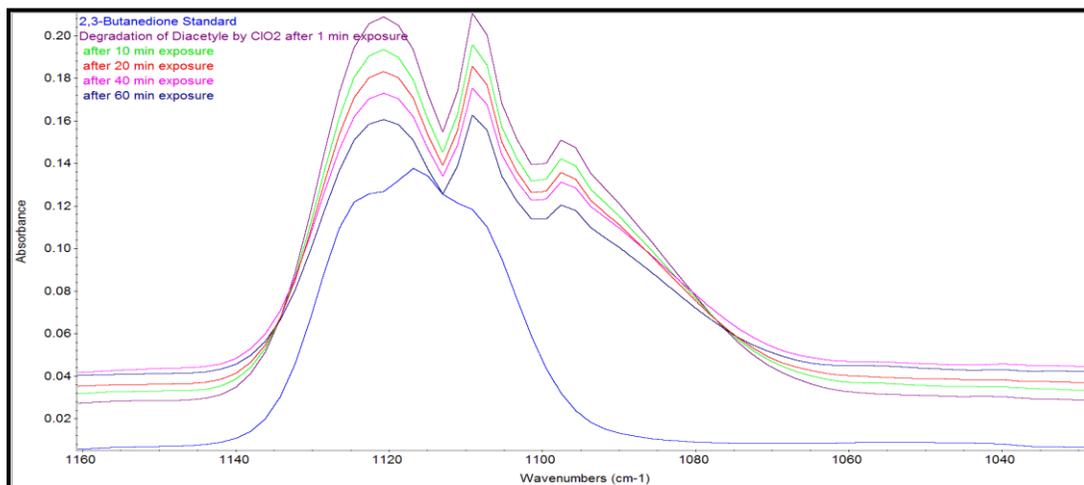


Figure 25: Comparison of FTIR spectra of 2,3-butanedione reacting with chlorine dioxide after different treatment periods. A peak in the range of 1080-1160 cm^{-1} represent the 2,3-butanedione and range of 1050-1150 cm^{-1} indicates the spectra of chlorine dioxide. A 15.5 ppm sample of 2,3-butanedione was treated with 30.7 ppm of chlorine dioxide in various time. The concentration of 2,3-butanedione and chlorine dioxide reduced to 10.5 ± 0.3 ppm and 17.1 ± 0.6 ppm after 120 minutes of reaction time respectively.

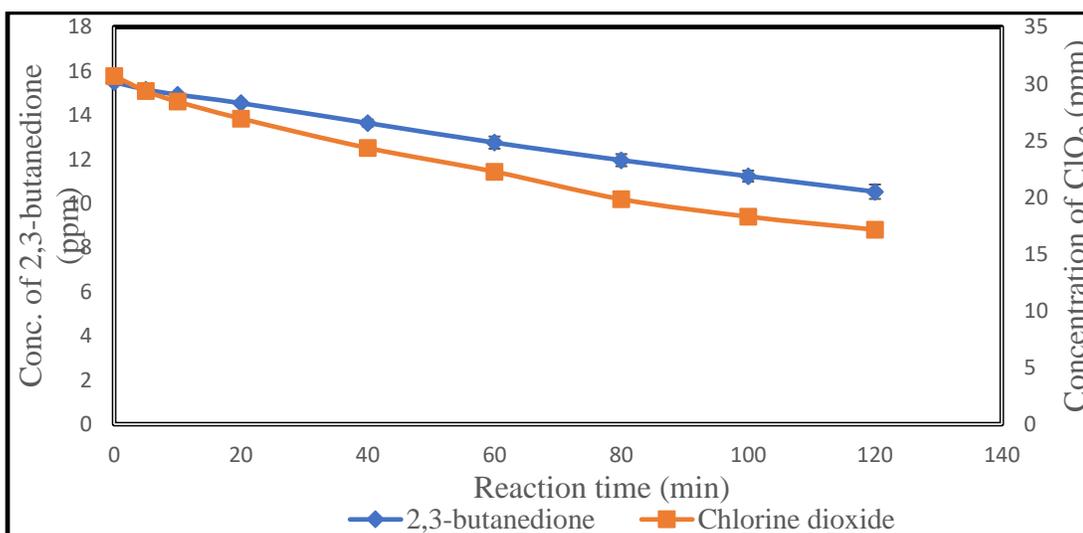


Figure 26: Plots showing decreasing concentration of 2,3-butanedione and chlorine dioxide as a function of their reaction time at room temperature. An initial concentration of 15.5 ppm of 2,3-butanedione was treated with 30.7 ppm of chlorine dioxide. The left and right Y-axes denote the concentrations of 2,3-butanedione and chlorine dioxide, respectively.

GC-MS analysis of 2,3-butanedione treated by chlorine dioxide was performed to study the by-products produced during the degradation process. A 15.5 ppm sample of 2,3-butanedione was treated with 25 ± 5 ppm of chlorine dioxide. The reaction was run up to 180 mins and 48% of 2,3-butanedione was broken down into other by-products after this time period. The overlay chromatograms of both treated and untreated 2,3-butanedione are shown in Figure 27 below. NIST search of treated spectra of 2,3-butanedione by chlorine dioxide tentatively identified dimethyl ether and formic acid as reaction by-products at retention times 3.76 min and 4.58 min, respectively. The peak at retention time 6.0 min was identified as chlorine dioxide which is an oxidative agent used for the degradation of 2,3-butanedione. The target compound 2,3-butanedione was detected in retention time 11.03 min in both treated and untreated compound spectra.

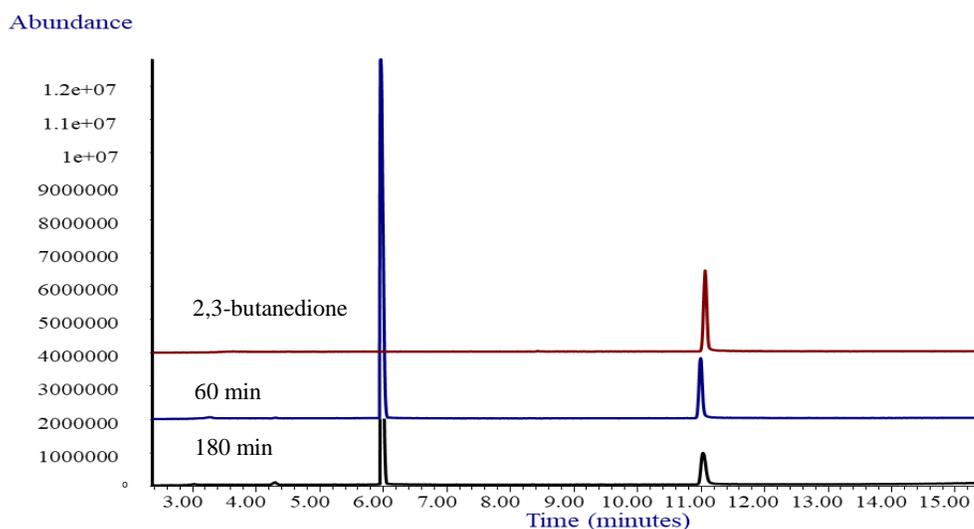


Figure 27: GC-MS overlay chromatograms of treated and untreated of 2,3-butanedione samples. A 15.5 ppm of 2,3-butanedione gas sample was exposed with 30.7 ppm of chlorine dioxide. The peak at retention time 11.15 min is 2,3-butanedione and peaks at the retention times 4.8 min and 6.0 min are dimethyl ether and chlorine dioxide respectively.

3.1.8 Degradation of 2,3-butanedione with ozone

Degradation of 2,3-butanedione by ozone was studied by FTIR analysis which helps to understand the degradation rate and the reaction efficiency of ozone with 2,3-butanedione. A gas sample of 15.5 ppm of 2,3-butanedione was prepared and treated with 30 ppm of ozone. Figure 14 shows the degradation of 2,3-butanedione by ozone where the range of 1080-1180 cm^{-1} indicates the 2,3-butanedione spectra and the range of 980-1080 cm^{-1} indicates the ozone spectra. The total reaction time was about 100 mins and degradation of 2,3-butanedione was very apparent after 100 minutes with ozone. The concentration of 2,3-butanedione was reduced to 12.3 ± 0.8 ppm after 100 minutes of treatment with ozone, and in the same time, the concentration of ozone was also reduced to 19.5 ± 0.5 ppm after 100 minutes of reaction.

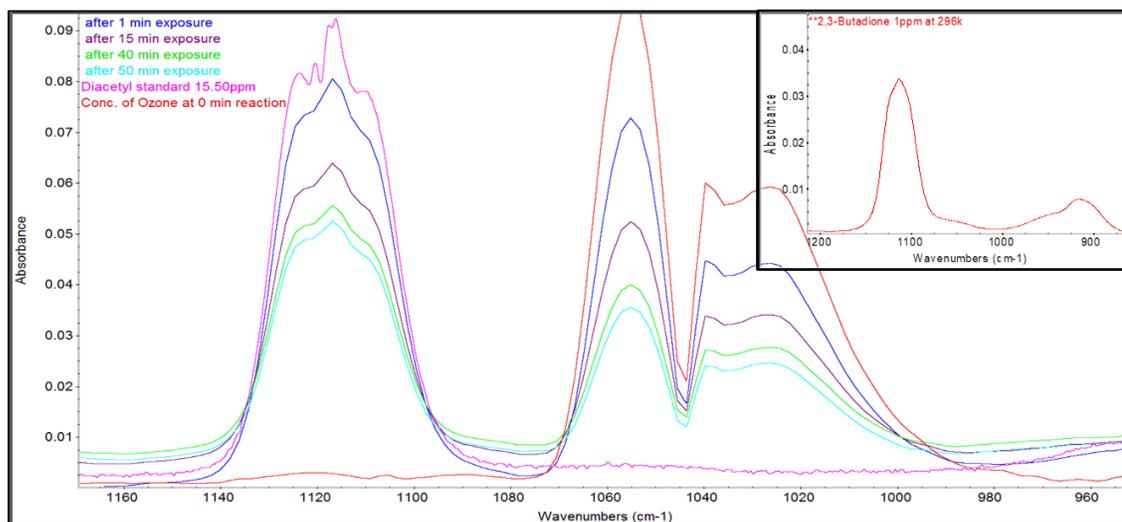


Figure 28: Comparison of FTIR spectra of 2,3-butanedione reacting with ozone after different treatment periods. A peak in the range of 1080-1160 cm^{-1} represent the 2,3-butanedione and range of 980-1080 cm^{-1} indicates the spectra of ozone. A 15.5 ppm sample of 2,3-butanedione was treated with 29.7 ppm of ozone. The concentration of 2,3-butanedione and ozone reduced to 12.3 ± 0.1 ppm and 19.5 ± 0.5 ppm after 100 minutes of reaction. The NIST standard spectra of 2,3-butanedione has shown above the right corner of the Figure 28.

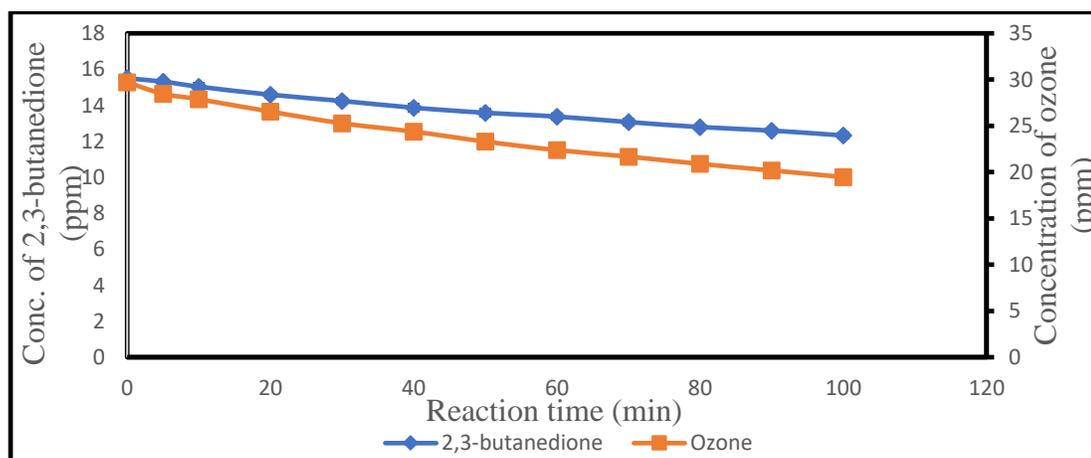


Figure 29: Plots showing decreasing concentrations of 2,3-butanedione and ozone as a function of their reaction time at room temperature. The initial reaction mixture was 15.5 ppm of 2,3-butanedione gas treated with 29.7 ppm of ozone. The left and right Y-axes denote the concentrations of 2,3-butanedione and ozone, respectively.

For the analysis reaction products of 2,3-butanedione and ozone, GC-MS analysis was performed at different reaction times. A 15.5 ppm sample of 2,3-butanedione gas sample was exposed with 25 ± 5 ppm of ozone and continued up to 250 minutes. Ozonation of 2,3-butanedione degraded 48% of this compound at the 250 min interval. The overlay chromatograms of treated and untreated spectra are shown in Figure 30. Primarily identified by-products of 2,3-butanedione were formic acid, 1,3-butadiene, acetone and acetic acid which appeared at retention times 5.26 min, 5.79 min, 7.68 min and 11.65 min respectively. The peak at retention time 6.41 min was identified as bromo-methane which might be contaminated from bromine compound. The compound 2,3-butanedione was identified at retention time 10.02 min in both treated and untreated sample spectra. The mass spectra of formic acid, acetone, and 1,3-butadiene are shown in the appendix, which were compared with NIST search library.

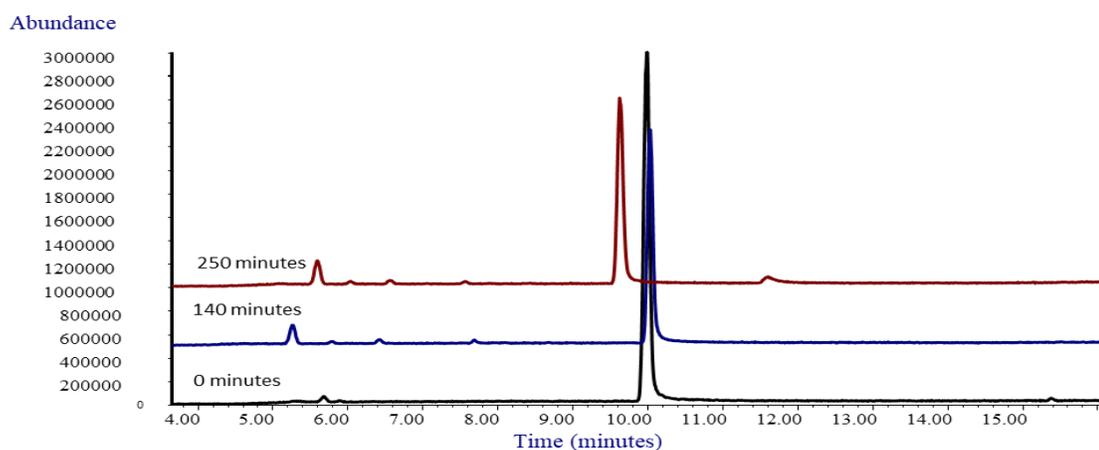


Figure 30: GC-MS overlay chromatograms of treated and untreated 2,3-butanedione. A 15.5 ppm sample of 2,3-butanedione gas was treated with 29.7 ppm of ozone. The peak at retention time 10.05 min is 2,3-butanedione and the peaks at the retention times of 5.25 min, 5.79 min, 6.41 min, 7.68 min, and 11.65 min are formic acid, bromomethane, acetone and acetic acid respectively.

3.1.9 Degradation of 1,1,2-trichloroethane with chlorine dioxide

In order to study the reactivity of chlorine dioxide with 1,1,2-trichloroethane FTIR analysis was performed. The peaks appeared in the range of 700-1000 cm^{-1} and 1000-1150 cm^{-1} which indicated 1,1,2-trichloroethane compounds and chlorine dioxide spectra respectively (Figure 31). A 13.7 ppm of 1,1,2-trichloroethane gas sample was prepared and exposed with 30 ppm of chlorine dioxide. After 100 mins of treatment, the remaining concentration of 1,1,2-trichloroethane was 8.40 ± 0.4 ppm (Figure 32) and the concentration of chlorine dioxide was 13.3 ± 0.6 ppm.

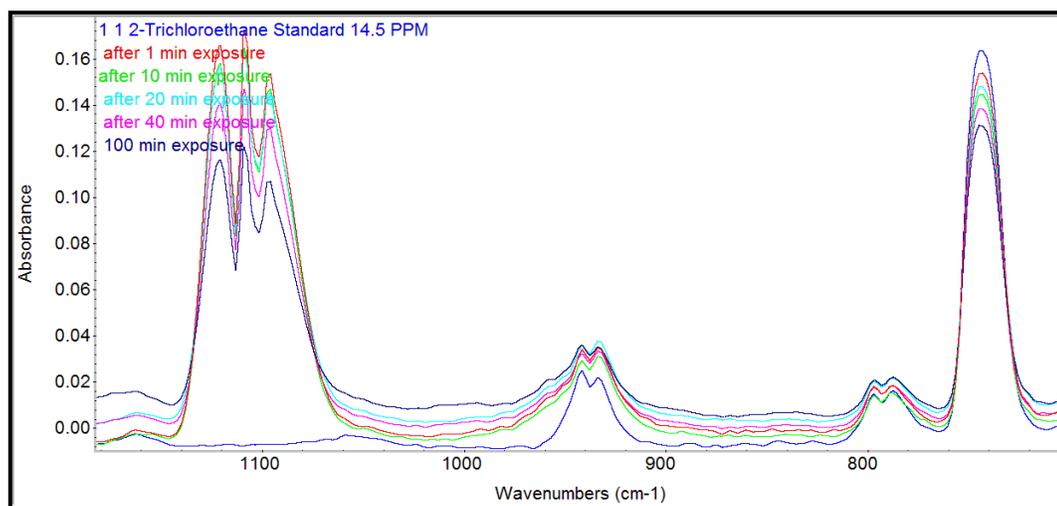


Figure 31: Comparison of FTIR spectra of 1,1,2-trichloroethane with chlorine dioxide after different treatment periods. A peak in the range of 700-1000 cm^{-1} represent the 1,1,2-trichloroethane and range of 1050-1150 cm^{-1} indicates the spectra of Chlorine dioxide. A 13.7 ppm of 1,1,2-trichloroethane gas sample was treated by 26.6 ppm of chlorine dioxide for different time interval. The concentration of 1,1,2-trichloroethane and chlorine dioxide were 8.4 ± 0.4 ppm and 13.3 ± 0.7 ppm after 100 min respectively.

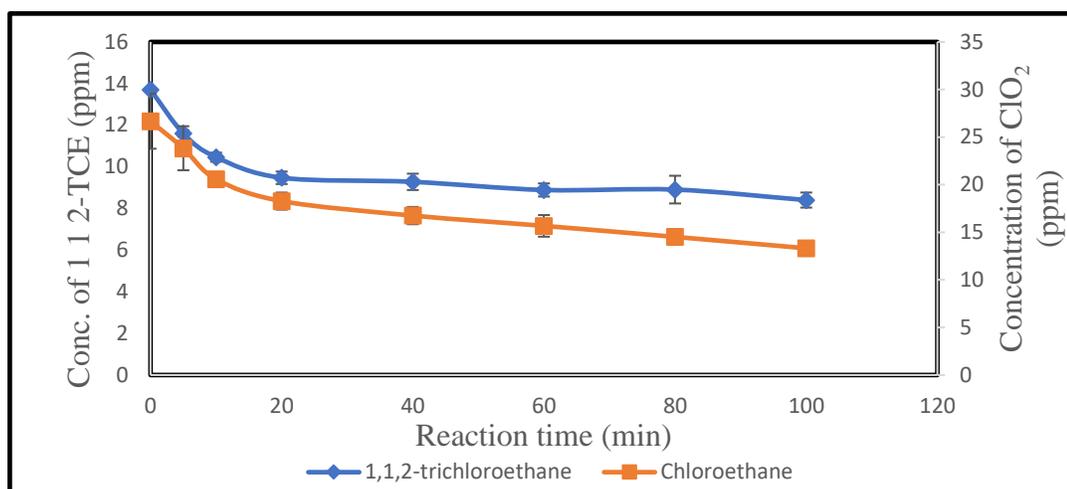


Figure 32: Plots showing decreasing concentration of 1,1,2-trichloroethane and chlorine dioxide as a function of their reaction time at room temperature. The initial reaction mixture was 13.7 ppm of 1,1,2-trichloroethane gas treated with 26.7 ppm of chlorine dioxide. The left and right Y-axes denote the concentrations of 1,1,2-trichloroethane and chlorine dioxide, respectively.

To study the reaction by-products of 1,1,2-trichloroethane treated by chlorine dioxide, a GC-MS analysis was performed. A gas phase sample of 13.7 ppm of 1,1,2-trichloroethane was prepared and exposed with chlorine dioxide. The reaction was carried out up to 180 minutes to see the reaction products during this time period. The total ion chromatograms indicated that only 14% of 1,1,2-trichloroethane degraded into other by-products with 30 ppm of chlorine dioxide at the 180 min interval. The peak of target compound 1,1,2-trichloroethane appeared at the retention time of 16.84 min and the chlorine dioxide peak is at 6.12 min. According to the FTIR study, chlorine dioxide was less reactive with 1,1,2-trichloroethane. The primarily identified by-products in this

reaction were dimethyl ether and ethyl ester carbon chloridic acid which appeared at the retention times of 4.54 min and 15.34 min, respectively.

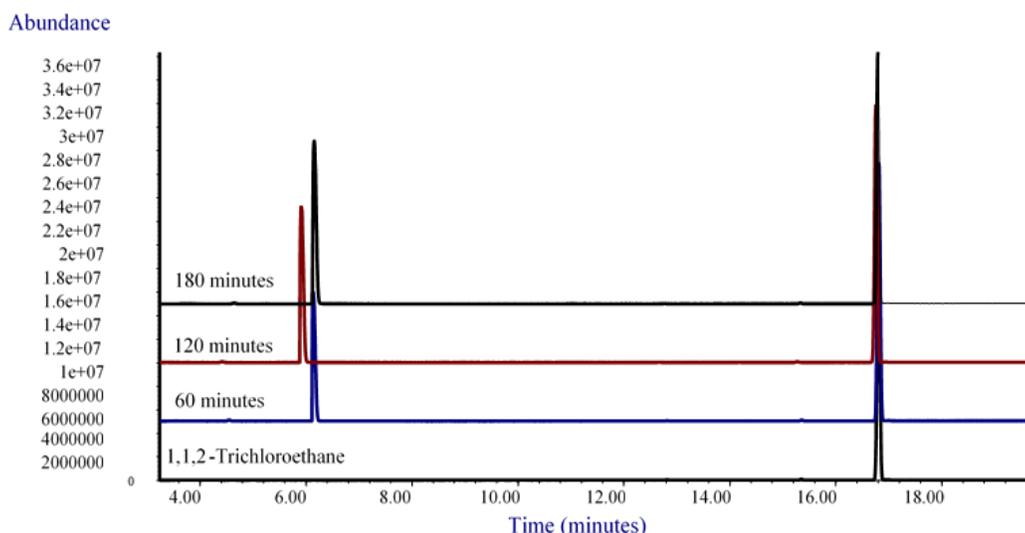


Figure 33: GC-MS overly chromatograms of treated and untreated 1,1,2-trichloroethane samples. A 13.7 ppm of 1,1,2-trichloroethane gas sample was exposed by 30 ppm of chlorine dioxide. The peak at retention time 17.0 min is the 1,1,2-trichloroethane compound and peaks in retention time 4.63 min, 6.23 min and 15.33 min are dimethyl ether, chlorine dioxide and ethyl ester carbon chloridic acid respectively.

3.1.10 Degradation of 1,1,2-trichloroethane with ozone

To study the reactivity of ozone with 1,1,2-trichloroethane FTIR analysis was performed. The peaks appeared in the range of 700-980 cm^{-1} which indicated 1,1,2-trichloroethane compounds, and ozone spectra is in the range of 980-1080 cm^{-1} . A gas sample of 13.7 ppm of 1,1,2-trichloroethane was prepared and exposed with 30.91 ppm of ozone. After 60 mins of treatment the remaining concentration of 1,1,2-trichloroethane was 7.5 ± 0.5 ppm and the concentration of ozone was 16.8 ± 2.3 ppm. Besides ozone, there

many other oxidants, such as persulfate, Fenton's reagent, permanganate, that are used for the degradation of volatile organic compounds like 1,1,2-trichloroethane.⁴⁰ Sodium persulfate was able to degrade 2% of 1,1,2-trichloroethane at 40 degrees Celsius during a 72 hour period whereas ozone showed better degradation results, which degraded about 54.7% at a normal temperature during an one hour period.⁴⁰

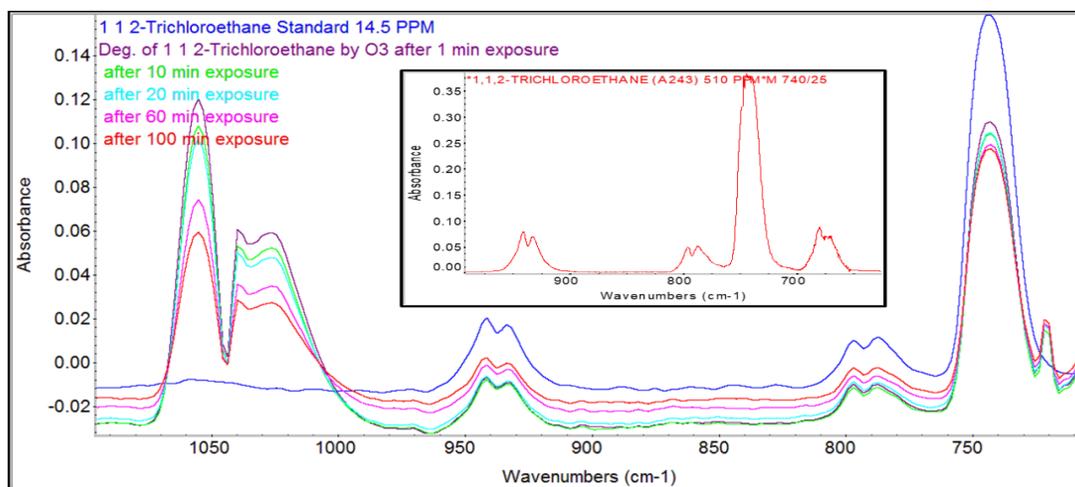


Figure 34: Comparison of FTIR spectra of 1,1,2-trichloroethane oxidized by ozone after different treatment periods. A peak in the range of 980-700 cm^{-1} represent the 1,1,2-trichloroethane and range of 980-1080 cm^{-1} indicates the spectra of ozone. A 13.7 ppm of 1,1,2-trichloroethane gas sample was treated with 30.91 ppm of ozone. The concentration of 1,1,2-trichloroethane and ozone reduced to 7.5 ± 0.5 ppm and 16.8 ± 2.3 ppm after 60 minutes of reaction respectively.

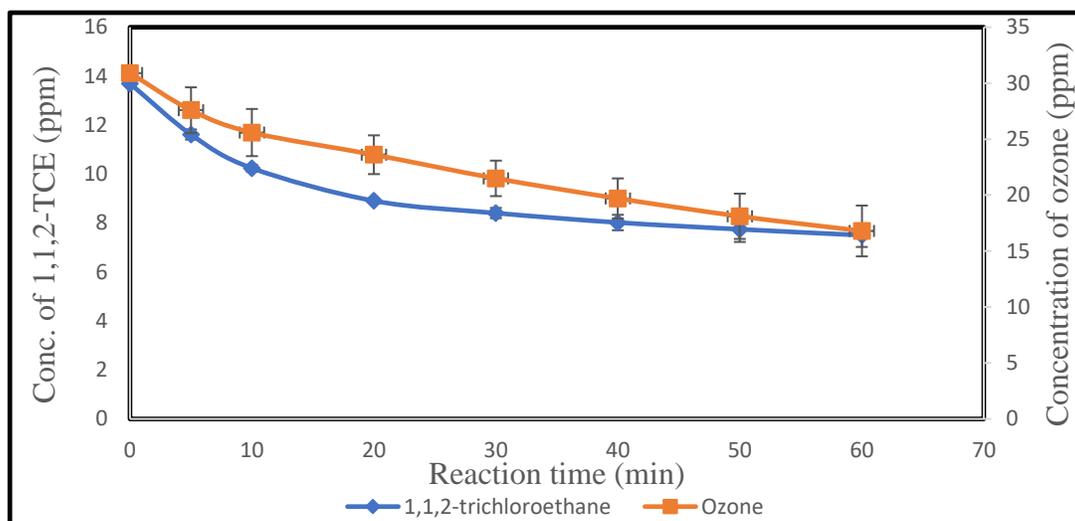


Figure 35: Plots showing decreasing concentration of 1,1,2-trichloroethane and ozone as a function of reaction time at room temperature. An initial concentration of 13.7 ppm 1,1,2-trichloroethane was treated with 30.91 ppm of ozone. The left and right Y-axes denote the concentrations of 1,1,2-trichloroethane and ozone, respectively.

Degradation by-products of 1,1,2-Trichloroethane treated by ozone were studied by GC-MS analysis. A 13.7 ppm of 1,1,2-Trichloroethane gas sample was prepared and treated with 25 ± 5 ppm of ozone in different time points and 35% of this compound was degraded within 80 min of reaction time with chlorine dioxide. The tentatively identified by-product from this oxidation reactions are methylene chloride, trichloro methane, 1,2-dichloroethane, and phosgene gas which detected in retention time 9.13 min, 11.84 min, 12.91 min, and 15.47 min, respectively. The target compound 1,1,2-trichloroethane was identified at retention time 16.91 min from both of treated and untreated sample spectra. Mass spectra search from NIST library and retention index vs retention time linearity relation was compared to confirm the reaction by-products for this analysis.

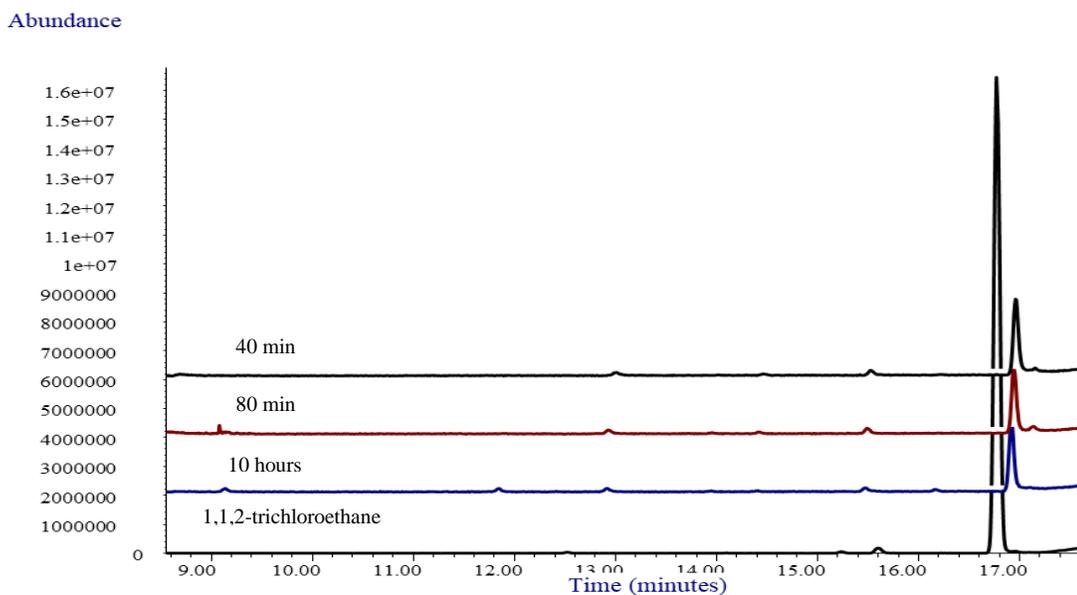


Figure 36: GC-MS overlay chromatograms of treated and untreated 1,1,2-trichloroethane. A gas sample of 13.7 ppm 1,1,2-trichloroethane was treated by 30.91 ppm of ozone. The peak at retention time 16.9 is the 1,1,2-trichloroethane and peaks at retention times 9.13 min, 11.84 min, 12.47, and 15.47 min are primarily detected by-products respectively

3.1.11 Degradation kinetics study of selected compounds with chlorine dioxide and ozone by FTIR analysis

Oxidation of dimethyl trisulfide, 1-bromopropane, isoprene, 2,3-butanedione, and 1,1,2-trichloroethane by chlorine dioxide and ozone were analyzed using Varian 7000 FTIR with MCT (Mercury Cadmium-Telluride) detector. Experiments were conducted between 25 ± 5 ppm of chlorine dioxide and different initial concentrations of those selected target compounds at room temperature. The $\ln[A]/[A^0]$ vs Time graphs were plotted for the first order reaction determination, where the x-axis represents the reaction time and the y-axis represents the $\ln[A]/[A^0]$. On the other hand, $1/[A]$ vs Time line

graphs were drawn for studying the second order reaction kinetics, where the x-axis indicated the reaction time and the y-axis represented the inverse concentration of target compounds. The linear correlation coefficient (r^2 value) demonstrated the reaction order for the degradation of different target compounds by using chlorine dioxide and ozone. The following formulas were used to determine the rate constant (K) and half-life ($t_{1/2}$) of these reactions.

$$K = -\text{slope} \dots \dots \dots (i)$$

$$t_{1/2} (1^{\text{st}} \text{ Order}) = 0.693/K \dots \dots \dots (ii)$$

$$t_{1/2} (2^{\text{nd}} \text{ Order}) = 1/K[A] \dots \dots \dots (iii)$$

The rate constant for the first order reaction kinetics of 1-bromopropane, isoprene and 2,3-butanedione by chlorine dioxide oxidations are 0.0128 min^{-1} , 0.02244 min^{-1} and 0.00546 min^{-1} with half-lives of 54 min, 31 min and 126 min respectively. The ozonation of isoprene and 2,3-butanedione also follow the first order reaction kinetics, having rate constants of 0.4051 min^{-1} and 0.0026 min^{-1} with half-lives of 2 min and 266 min respectively. The degradation of dimethyl trisulfide and 1,1,2-trichloroethane follow the second order reaction kinetics with both oxidants, chlorine dioxide and ozone. The half-lives of dimethyl trisulfide by chlorine dioxide and ozone oxidation are 2.2 min and 24 min respectively; half-lives for 1,1,2-trichloroethane are 58 min and 43 min with chlorine dioxide and ozone. The second order rate constant for the ozonation of 1-bromopropane is $0.000489 \text{ ppm}^{-1} \text{ min}^{-1}$ with half-life of 141 min.

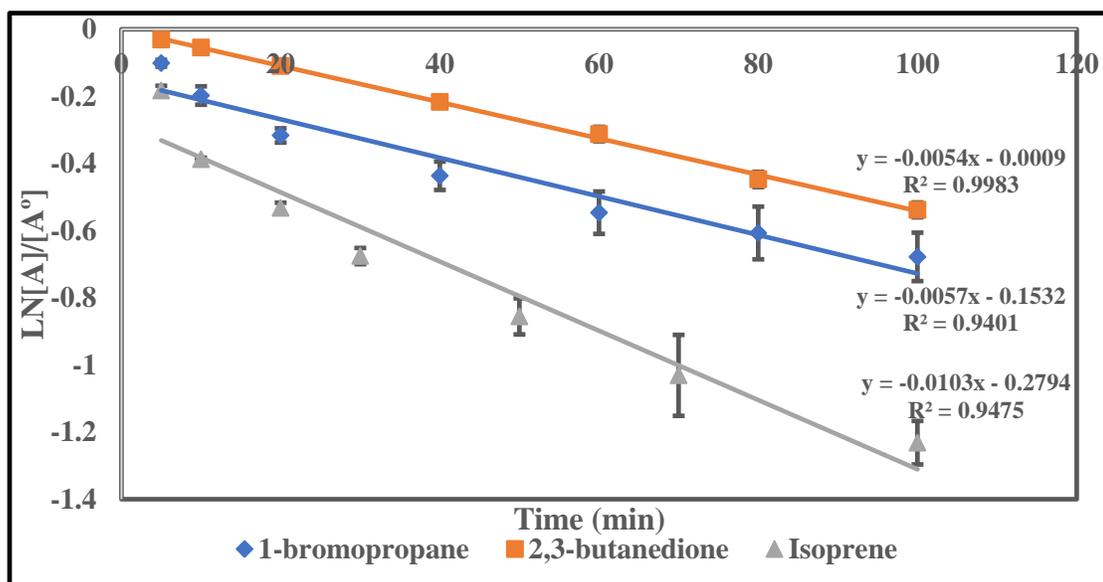


Figure 37: Plot of $\ln[A]/[A^\circ]$ vs Reaction Time (min) at time-dependent reaction concentration of the compounds at room temperature. The first order reaction kinetics for the degradation of 1-bromopropane, 2,3-butanedione and isoprene treated with chlorine dioxide.

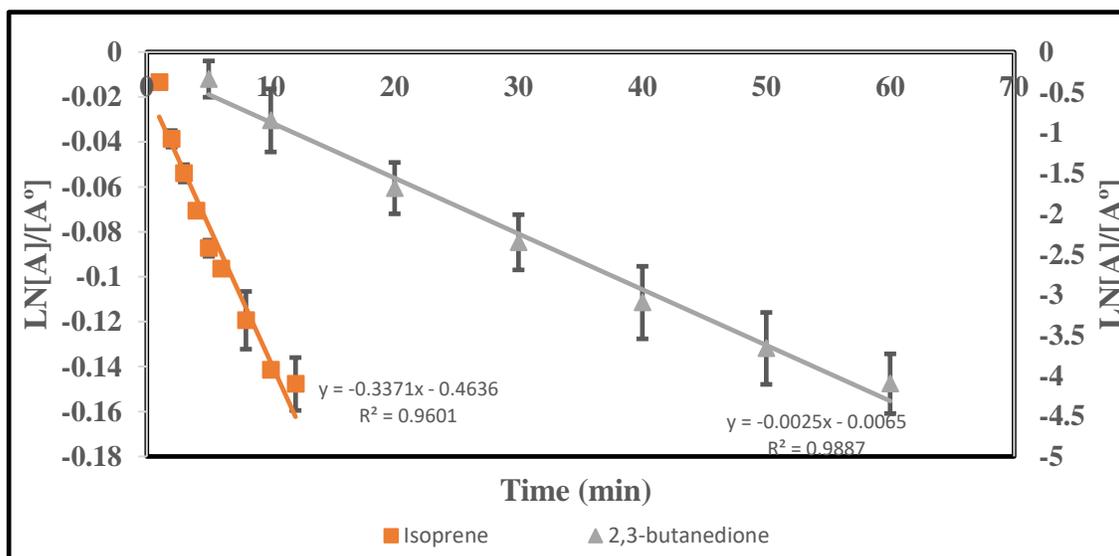


Figure 38: Plot of $\ln[A]/[A^\circ]$ vs Reaction Time (min) at time-dependent reaction concentration of the compounds at room temperature. The first order reaction kinetics for the degradation of 2,3-butanedione and isoprene treated with ozone.

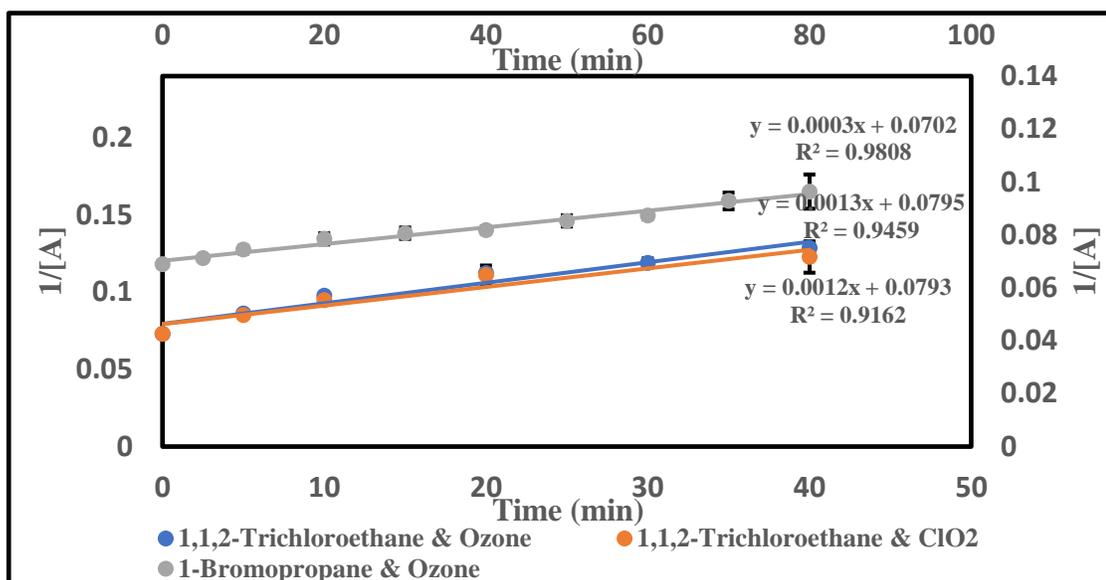


Figure 39: Plot of $1/[A]$ vs Reaction Time at time dependent concentration of compounds at room temperature. The second order reaction kinetics for the degradation of 1-bromopropane and 1,1,2-trichloroethane treated by ozone and chlorine dioxide treatment of 1,1,2-trichloroethane.

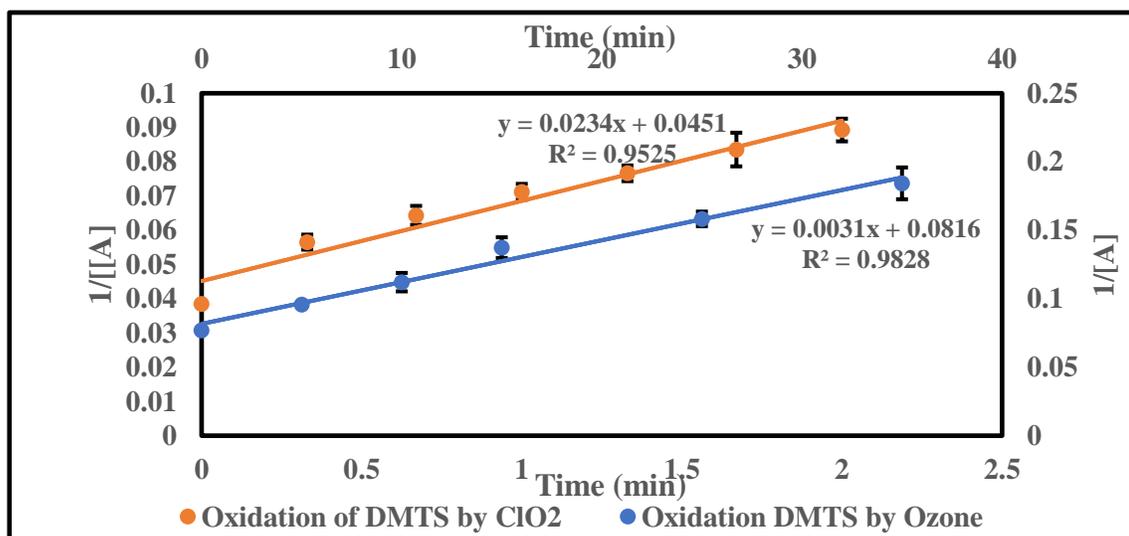


Figure 40: The plot of $1/[A]$ vs Reaction Time (min) in time-dependent concentration of compounds at room temperature. The second order reaction kinetics for the degradation of dimethyl trisulfide treated by ozone and chlorine dioxide.

CHAPTER 4

CONCLUSION

Toxic and odorous volatile organic compounds (VOCs) in the workplace or from natural sources may cause chronic disease or adverse effects in humans. It is therefore necessary to remove or reduce such kinds of atmospheric contaminants. The chemical degradation of harmful VOCs by using oxidants like chlorine dioxide or ozone could be a useful method for preventing or reducing the undesirable human exposure to toxicants. So, it is important to investigate the feasibility of chlorine dioxide and ozone as gas phase oxidants and to evaluate the degradation characteristics of dimethyl trisulfide, isoprene, 1-bromopropane, 2,3-butanedione, and 1,1,2-trichloroethane in the presence of these oxidants. The results show that dimethyl trisulfide and isoprene were substantially degraded into other by-products, including methane sulfonyl chloride and sulfur dioxide, during oxidation by chlorine dioxide and ozone, respectively. In contrast, 1-bromopropane, 2,3-butanedione and 1,1,2-trichloroethane have slow reaction kinetics and did not break down completely. Degradation of dimethyl trisulfide by chlorine dioxide and ozone follows the second order kinetics with rate constants of $2.31 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $2.11 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Their respective half-lives of 2.2 min and 24 min indicate that chlorine dioxide is a more effective oxidant compared to ozone. On the other hand, isoprene follows the first order reaction kinetics with rate constant of 0.00675 s^{-1} and 0.000374 s^{-1} and half-lives of 1.73 min and 32 min for degradation using ozone and chlorine dioxide, respectively. The degradation of 2,3-butanedione follow the first order reaction kinetics with half-lives of 126 min and 266

min whereas 1,1,2-trichloroethane follows the second order kinetics with half-lives of 58 min and 43 min by chlorine dioxide and ozone, respectively. The oxidative degradation of 1-bromopropane, dimethyl trisulfide, and 2,3-butanedione by chlorine dioxide were more efficient compared to their reaction with ozone. However, the degradation of isoprene and 1,1,2-trichloroethane showed a greater reactivity toward ozone compared to chlorine dioxide. Though the degradation of 1-bromopropane, 2,3-butanedione, and 1,1,2-trichloroethane have slower reaction rates compared to dimethyl trisulfide and isoprene, the higher concentration of chlorine dioxide and ozone might be efficient to breakdown those compounds completely. Most of the reaction products of oxidative degradation include acetone, ethanol, formic acid, and dimethyl ether that are chemically benign. But there are also by-products such as methane sulfonyl chloride, sulfur dioxide, chloroform, and cyanogen bromide that require further toxicological studies.

To understand the applicability of chlorine dioxide and ozone as oxidants for the degradation of harmful volatile organic compounds, we need to study more additional class of compounds by using these oxidants. Combination of chlorine dioxide and ozone also can be used for the complete destruction of VOCs. Degradation kinetics with high temperature should be studied for rapid destruction of volatile organic compounds.

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Appendix A

Preconcentrator conditions

The Nutech 8900DS preconcentrator consists of 3 traps. The different steps and conditions used are summarized in the Table 1 and Table 2, respectively.

Table 1: Nutech preconcentrator steps

Step N	Steps of Nutech Preconcentrator	Conditions	Time Elapsed (min)
1	Setting Inlet Position	N/A	0:00-1:00
2	Venting	N/A	1:00-1:30
3	Cooling trap 1	-150°C	1:30-2:40
4	Purging the ISTD line	120mL/min	2:40-2:50
5	Loading the ISTD	200mL/min	2:50-3:30
6	Purging the sample line	20mL/min	3:30-4:06
7	Loading sample	100mL/min	4:06-4:40
8	Flushing the line, cooling trap 2	N/A	4:40-5:20
9	Sweeping the trap, cooling trap 2	20mL/min	5:20-6:50
10	Preheating Trap 1	25°C	6:50-7:40
11	Transferring trap 1 to trap 2	50mL/min	7:40-8:20
12	Cooling the cryofocuser	-165°C	8:20-12:30
13	Transferring Trap 2 to cryofocuser	N/A	12:30-13:05
14	Injecting sample into GC	30 seconds	13:05-13:35
15	Trap 2 bakeout	N/A	13:35-19:20
16	GC delay	100mL/min	18:20-40:00

Table 2: Conditions used for Nutech 8900DS preconcentrator

Parameter	Trap 1	Trap 2	Cryofocuser
Cooling temperature	-150°C	-160°C	-165°C
Preheating temperature	25°C	N/A	N/A
Preheating time	20 sec	-150°C	N/A
Desorb temperature	140°C	140°C	N/A
Desorb time	90 sec	90 sec	N/A
Bakeout temperature	183°C	180°C	N/A
Bakeout time	N/A	180 sec	N/A
Injection time	N/A	N/A	30 sec

Appendix B

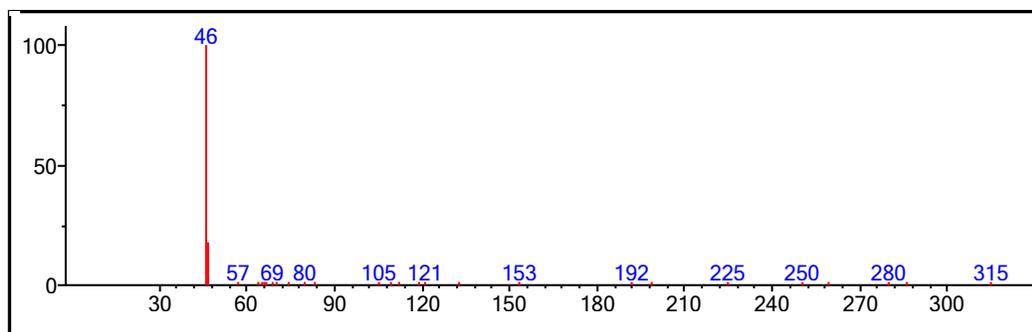


Figure 1: Mass spectrum of formic acid

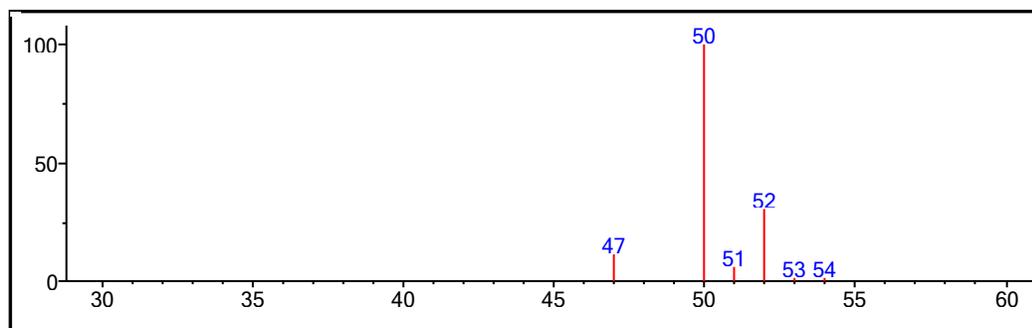


Figure 2: Mass spectrum of Chloromethane

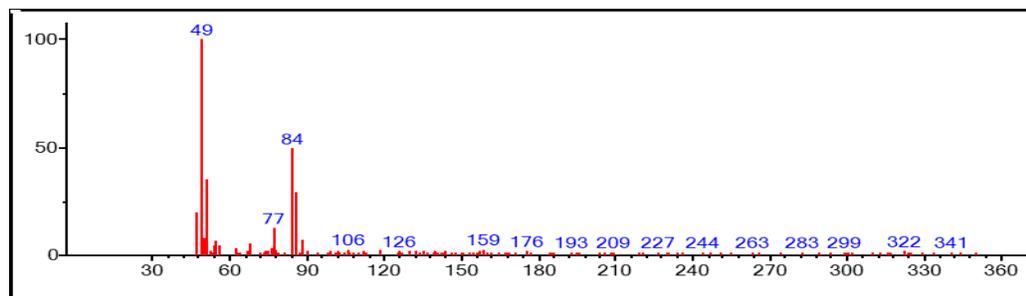


Figure 3: Mass spectrum of methylene chloride

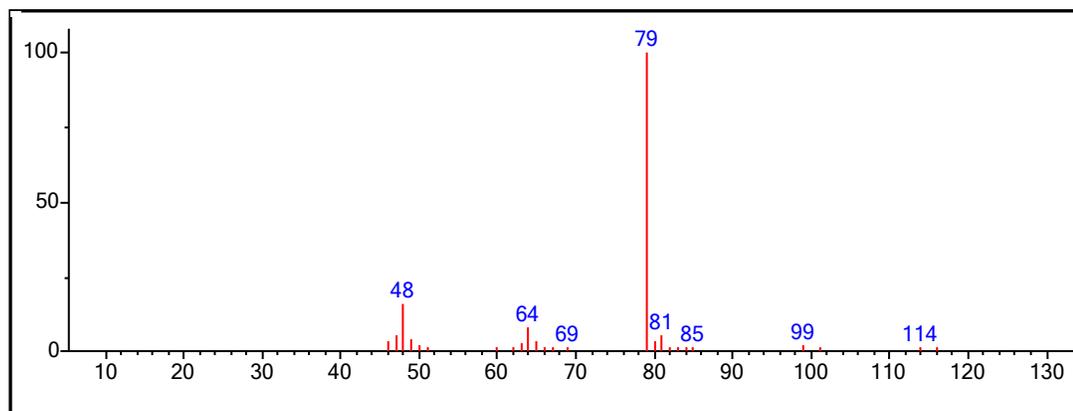


Figure 4: Mass spectrum of methane sulfonyl chloride

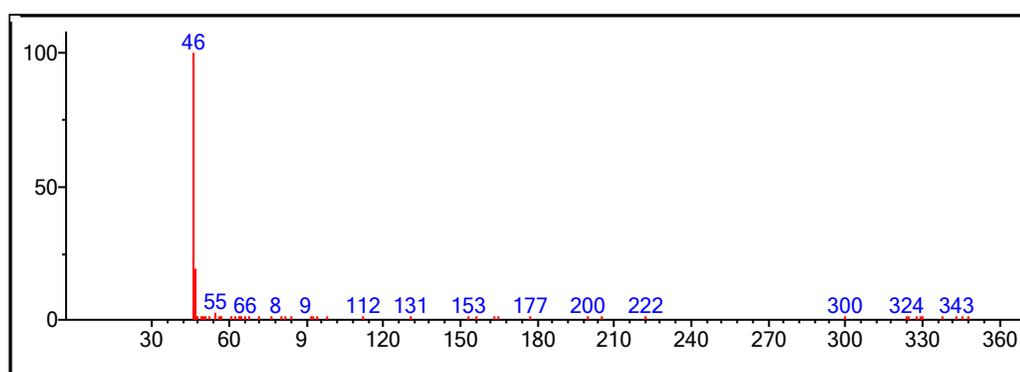


Figure 5: Mass spectrum of Dimethyl ether

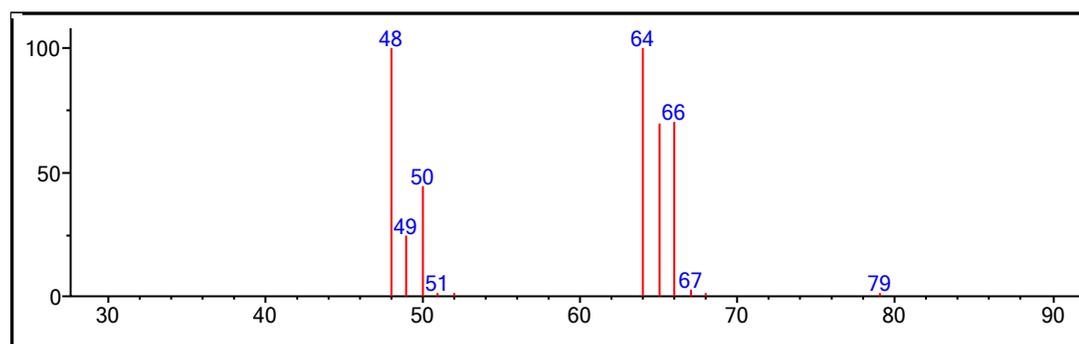


Figure 6: Mass spectrum of sulfur dioxide

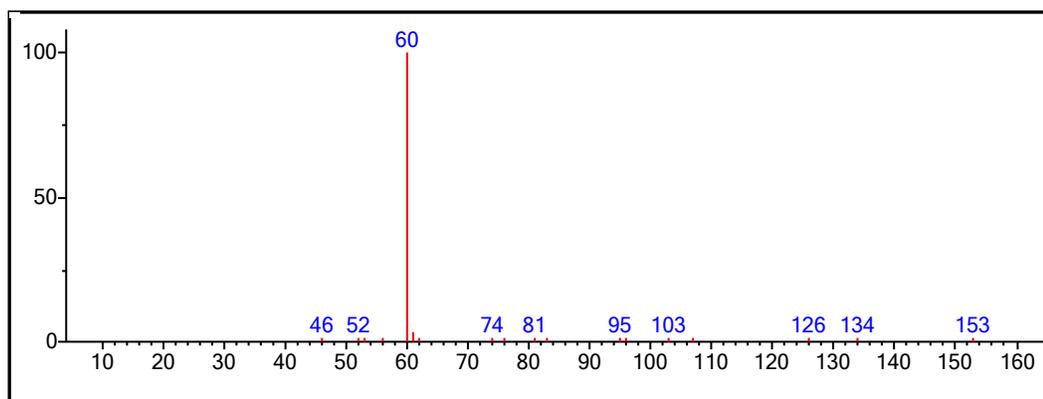


Figure 7: Mass spectrum of methyl formate

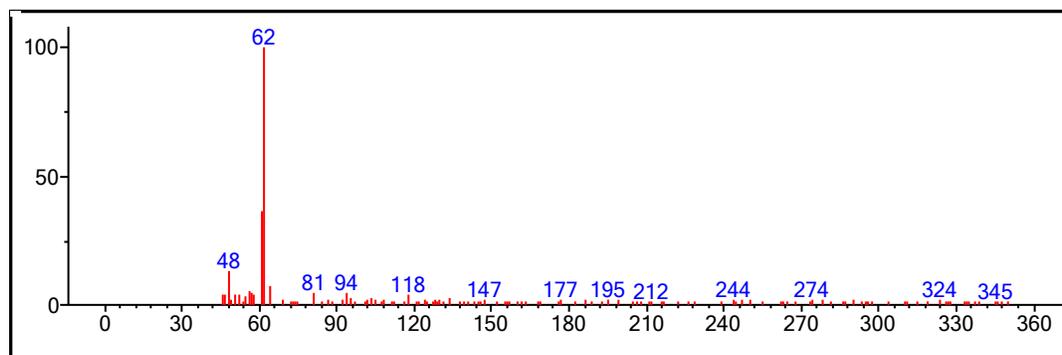


Figure 8: Mass spectrum of dimethyl peroxide

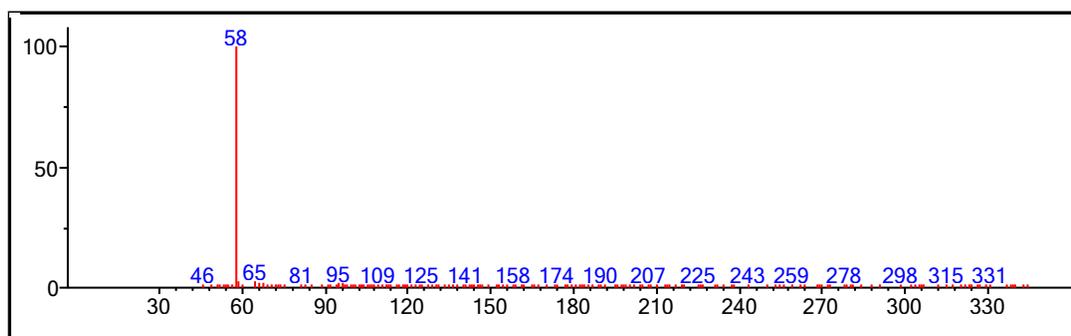


Figure 9: Mass spectrum of acetone

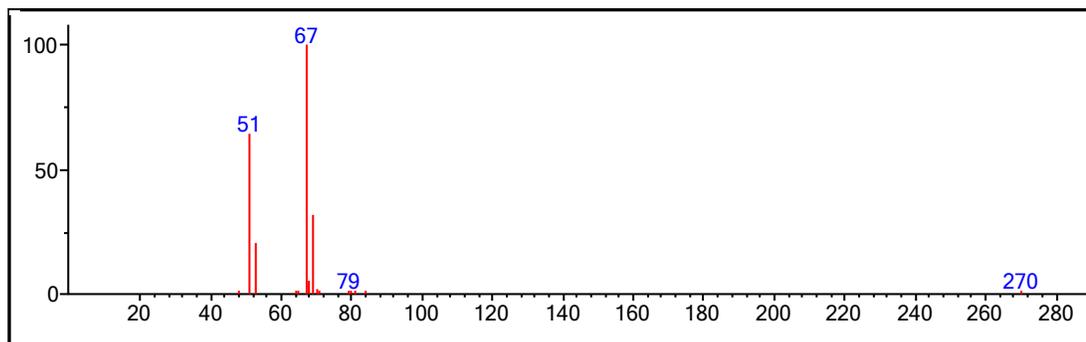


Figure 10: Mass spectrum of chlorine dioxide

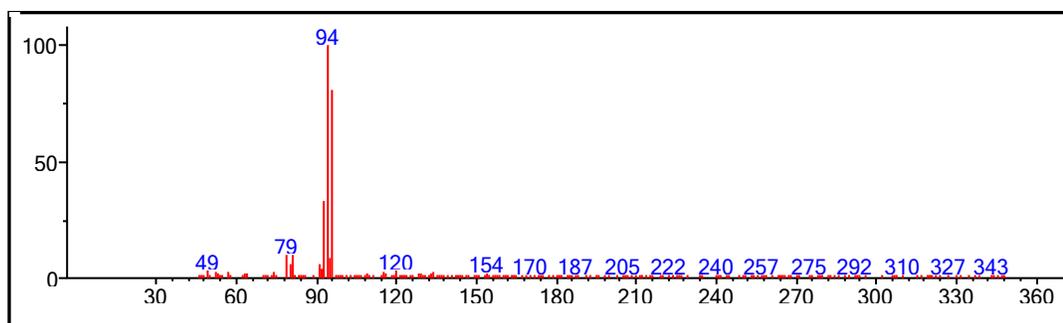


Figure 11: Mass spectrum of bromomethane

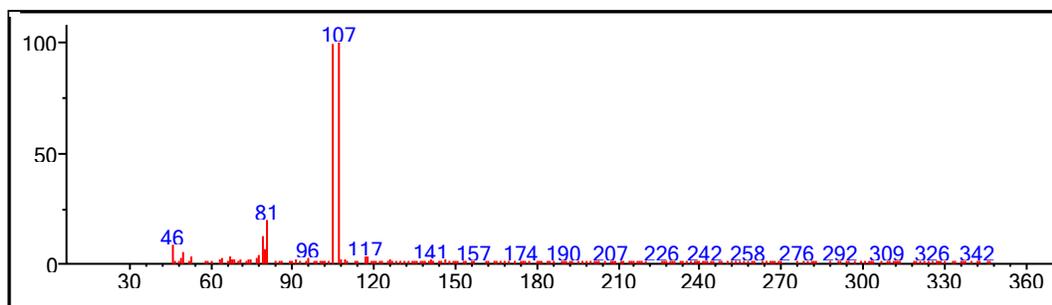


Figure 12: Mass spectrum of cyanogen bromide

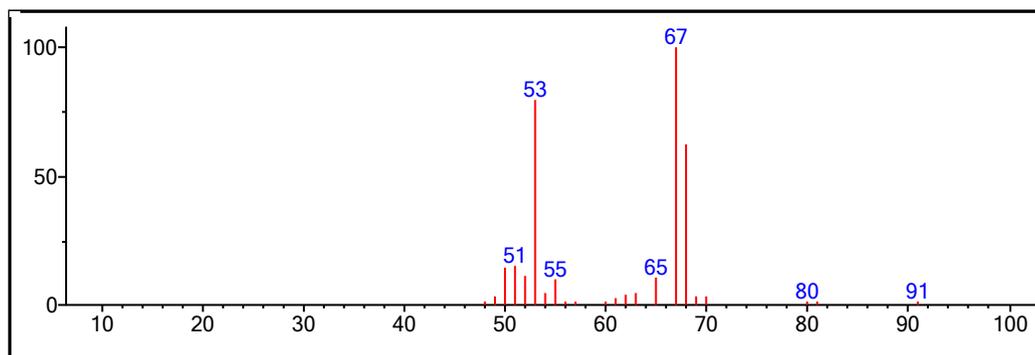


Figure 13: Mass spectrum of 1,3-pentadiene

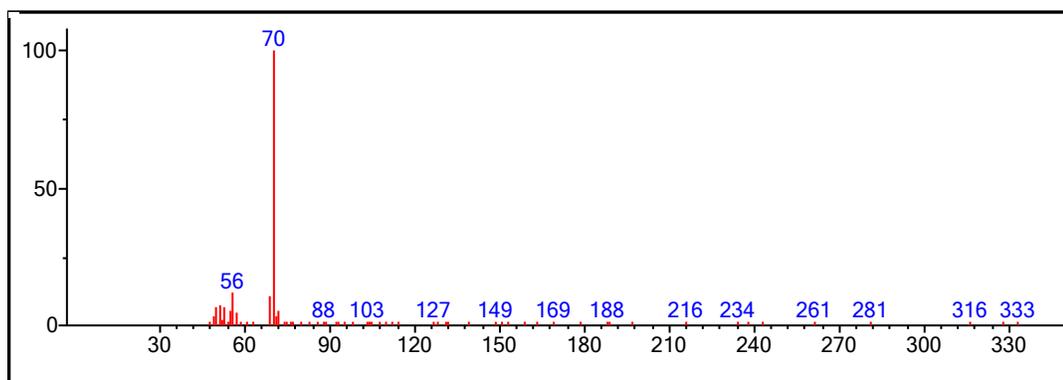


Figure 15: Mass spectrum of 2-butenal

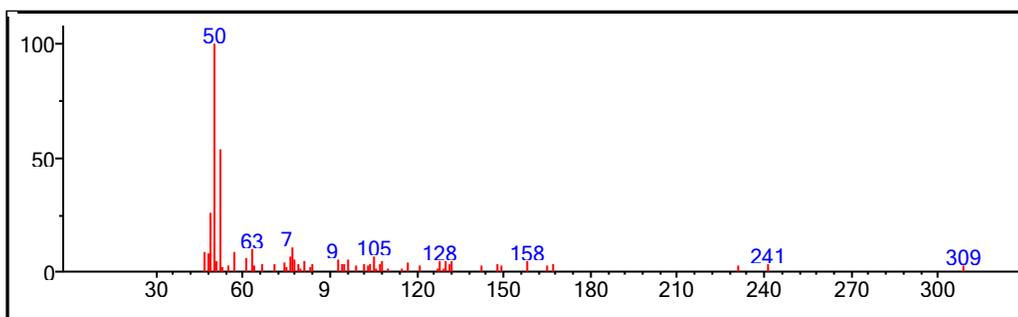


Figure 16: Mass spectrum of chloro-acetaldehyde

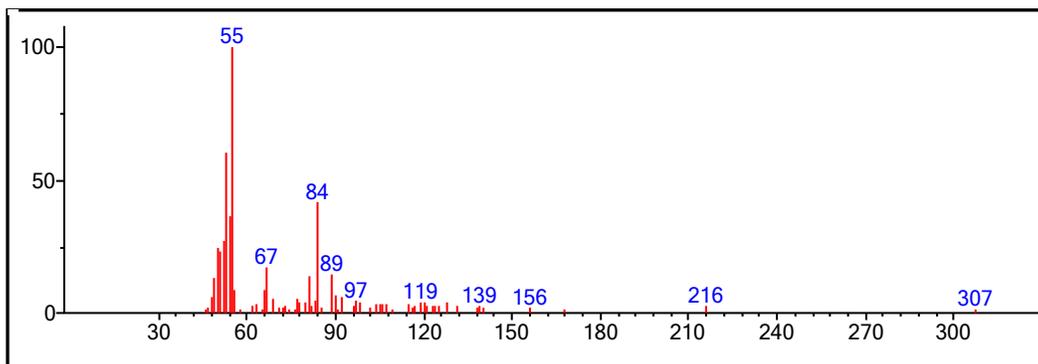


Figure 17: Mass spectrum of 2-methyl 2-butenal

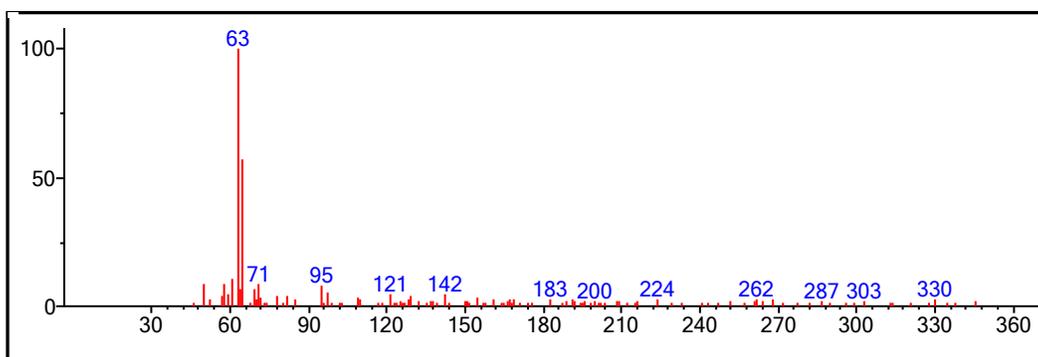


Figure 18: Mass spectrum of Ethyl ester carbon chloridic acid

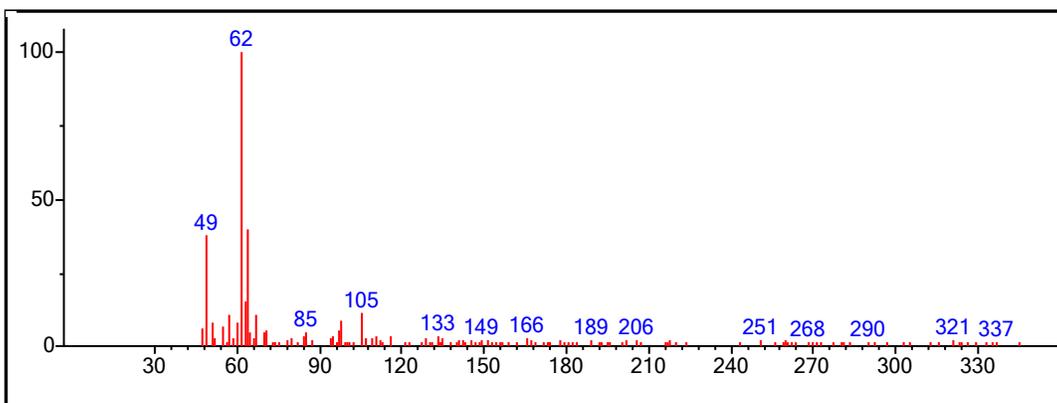


Figure 19: Mass spectrum of 1,2-dichloroethane

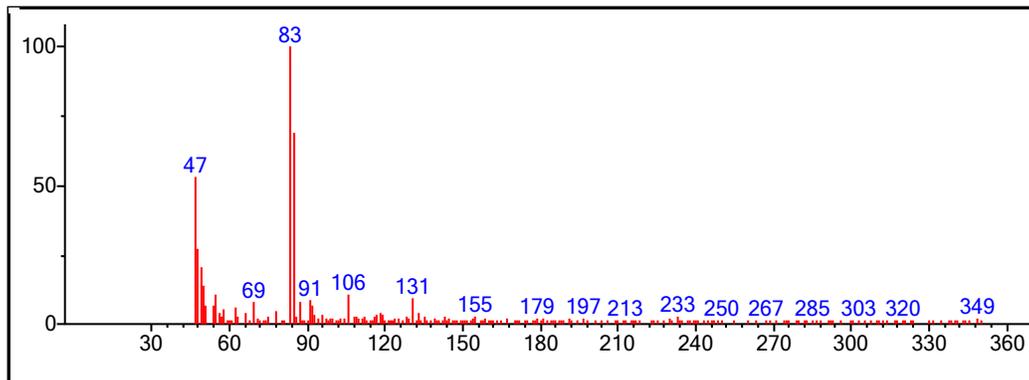


Figure 20: Mass spectrum of tri-chloromethane

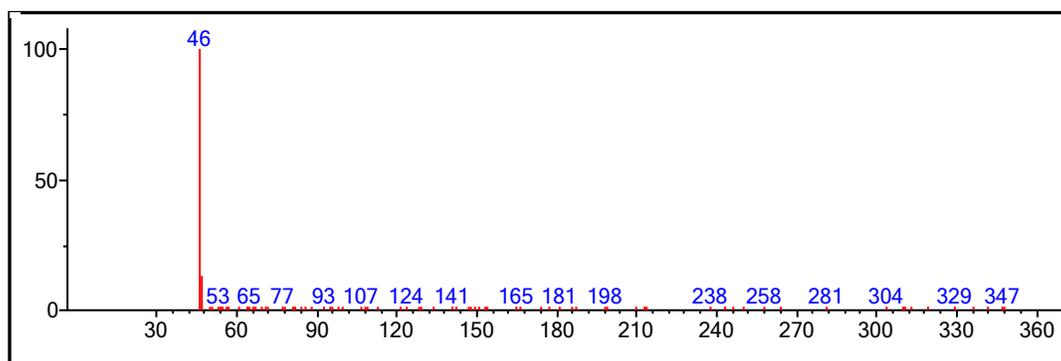


Figure 22: Mass spectrum of ethanol

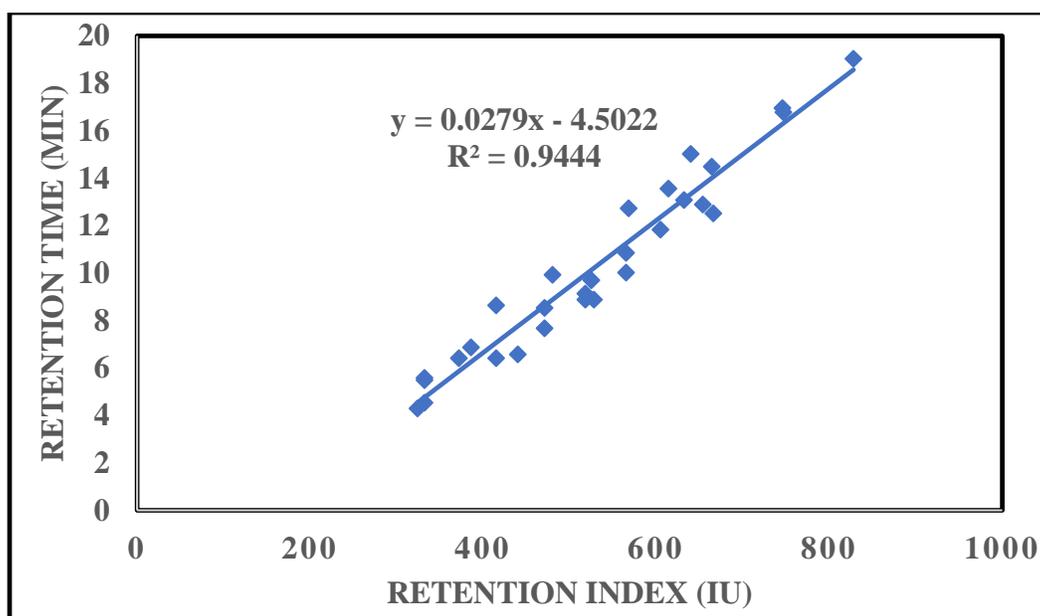


Figure 23: Retention index vs Retention time linearity graph for the produced by-products during degradation reactions.

Table 1: Retention time and R match of dimethyl trisulfide and its reaction by-products with chlorine dioxide.

Reaction of dimethyl trisulfide with chlorine dioxide			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Formic Acid	4.832	512	845
Chloromethane	5.58	332	902
Methylene chloride	8.879	528	888
Methane sulfonyl chloride	19.037	828	935
Dimethyl Trisulfide	11.403		898

Table 2: Retention time and R match of dimethyl trisulfide and its reaction by-products with ozone.

Reaction of dimethyl trisulfide with ozone			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Dimethyl ether	3.50	324	820
Sulfur dioxide	5.33	869	813
Methyl formate	6.80	386	993
Dimethyl peroxide	6.41	372	873
Dimethyl Trisulfide	11.403		898
Acetone	8.583	471	896
Methyl nitrate	9.70	525	909

Table 3: Retention time and R match of 1-bromopropane and its reaction by-products with chlorine dioxide.

Reaction of 1-bromopropane with chlorine dioxide			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Dimethyl ether	3.739	328	877
Formic acid	4.55	512	854
Chlorine dioxide	6.04		803
1-bromopropane	11.53	614	938

Table 4: Retention time and R match of 1-bromopropane and its reaction by-products with ozone.

Reaction of 1-bromopropane with ozone			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Ethanol	6.57	440	858
Chloromethane(cont)	7.54	332	859
Bromomethane	8.64	415	890
Acetone	10.47	471	897
Cyanogen bromide	11.61	482	951
1-bromopropane	13.57	627	919

Table 5: Retention time and R match of isoprene and its reaction by-products with chlorine dioxide.

Reaction of isoprene with chlorine dioxide			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Carbamic acid	8.95	512	878
Chlorine dioxide	11.6		893
Isoprene	13.5	498	900
2-methyl butene	17.85	568	901

Table 6: Retention time and R match of isoprene and its reaction by-products with ozone.

Reaction of isoprene with ozone			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Ethanol	6.63	440	858
Chloromethane(cont)	7.6	332	876
1,4-pentadiene	9.93	480	955
Acetone	10.48	471	977
2-butenal	12.22	666	910
Isoprene	6.48	498	940
Methyl vinyl ketone	13.03	568	926

Table 7: Retention time and R match of 2,3-butanedione and its reaction by-products with chlorine dioxide.

Reaction of 2,3-butanedione with chlorine dioxide			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Dimethyl ether	4.29	328	875
Chlorine dioxide	6.002		972
2,3-butanedione	11.03	565	899

Table 8: Retention time and R match of 2,3-butanedione and its reaction by-products with ozone.

Reaction of 2,3-butanedione with chlorine ozone			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Formic acid	5.258	512	858
Bromomethane(cont.)	6.41	415	909
Acetone	7.68	471	951
2,3-butanedione	10.023	565	937

Table 9: Retention time and R match of 1,1,2-trichloroethane and its reaction by-products with chlorine dioxide.

Reaction of 1,1,2-trichloroethane with chlorine dioxide			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Dimethyl ether	4.54	332	909
Chlorine dioxide	6.166		887
Ethyl ester carbon chloridic acid	15.341	640	893
1,1,2-trichloethane	16.79	747	956

Table 10: Retention time and R match of 2,3-butanedione and its reaction by-products with ozone.

Reaction of 1,1,2-trichloroethane with ozone			
Name of by-products	Retention time(min)	Retention index(iu)	R match
Methylene chloride	9.131	518	917
Tri-chloromethane	11.84	605	872
1,2-dichloroethane	12.91	632	934
Ethyl ester carbon chloridic acid	15.52	598	858
1,1,2-trichloroethane	16.91	746	920