OXIDATIVE DESTRUCTION OF ORGANIC CONTAMINANTS UTILIZING ULTRASOUND

by

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CHAPTER I

INTRODUCTION

Mankind, over the many years of the industrial age, has made and utilized many useful chemicals. Not all of these chemicals are benign, and it becomes a particular problem when they come in contact with the environment. Whether or not the introduction of these chemicals into the environment was deliberate, mankind has a duty to address and solve these contamination problems.

Environmental Contaminants

Environmental contaminants are hazardous materials that have been introduced into or have migrated into the environment. These materials consist of individual materials or combinations of materials that are presently or potentially dangerous to humans or other living organisms. Currently, the Environmental Protection Agency (EPA) segregates hazardous wastes into three categories[1]: organic wastes, aqueous wastes and sludges. Organic wastes are further divided into two categories: halogenated and oxygenated compounds. Within the halogenated category, polychlorinated biphenyls (PCBs) are separated from the other halogenated compounds due to their persistence in the environment.[1] Oxygenated organics are further divided into alcohols, aldehydes, ketones, organic acids, ethers, phthalates and phenols. Oxygenated organics also include other heteroatom compounds, including amines, heterocyclic nitrogen compounds, nitro compounds, nitriles, nitrosamines, sulfur-containing compounds and aromatics. This work will concentrate on the organic contaminants.

The health effects of halogenated organic compounds range from breathing difficulty to cancer and even death. The International Agency for Research on Cancer of the World Health Organization (IARC), and the National Toxicology Program (NTP) have three categories of carcinogens, or cancer-causing substances: confirmed carcinogens, probable human carcinogens and possible human carcinogens.[2] Both groups have labeled chloroform and carbon tetrachloride as possible carcinogens, while benzene is a confirmed carcinogen.

The Occupational Safety and Health Administration, OSHA, has set exposure limits in the workplace for a number of chemicals.[3] For example, carbon tetrachloride's legal airborne permissible exposure limits (PEL) are 10 parts per million (ppm) averaged over an 8-hour workshift, and up to 25 ppm for a maximum time of 5 minutes in a 4-hour time span, but not to exceed 200 ppm,. Methylene chloride's PEL is 500 ppm averaged over an 8-hour workshift, with an acceptable ceiling level of 1,000 ppm and a maximum concentration of 2,000 ppm for a 5 minute limit in any 2-hour time frame. On the other hand, chloroform has a PEL of 50 ppm, but is never to be exceeded. The acute, short-term effects for all three compounds are quite similar: dizziness and lightheadedness, irritation of the eyes and an irregular heart beat. The chronic, long-term effects are also quite similar and include possible reproductive hazards, damage to the liver and kidney and cancer in animals. Repeated exposure to chloroform may affect the nervous system as well. Exposure to methylene chloride can cause damage to the brain resulting in memory loss, poor coordination and reduced thinking ability; repeated exposure, especially in the presence of a combustion source, can also cause

bronchitis with cough, phlegm and/or shortness of breath due to the byproduct phosgene, which is a lung damaging gas.[3]

Trichloroethylene (TCE), another halogenated organic compound, is a commercially produced chemical used to remove grease. Exposure to low levels of TCE can cause dizziness, headaches, slowed reaction times, sleepiness and facial numbness, while higher levels of exposure may cause unconsciousness or even death. Long-term effects are thought to include liver and kidney damage; blood disorders; tumors of the liver, kidney, lung and male sex organs; and possibly cancer of the tissues that form the white blood cells, causing leukemia.[4] The limits for TCE are set by the EPA at 5 parts per billion (ppb) for drinking water.[4] The PEL, as set by OSHA, for TCE is 50 ppm for an 8-hour workday, while 200 ppm should never be exceeded.[3]

The oxygenated organics also cause a wide range of health effects. Toluene is not considered to be a carcinogen, but exposure to it can lead to difficulty in breathing and unconsciousness, which ultimately can lead to suffocation. Chronic overexposure can lead to kidney and liver damage. The PEL is 200 ppm averaged over an 8-hour workshift, with a maximum concentration of 500 ppm.[3] Benzene, however, is considered a carcinogen since it has been shown to cause leukemia in humans.[4] There is some limited evidence that benzene causes birth defects in animals; benzene is therefore considered a possible mutagen in humans as well.[5] Exposure to benzene can cause dizziness, lightheadedness, and at higher concentrations can cause convulsions and death. It can also cause an irregular heart beat and aplastic anemia, both of which can also lead to death. The PEL for benzene is 1 ppm averaged over an 8-hour workshift and a maximum of 5 ppm.[3]

Environmental contamination is problematic throughout the entire world. In the United States, all 50 states have disposal sites that are contaminating the surrounding land.[4] Most of Europe and Asia have similar problem sites. Contamination can occur through several routes. Once in the ground, organic contaminants can leach into groundwater systems, and from there into lakes, rivers, oceans and ultimately into drinking water. Polychlorinatedbiphenyls and similar compounds such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are especially problematic, in that they are bioaccumulated. Once in the water, these compounds can enter the food chain and ultimately end up in humans. Since they are fat soluble, they remain in the body. Studies have shown that human breast milk contains PCBs, PCDDs or PCDFs in women in Africa,[6] Canada,[7, 8] England,[6, 9] France,[10] Japan,[11] the Netherlands,[12-14] Pakistan,[6] Spain,[15, 16] Vietnam,[6] and the United States.[6, 17] Through evaporation, organic contaminants are carried into the atmosphere, which allows distribution throughout the world via wind currents. Polychlorinatedbiphenyls have been detected in snow in such remote places as Finland[18] and Antarctica,[19, 20] far from the initial disposal site. Another common method of contamination in the past was the application of used oil as a dust suppressant on roads and other nonpaved surfaces; some of this oil had been contaminated with compounds such as dioxin. A number of rural areas have been affected.[4]

In the United States, there are many cities that have problems due to the leaching of organic contaminants from nearby landfills into either surface water or groundwater. Several of the cities with hazardous waste contamination problems, specifically trichloroethylene contamination, include: Fridley, MN; Pleasantville, NJ; Manua Township, NJ;[21]

Tucson, AZ;[22] Silver Creek, MO;[23] Waldoboro, ME;[24] Moses Lake, WA;[25] and Orlando, FL.[26] The New York towns of Wellsville and Oswego both have water contaminated with PCBs.[21] Both Love Canal in Niagara Falls, NY and Times Beach, MO[4, 27, 28] are well known for their contamination with dioxin.

Polychlorinated biphenyls (PCBs), their degradation products and dioxin are among the organic contaminants that have received a great deal of media attention because of human contamination at places such as Love Canal, NY and Times Beach, MO and during the Yusho incident in Japan[29, 30] and the Yu-Chen incident in Taiwan.[30, 31] In the Love Canal incident, a subdivision was built near an old chemical disposal site where dioxin had been dumped. The residents developed numerous health problems and the chemicals that had been placed in the dump were to blame. The Times Beach incident also involved dioxin, a contaminant in the oil that was sprayed to keep down dust. Both the Yu-Chen and Yusho incidents involved PCB-contaminated cooking oils.

Studies of men and boys from the PCB spill in Taiwan, the Yu-Chen incident, show that men who have been exposed to PCBs have a higher incidence of testicular deformities, low sperm counts and undersized penises than males who were not exposed to PCBs.[32] Studies done in Michigan and Taiwan on children born to women who had high levels of PCBs in their breast milk show much higher levels of deformities than those in control groups.[32] There is a higher incidence of endometriosis, a condition that can lead to infertility, in women who were exposed to PCBs and other pesticides than in women who were not exposed. Studies are linking both endometriosis and breast cancer to these pollutants.[32] Symptoms of PCB poisoning include constant abdominal pain, poor

appetite, general fatigue, acneform eruption, pigmentation, swelling of eyelids, eye discharge and deformation of nails.[33]

Numerous scientific studies involving PCBs and the environment have been published.[1, 19, 20, 33-43] An excellent review of the effect PCBs have had on the Great Lakes area and wildlife has been published.[34] In 1966, Jensen tested eagle feathers dating back to the 1920's and discovered PCBs in feathers from as early as 1944.[35] Herring gulls have been widely studied to determine how PCBs get into tissues as well as how they are stored.[36-39] The fish of the Great Lakes are found to have much higher PCB content than fish of other areas,[35] as do mink populations which are fed fish from the Great Lakes.[40-42, 44] Both the mink and the gulls have reproduction problems which are attributed to PCBs. Humans who live in contaminated areas, or have become contaminated, are having some of the same reproductive problems as laboratory mice and alligators in Florida that have been exposed to PCBs.[32]

Methods of Treatment for Environmental Contaminants

Numerous methods are currently available for treatment of organic contaminants and other wastes.[1, 4, 45-47] Some are economically or systematically feasible, while others are not. These methods include biodegradation,[1, 4, 46] ion exchange,[46] oxidation by such methods as chlorinolysis,[4] UV radiation,[47] hypochlorites,[4] ozone,[47] peroxides[47] or electrolysis, as well as reduction by methods[4] including treatment with sulfur dioxide, ferrous sulfate or sulfites. Problematic acid and base streams can be neutralized by simply mixing them with each other,[4] while in the absence of a suitable base stream, acid streams can be neutralized by passing through limestone beds or caustic soda, while base

streams can be neutralized using CO_2.[4] Solids can be removed from aqueous solutions by sedimentation, precipitation, centrifugation, filtration, magnetic separation or with the use of carbon or resin sorption.[46] Separation technologies that are being examined for remediation of organic contamination include oil/water separation, dissolved air flotation, evaporation, both air and stream stripping, reverse osmosis, and liquid/liquid extractions.[46] Membrane-assisted extractions,[47] as well as non-foaming adsorptive bubble separation processes[45] are also being considered.

Cementation of solid wastes, to isolate them from the environment, is a common method of waste treatment.[4] Thermoplastic solidification,[4] a process similar to cementation but considerably more expensive, is seeing more application. With these techniques the wastes can then be stored underground with greatly minimized danger of leaching into the soil or groundwater. Deep well injection is also utilized, but only where oil technologies are already in place. The organics are injected into highly porous rock well below the water table where no leaching into the ground water is thought to occur. Problems have arisen in Wyoming, where organic contaminants were injected into an old uranium mine. The organics migrated from the injection site in the mine and contaminated the groundwater nearby. Landfills are still in use, although care is taken to make sure they are "secure," i.e., isolated from people and from water, and in poorly permeable high clay soils that minimize leaching. A newer alternative is deep burial. Abandoned underground military silos, which are designed to withstand earthquakes and bombing attacks, are being used to store hazardous wastes with little or no danger of leakage.[4]

Some disposal methods actually degrade the waste. Incineration is a very common degradation method. Fluidized alkaline-bed incineration is another common method of destruction. Care must be taken that the temperatures utilized are high enough to completely destroy the hazardous component. In some instances, the by-products of thermal degradation are at least as toxic as the original waste if sufficiently high enough temperatures are not employed.[43] One of the newest methods being considered for degradation of hazardous wastes is sonication. Sonication can be used to degrade solutions to either non-toxic materials or less toxic materials which have easier disposal methods.

Ultrasound

Sonochemistry utilizes ultrasound, sound waves which are generally above the range of human hearing (>16 kHz).[48] Sound waves can travel through any substance that has elastic properties, including liquids. These sound waves impart their movement to the medium through which they travel, resulting in both expansion waves and compression waves. In liquids, this creates numerous bubbles. The rapid birth, growth and violent collapse of these bubbles within the solution is termed cavitation.

There are two types of cavitation, stable and transient. Transient bubbles last only a few acoustic cycles as they expand and collapse, while the stable bubbles maintain a relatively small equilibrium size and last much longer before collapsing, with a decreased intensity of collapse.[49] Sonochemistry principally occurs at the sites of transient cavitation. There are two areas where reactions take place around the transient bubble,[50-52] one inside the bubble itself and the other in the interface

between the bubble and the solvent. Temperatures of the bubble and the liquid phase directly around the bubble are approximately 5000 K and 2000K, respectively, and there are intense pressures generated, as high as several hundred atmospheres.[53, 54] The extreme temperatures are caused by the collapse of the bubble and the compression of the vapors inside the bubble.[55] These high temperatures are responsible for thermal reactions which can occur in the liquid phase around the bubble. In aqueous solutions, one reaction that occurs is the formation of radicals, due to the homolytic cleavage of water molecules into hydrogen radicals and hydroxy radicals upon sonication:

$$H_2O \longrightarrow H\bullet + \bullet OH$$

The occurrence of chemical activity via cavitation was first mentioned in 1895 by John Thornycroft and Sidney Barnaby when they reported on problems that the destroyer H.M.S. Daring was experiencing with its propellers.[52] They investigated the propeller degradation and determined it was due to the cavitation. While chemical reactions of ultrasound have been known as far back as 1929,[56] the use of sonochemistry has not come into prominence until the last 10-15 years. In the last few years several books and reviews on sonochemistry have been published.[48, 50, 52, 55, 57-59]

Since the initial exploration of ultrasound's usage in the early part of the century, a myriad of applications have come into use. These include degassing, flaw detection, thickness gauging, cleaning and sterilization, welding of plastics, cell disruption in biological areas, and emulsification of such solutions as inks and paints. It is used in dentistry

for both cleaning and drilling; in the medical field it is used for both imaging and physical therapy.[52, 60-62]

The use of ultrasound in the realm of chemistry is quickly increasing. There are a number of synthetic applications for ultrasound.[58, 63] Sonication leads to more effective mixing of reactants, especially for heterogeneous reactions, which increases reaction rates. Ultrasound often eliminates the need for a phase transfer catalyst due to the emulsion that is created during cavitation. Ultrasound can also remove inert coatings, such as oxides, from metal surfaces, again increasing the reaction rate. Much of the chemistry that involves ultrasound is a result of the increased pressures and temperatures which occur during cavitation. Reductions, alkylations, acylations, and ester hydrolyses are some of the chemical reactions that can be accomplished via ultrasound,[62] as well as a host of free radical reactions which are initialized by sonication.

Several sources of ultrasound are available. Ultrasonic cleaning baths are widely used in industry, especially for synthesis. They are inexpensive, give an even distribution of energy, and have a low power output. A direct immersion system employs a piezeoceramic coupled to a horn which is placed directly into the reaction media. It has a higher power output, has a more direct application of energy, and requires specific glassware for its use.

Use of Sonication for Waste Degradation

Degradation of organic waste is a current chemical application of ultrasound. Hart, Fischer and Henglein have looked at hydrocarbon destruction by sonochemical means. They studied the effects of

ultrasound on acetylene[64] and the C_4 and shorter hydrocarbons.[65] For acetylene, a great number of sonication products were found. The products range from gases such as carbon monoxide and methane, through the middle molecular weight gases including ethylene and propene, to higher molecular weight species such as benzene and naphthalene. The more abundant products were the middle weight species. The concentration of the products was found to be proportional to the sonolysis time in all cases, indicating constant rates of formation. Acetylene itself had greater than 90% destruction occurring within 8 minutes. The products that appear upon sonolysis of either methane or ethane include most of the hydrocarbons in the C_2 to C_4 range. Methane decomposed rather quickly, but could not be driven to completion. Ethane decomposed at a slow rate, but decomposition was complete as shown by gas chromatography/mass spectrometer (GC/MS). Both produced proportional amounts of H_2, dependent upon the initial concentration of the methane or ethane. For other hydrocarbons studied in the C_2-C_4 range, less H_2 evolved than expected for unsaturated hydrocarbons and greater decomposition was observed than that with the saturated hydrocarbons, which Hart *et al.* attributed to polymerization or oligomerization.

Beginning in 1958, ultrasound has been used in the degradation of a number of compounds which contain nitrogen. Zechmeister and Magoon[66] used silver nitrate and ultrasound to decompose up to 5% of a pyridine solution, forming the silver salts of acetylene, diacetylene and hydrogen cyanide. They had similar results for nicotine, which is a substituted pyridine.

Currell and Zechmeister[67] studied the effect of silver nitrate on the degradation of pyridine, pyrazine and pyrrole via ultrasound. The silver was not necessary for the degradation, but enhanced the degradation of pyrazine and pyrrole, as determined by the amount of acetylene produced. In all cases the cyanide yields were lower in the presence of silver nitrate.

Currell, Wilheim and Nagy[68] looked at the effects of various conditions on the destruction of a pyridinium salt. The pH under which the sample was sonicated played an important role in the destruction of the salt. Low pH seemed necessary for the destruction, which was monitored by the production of acetylene. Surface tension appeared to have no effect on the rate of acetylene production. Different atmospheres affected the production of acetylene; an argon atmosphere increased production of acetylene, while an atmosphere of sulfur hexafluoride gave only a trace of acetylene.

Anbar and Pecht[69] studied the free radical destruction of ethylenediamine via the oxidative deamination to ammonia. The yield eventually reached a plateau which indicates the degradation occurs through a pathway involving the products of the sonolysis of water. Hydroxy radicals, instead of hydrogen radicals, were identified as the active species by two pieces of evidence. First, a diminished yield was observed in the presence of Ti^{+} and Cu^{2+} ions, which are known hydroxy radical scavengers. Second, the rate did not change when a small amount of O_2, a hydrogen radical scavenger, was present.

Gutiérrez and Henglein[70] studied the sonochemical degradation of tetranitromethane, utilizing ion chromatography and gas chromatography. It was completely degraded after 8 minutes of

sonication time. The degradation products included NO_2, NO_3 and $C(NO_2)_3^-$ as well as N_2, CO and CO_2.

Kotronarou, Mills and Hoffmann[71] investigated the decomposition of *p*-nitrophenol. The major sonication products were NO_2^-, NO_3^-, *p*-benzoquinone and H^+ while HCO_2^-, $C_2O_4^{2-}$, 4-nitrocatechol and H_2O_2 were minor products. NO_2^- was the primary product of short-term sonication, while NO_3^- was the primary long-term product. Decreases in hydrogen peroxide concentrations indicated the reaction of NO_2 and the peroxide to form NO_3. The efficiency of ultrasound to degrade the *p*-nitrophenol was found to be better than that observed with photolysis.

Kotronarou, Mills and Hoffmann[72] also investigated the sonochemical destruction of parathion, O,O-diethyl O-*p*-nitrophenyl thiophosphate. The first products were *p*-nitrophenol and sulfate, while degradation of the diethyl phosphate moiety led to the formation of phosphate and oxalate. The *p*-nitrophenol further decomposed to NO_3 and NO_2, as discussed above. Parathion has a low vapor pressure and is thought to undergo thermal decomposition in the hot interface region around the cavitation bubbles. Complete destruction of parathion occurred in about 2 hours.

Toy, Stringham and Woodward[73] investigated the sonolysis of acetone, 2-butanone, formaldehyde and acetaldehyde. The sonication products for a low concentration, aqueous acetone solution were formate and acetate. They achieved 13.4% degradation of the acetone. A similar solution of 2-butanone gave identical sonication products, but had a lower degradation of only 3.4%. A slightly higher concentration of acetaldehyde had the same products, with comparable degradation, 14.1%. With a slightly higher starting concentration of formaldehyde, only the formate

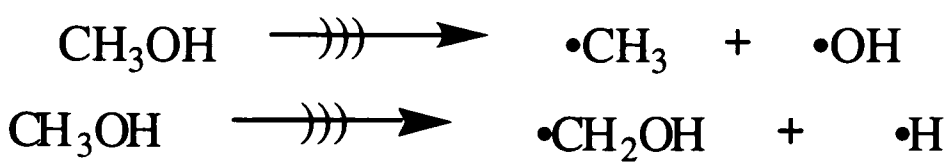
ions were detected, with a much higher degradation level, 78%. The percent destruction did correlate to the ease of oxidation for the four compounds.

Hart and Henglein[74] studied formic acid-water mixtures. Upon sonication, they found large amounts of CO along with H_2 and CO_2 as the major products. Oxalic acid was produced as a minor product. The product distribution indicated that most of the degradation was done by decarboxylation, with only a small amount of radical decomposition taking place. Hart and Henglein[75] also studied sonication of aqueous sodium formate. The sonication products were H_2O_2, H_2, CO_2 and oxalic acid. This time the oxalic acid concentration increased, while the CO_2 concentration remained constant. The concentration of H_2 indicated that the H radicals formed in the sonolysis of water did not escape the hot spots to react with the formate ions. In the absence of O_2, oxidation of formate is a chain reaction as CO_2^- reacts with H_2O_2 to form CO_2 and regenerates an OH radical, which in turn reacts with a formate ion to form another CO_2^-. The use of a known radical scavenger indicated a radical pathway.

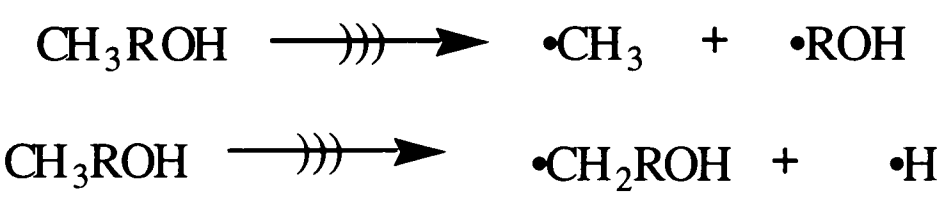
Schmitt, Johnson and Olson[56] found that sonication, in air, of aqueous solutions of H_2S gave elemental sulfur. They established that when a 5 mL sample was sonicated for a 3-minute period, H_2S oxidation occurred at a much faster rate than that at which a hydrogen peroxide solution could oxidize similar solutions of H_2S. Kotronarou, Mills and Hoffmann[76] also looked at the oxidation of H_2S that occurs upon sonication. They found sulfate, sulfite, thiosulfate and elemental sulfur to be the degradation products. They found that the degradation pathway was pH dependent. At higher pH levels, the pathway was a radical pathway, while at a lower pH, a thermal pathway dominated. They

concurred with Schmitt *et al.* that elemental sulfur was the primary degradation product for the sonication of aqueous solutions of H_2S.

The degradation of alcohols as a group has been studied in great detail. Spin trapping studies have been done to determine radical intermediates during the degradation of several alcohols.[77-79] Methanol was decomposed by homolytic cleavage of the C-O or C-H bond, with the first mechanism predominating:



Other alcohols gave similar results:



Büttner, Gutiérrez and Henglein[80] reported the major degradation products of methanol as H_2, CO, CH_2O, CH_4 and minor degradation products as C_2H_4 and C_2H_6. In comparison to combustion, some of the products are similar, while some of the sonication products found are not present in pyrolysis. Toy, Stringham and Woodward[73] utilized a flow-through sonication system rather than a closed system, and reported the formation of HCO_2^-, $H_3CO_2^-$ and small amounts of CO_3^- upon sonication of methanol. The highest reported decomposition is 7%, but they noted that a faster flow rate gave lower decomposition.

Toy *et al.* [73] reported a decomposition level of 5% for ethanol, once again with lower decomposition due to faster flow rates. Gutiérrez *et al.*[70] found methane, ethane, ethylene, formaldehyde and acetaldehyde as decomposition products of ethanol. They noted that acetaldehyde is the only product that resulted from a radical pathway; all others resulted from pyrolysis.

Serpone *et al.*[81] and Lur'e, Kandzas and Mokina[82] looked at the effects of ultrasound on phenol. While both groups reported catechol as a major degradation product, they differed on the other products. Serpone *et al.* reported major amounts of hydroquinone and benzoquinone, with further oxidation of all three products to yield hydroxy-*p*-benzoquinone. Lur'e *et al.* reported two other products, pyrogallol and traces of quinol; the quinol could be further oxidized to *o*-quinone. Serpone *et al.* did not give a quantitative report of the degradation, but Lur'e *et al.* reported the concentration of phenol decreased by 95.5%. Lur'e *et al.* also reported that decomposition of phenol was similar in acidic, neutral and weakly alkaline media, but a strongly alkaline medium greatly slowed the decomposition. Kotronarou *et al.*[71] investigated the decomposition of *p*-nitrophenol. Sonication gave NO_2^-, NO_3^-, *p*-benzoquinone and H^+ as primary products, while HCO_2^-, $(C_2O_4)_2^-$, 4-nitrocatechol and hydrogen peroxide were secondary products. These are analogous to the degradation products of phenol found by Serpone *et al.* and Lur'e *et al.*

Currell *et al.*[68] looked at the effects of various conditions on the destruction of phenol, with either acetylene or carbon dioxide as destruction products. The highest amount of destruction was about 16.2%, under an argon atmosphere, with acetylene as the degradation product. Different atmospheres affected the production of acetylene; while

an argon atmosphere increased production of acetylene, an atmosphere of sulfur hexafluoride resulted in only a trace of acetylene. In acidic conditions, only a trace amount of acetylene was given off, which was credited to reduced vapor pressure.

The use of ultrasound for polymer destruction has been extensively studied. As this class of materials is the subject of a review by Basedow,[83] polymers will just be briefly mentioned here. Gutiérrez *et al.*[70] investigated poly(vinylpyrrolidone) and found that sonication degraded this polymer to smaller molecules. The products which formed after 20 minutes of sonication time were CH_4, C_2H_6, C_2H_4, CO_2, CO, formaldehyde and acetylaldehyde. These products indicated rearrangement of the polymer by pyrolysis in the zone just outside the gas bubbles.

Chlorinated hydrocarbons are a major constituent of organic contaminants in drinking water, and thus a major thrust of remediation work should concentrate around them. Sonication is a topic of great interest as a method of destruction for these chlorinated compounds. The chlorinated compounds that have been sonically destroyed include carbon tetrachloride,[84-92] methylene chloride,[84, 87] chlorophenol,[93] pentachlorophenate,[94] *o*-dichlorobenzene,[91] trichloroethylene,[84, 87, 88] tetrachloroethylene,[88] 1,1,1-trichloroethane,[87, 88, 95] PCBs[96] and chloroform.[84, 88-90, 97]

The sonochemical destruction of PCBs is discussed by Connors and Rushing.[96] They used sonochemistry to assist the electrocatalytic dechlorination of PCBs. They reported that ultrasound not only increased the electrocatalytic conversion of PCBs to biphenyl, but also decreased the time required for the conversion.

The sonolysis of aqueous carbon tetrachloride has been studied as early as 1929.[56] The early work concentrated on the mechanism of the oxidation of CCl_4 to Cl_2.[56, 90-92]

$$CCl_4 + H_2O \xrightarrow{\quad))) \quad} CO + Cl_2 + 2HCl$$

The sonochemical destruction of aqueous carbon tetrachloride can be done using both horns and baths with similar success. Chendke and Fogler[86] Cheung, Bhatnagar and Jensen,[87] as well as Inazu, Nagata and Maeda[88] used horns, while Alippi, Cataldo and Galbato[84] and Jennings and Townsend[89] used baths. Different analytical methods were used: monitoring the production of I_2 from reaction of halocarbons with KI,[56, 84, 86, 90, 92] gas chromatography,[85, 86, 88, 89] pH and titration of HCl[86, 87] and conductivity.[91] The results for all methods were similar; HCl was observed by all who analyzed by-products, and destruction times were similar. Other common by-products were Cl_2, C_2H_6, CO_2, O_2, C_2Cl_4, C_2Cl_6 and HOCl. Wu, Huang and Livengood[85] reported the best results for destruction of carbon tetrachloride: greater than 99% destruction of starting concentrations of 130 ppm in 6 minutes. Several groups detected small amounts of chlorinated products upon the sonication of aqueous carbon tetrachloride. Jennings *et al.*[89] detected trace amounts of hexachloroethane and tetrachloroethylene, while Prakash *et al.*[91] and Spurlock and Reifsneider[98] only detected hexachloroethane. Sonication of nonaqueous carbon tetrachloride by Henglein and Fischer[99] gave more products. They detected methylene chloride, carbon tetrachloride, tetrachloroethane, pentachloroethane,

hexachloroethane, trans-1,2-dichloroethane, trichloroethane, and tetrachloroethane.

Aqueous chloroform solutions were also investigated by many of the groups who studied aqueous carbon tetrachloride.[84, 88-91, 97] Once again, both baths and horns were utilized, with similar results. The same analytical techniques were used with most of the same byproducts generated. Chen *et al.*[97] reported that location of the flask in the ultrasound tank greatly affected the destruction of chloroform, with results ranging from 14% to 90% destruction. Inazu *et al.*[88] reported similar degradation results for chloroform as for carbon tetrachloride, greater than 75% destruction in the first 10 minutes and up to 81% destruction in 20 minutes. Alippi *et al.*[84] reported that using an atmosphere of N_2 instead of air does not affect degradation. Henglein and Fischer[99] studied the sonolysis of neat chloroform. They identified several byproducts, including H_2, HCl, methylene chloride, carbon tetrachloride, tetrachloroethane, pentachloroethane, hexachloroethane, trans-1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene. They also found that a carbene was an intermediate in the formation of these products.

Alippi *et al.* [84] and Bhatnagar and Cheung[100] reported the destruction of methylene chloride from aqueous solutions, with Alippi *et al.* using a bath and Bhatnagar *et al.* using a horn. Both reported HCl as the degradation product. Bhatnagar *et al.* used GC-MS for analysis and reported an 80% destruction in 40 minutes, while Alippi *et al.*, who used pH to detect the formation of HCl as a degradation product, also reported approximately 80% destruction in 150 minutes.

Cheung *et al.*,[87] Inazu *et al.*[88] and Toy, Stringham and Passell[95] all report degradation of aqueous 1,1,1-trichloroethane upon sonication. All three used horns and reported HCl as products. Toy *et al.* was the only group to report percent degradation, 91.4% after 18 minutes, by GC, while the others all used pH to determine the degradation of trichloroethane. Toy and Carter[101] reported the synergistic effects of sonochemistry and the photochemical destruction of aqueous 1,1,1-trichloroethane.

Cheung *et al.* [87] and Inazu *et al.* [88] reported destruction of aqueous trichloroethylene, and Inazu *et al.* also reported the destruction of tetrachloroethylene. The pH was used to determine the degradation. Inazu *et al.* reported greater than 75% of both trichloroethane and tetrachloroethylene decomposed in the first 10 minutes of sonication. Inazu reported trace amounts of dichloroethylene in the aqueous trichloroethylene degradation.

Statement of Research Goals

Organic contaminants in the environment are a problem that must be dealt with. Although there are various methods of removal of these contaminants from the environment, ultimately, degradation of these contaminants to nonhazardous forms is the ideal solution. With this in mind, the degradation of chlorinated hydrocarbons utilizing ultrasound will be attempted. Sonication of methylene chloride, chloroform, carbon tetrachloride and trichloroethylene will be done to study the degradation and possible product formation during sonication. Although sonolytic degradation of the chlorocarbons and identification of degradation species is the primary focus of this research, mechanistic investigation will be undertaken where feasible.

CHAPTER II

RESULTS AND DISCUSSION

Methylene Chloride

The destruction of methylene chloride via sonication was studied over a range of concentrations from as low as 15 ppm aqueous methylene chloride to that of neat methylene chloride. At all aqueous concentrations, the pH dropped, which has been previously attributed to the formation of HCl, and possibly HOCl which would come from the hydrolysis of Cl_2.[86] At initial concentrations lower than 2500 ppm, there were no degradation products detected by GC-MS. Above that level, there were several products that formed and were subsequently degraded themselves. These products included 1,1-dichloroethylene, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, chloroform, 1,2-dichloroethane, trichloroethylene, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane.

Figure 1 shows the degradation of 15 ppm aqueous methylene chloride. The degradation was 75% in 10 minutes of sonication time in that only 25% of the initial methylene chloride concentration remained. There were no degradation products detected. Concentrations of 50 ppm were observed to have methylene chloride levels declining rapidly, with greater than 90% degradation in 30 minutes, and only 4 ppm remaining (see Figure 2). Again, no degradation products were detected. It took 60 minutes of sonication time to degrade the 50 ppm of methylene chloride to below the detection limit, which is between 500 ppb and 1 ppm. The pH of the 50 ppm solution dropped during sonication from 7.0 to just under 2.8 in 20 minutes (see Figure 3).

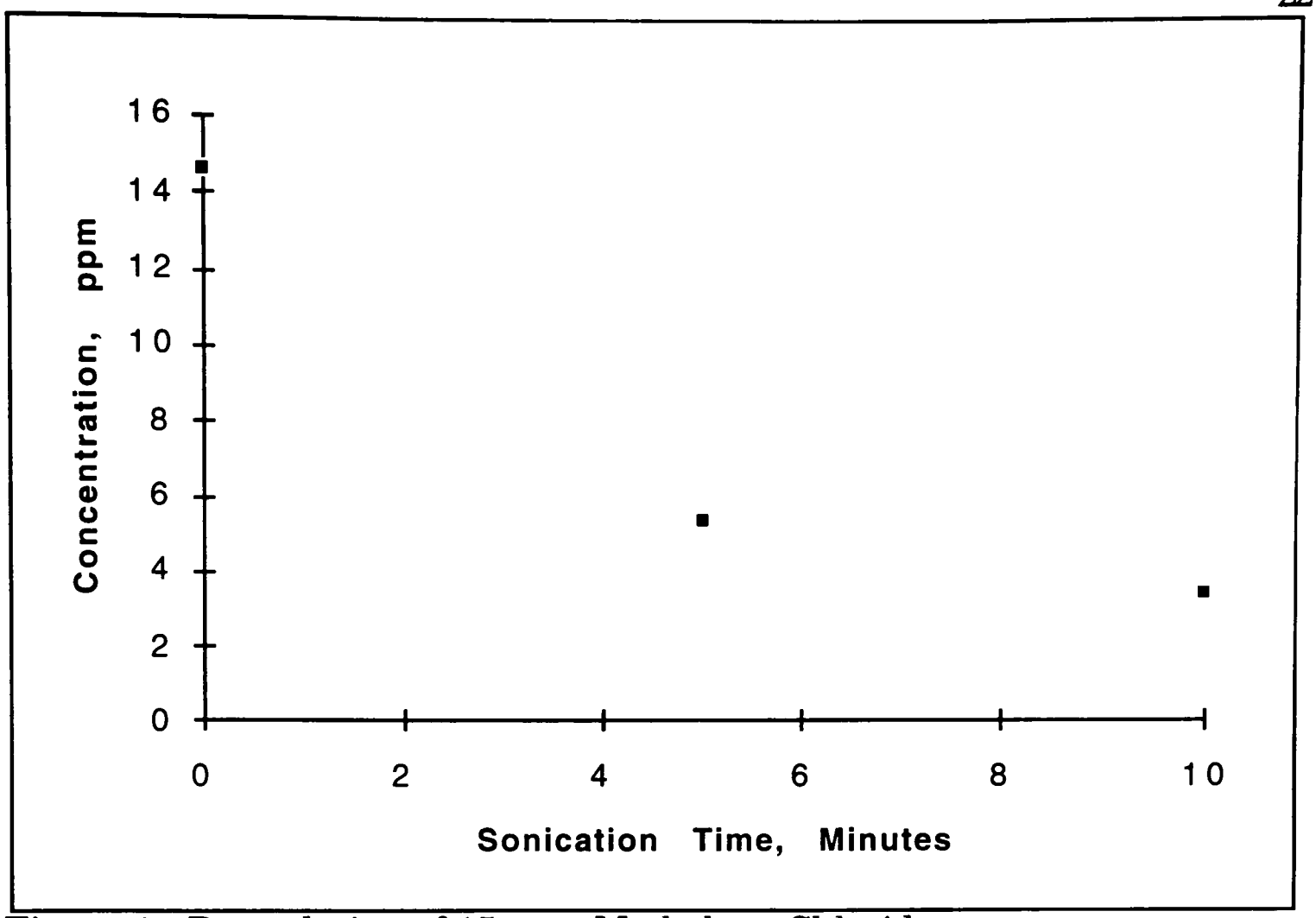


Figure 1. Degradation of 15 ppm Methylene Chloride.

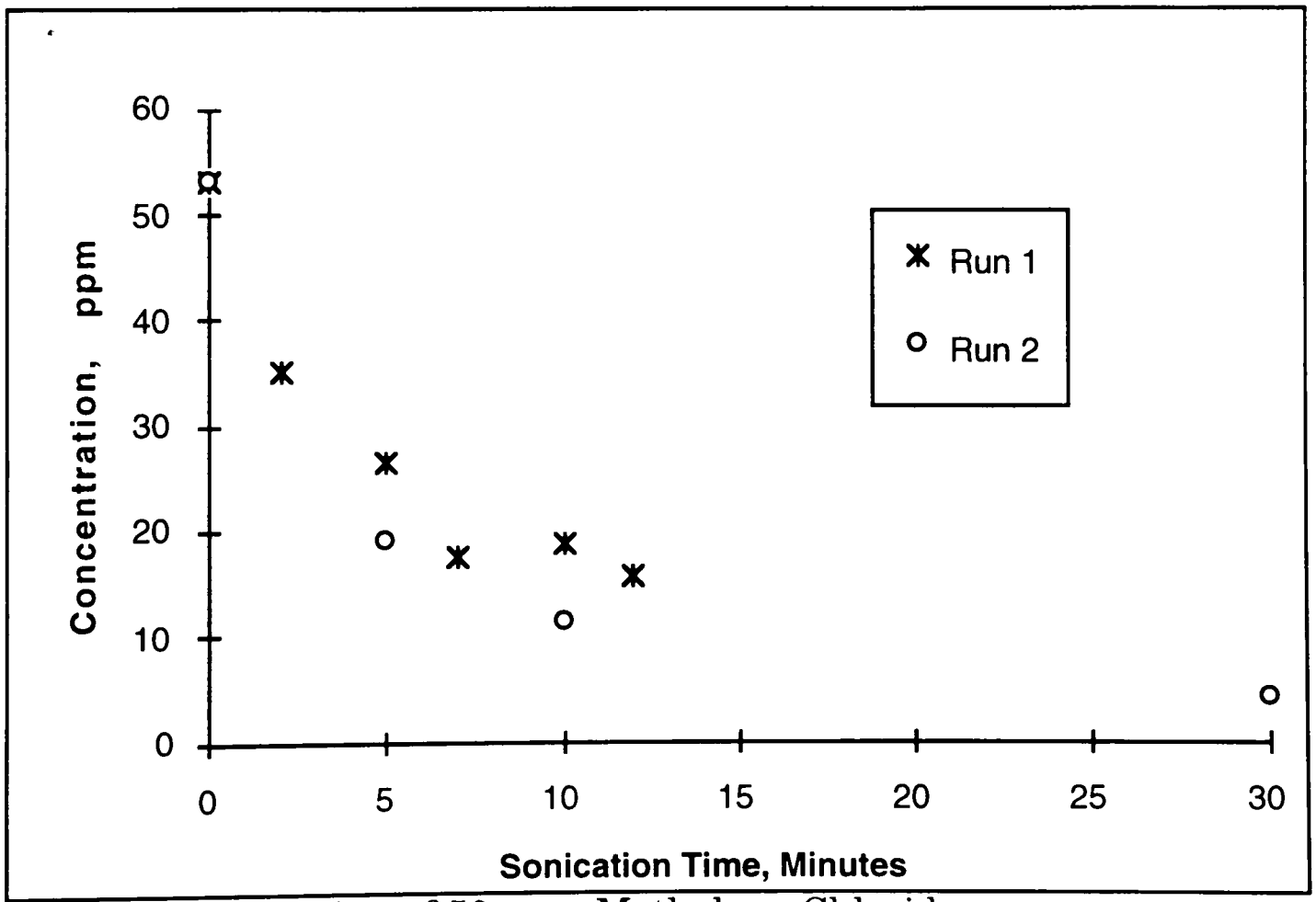


Figure 2. Degradation of 50 ppm Methylene Chloride.

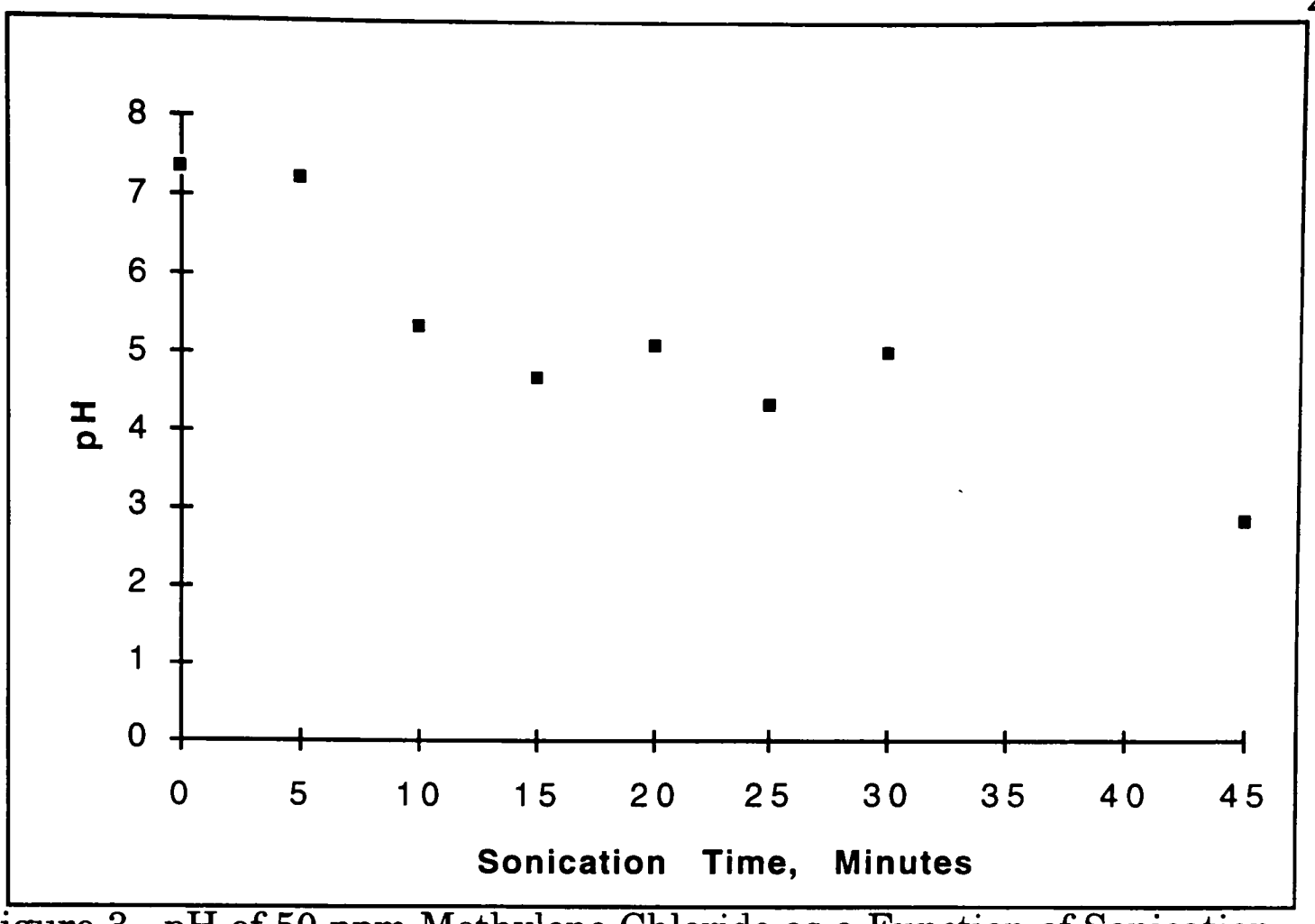


Figure 3. pH of 50 ppm Methylene Chloride as a Function of Sonication Time.

Figure 4 shows that for higher concentration levels of aqueous methylene chloride, such as 100 ppm, the degradation was not nearly as complete as that seen at the lower concentrations. In 20 minutes of sonication time, 56% of the methylene chloride remained. Sonication of these concentrations of methylene chloride showed no detectable products.

A solution of 200 ppm methylene chloride was sonicated, using the conditions set forth in the article by Bhatnagar and Cheung.[100] Degradation results after 35 minutes (see Figure 5) were similar to the results of Bhatnagar and Cheung; however, they reported a first order rate, which did not agree with current results. A conculsive first order rate could not be determined. Figure 6 shows the similarity between the first and second order rates. Additionally, repoducibility of the rates was not achieved.

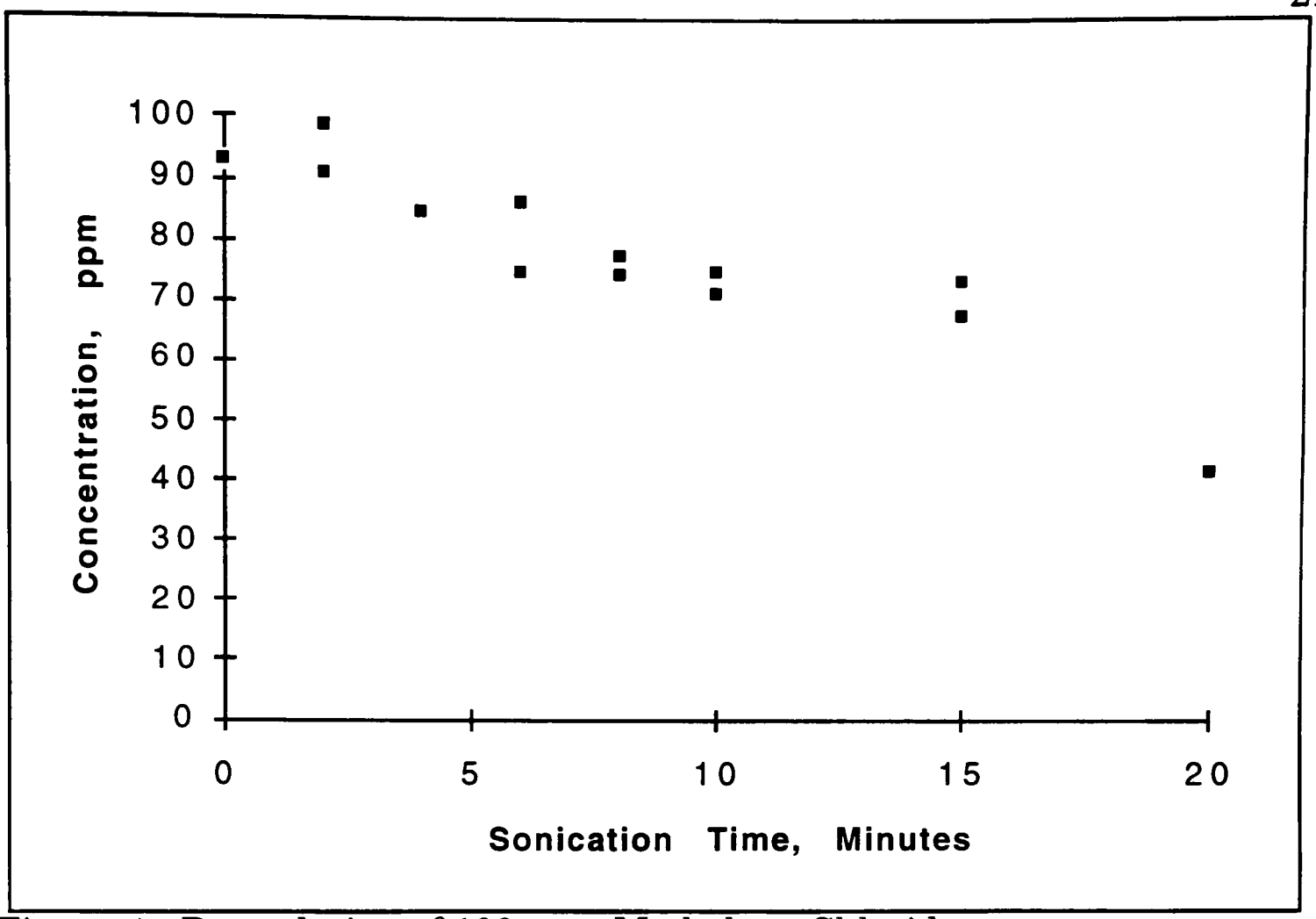


Figure 4. Degradation of 100 ppm Methylene Chloride.

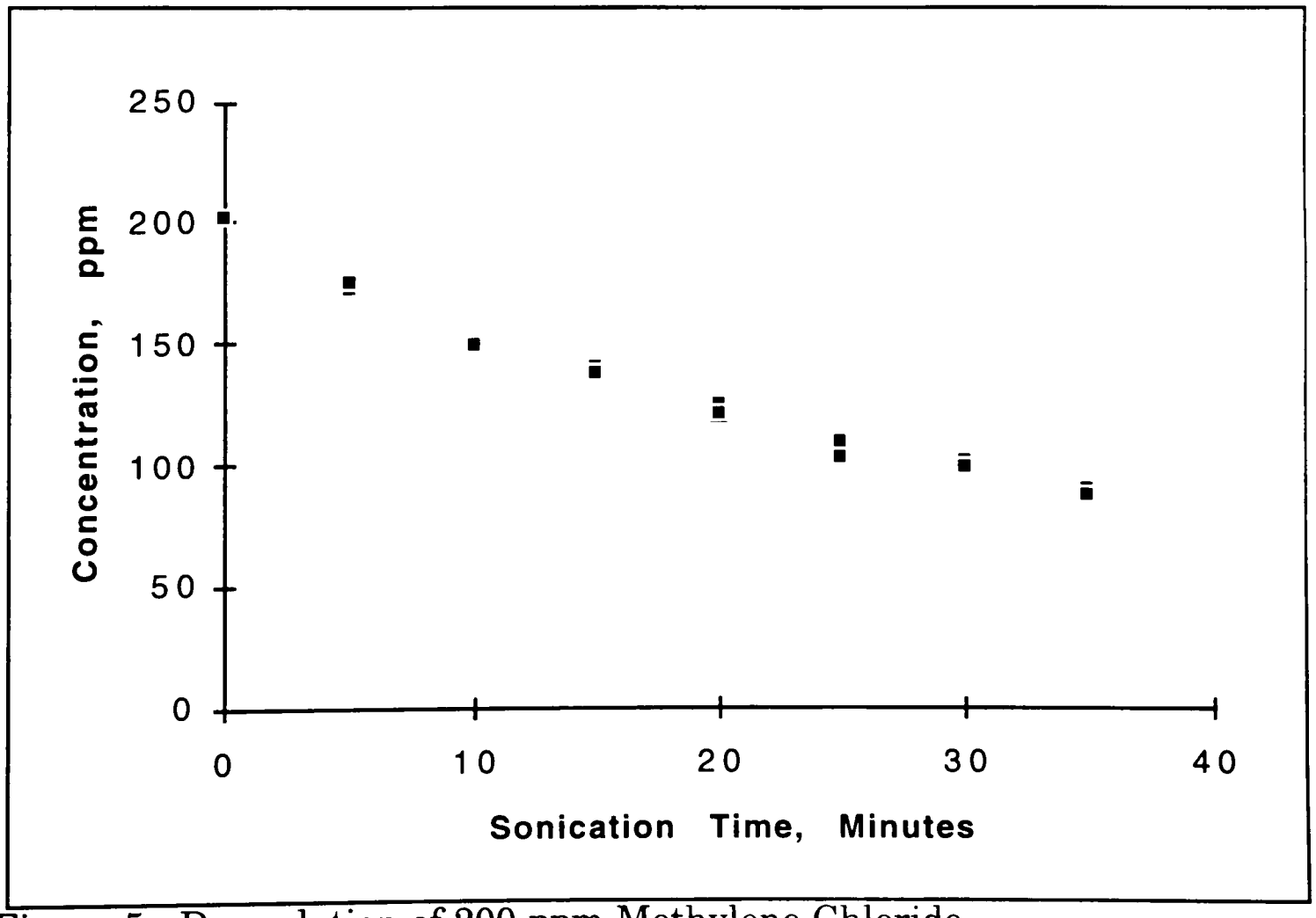


Figure 5. Degradation of 200 ppm Methylene Chloride.

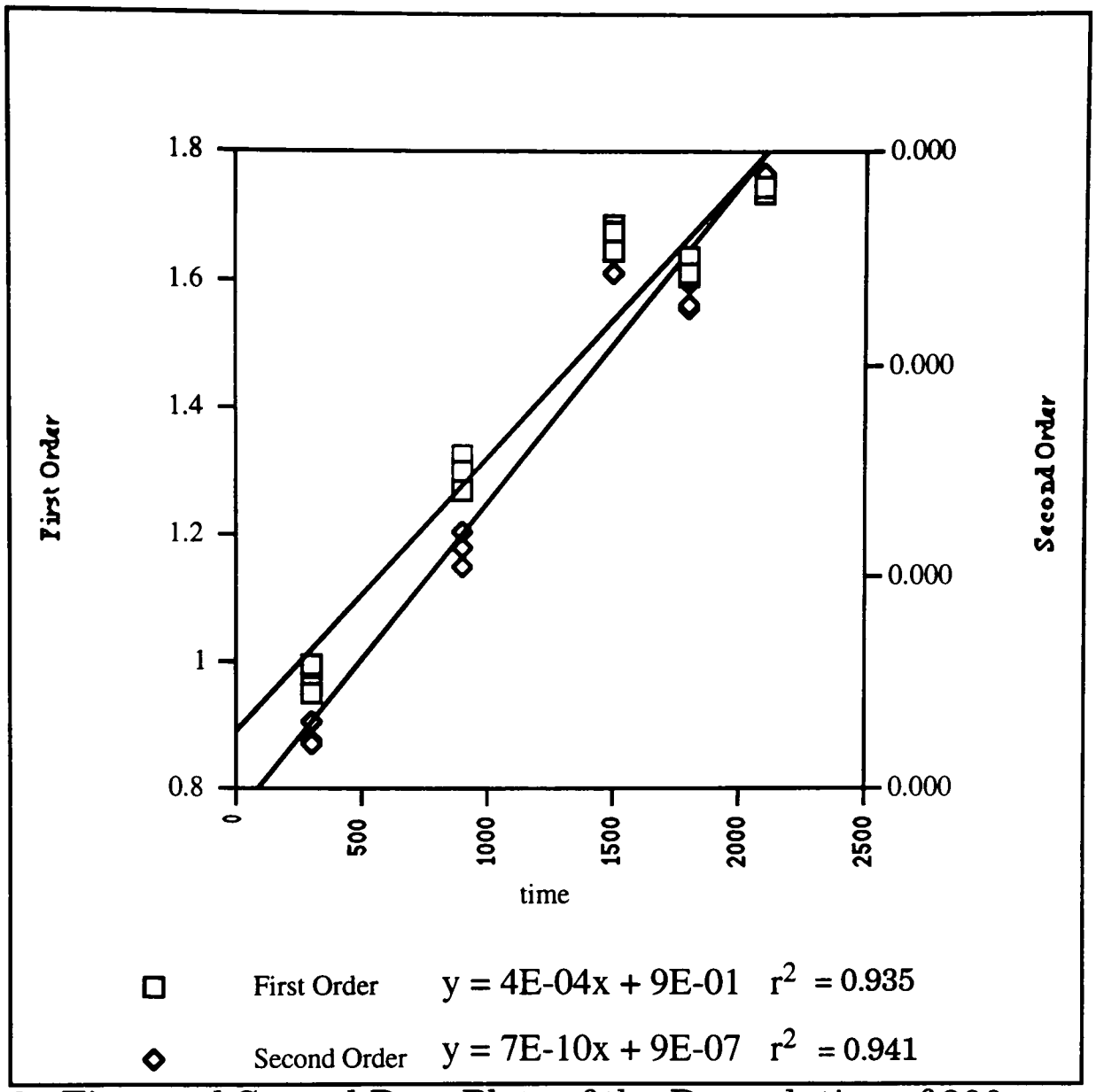


Figure 6. First and Second Rate Plots of the Degradation of 200 ppm Methylene Chloride.

Figure 7 shows the comparison of degradation for the 50 ppm, 90 ppm and 200 ppm concentrations of methylene chloride. The degradation appears to diminish as the initial concentration increases.

Aqueous solutions with methylene chloride concentrations of 2500 ppm that were sonicated for 10 minutes were found to have several degradation products present. These products can arise from the recombination of the various chlorinated radicals that are formed in the aqueous solution while it is being sonicated. Some of these recombinations are shown in Scheme 1. These products were identified by the mass spectrometer as 1,1-dichloroethylene (retention time of 2.3

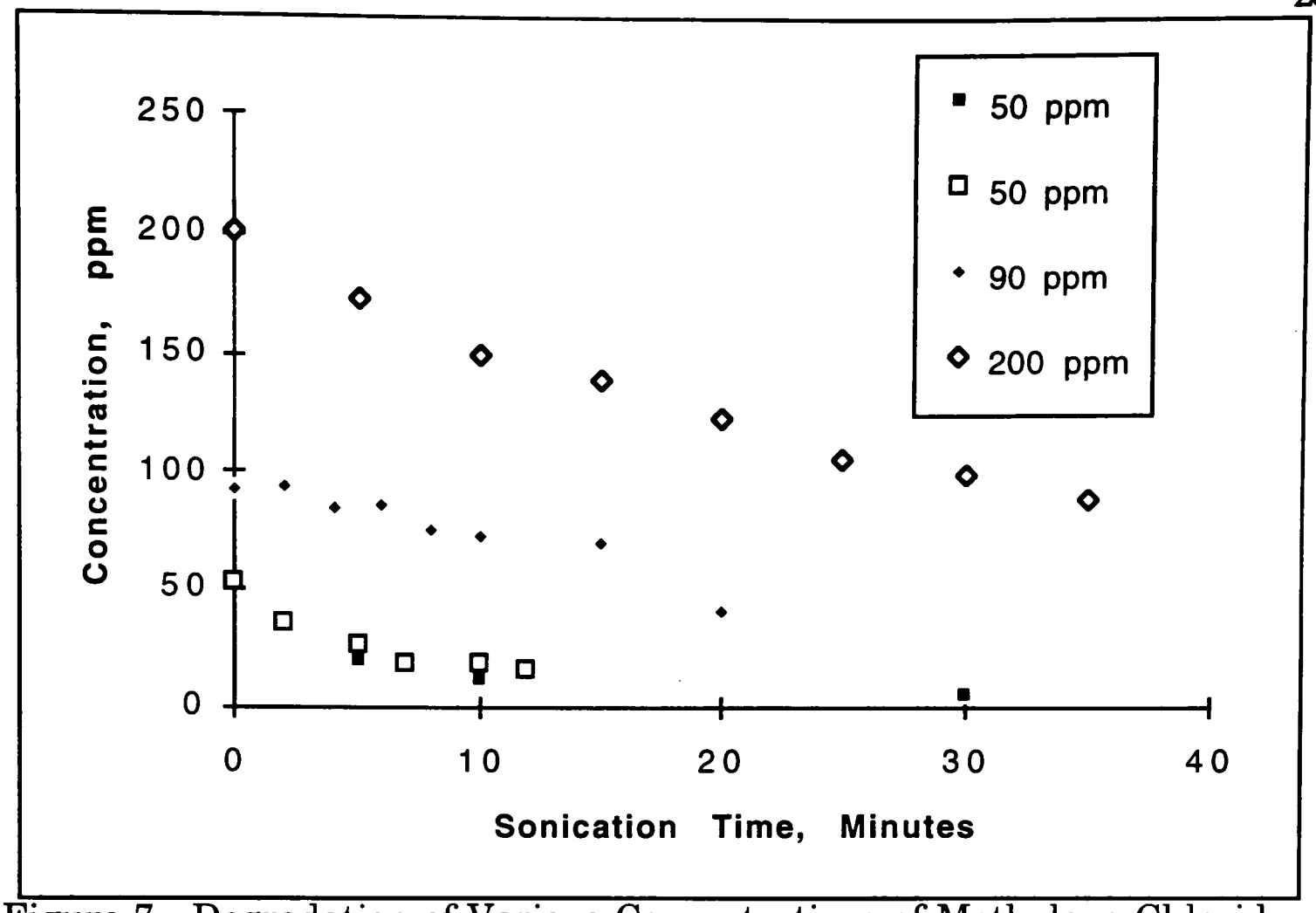


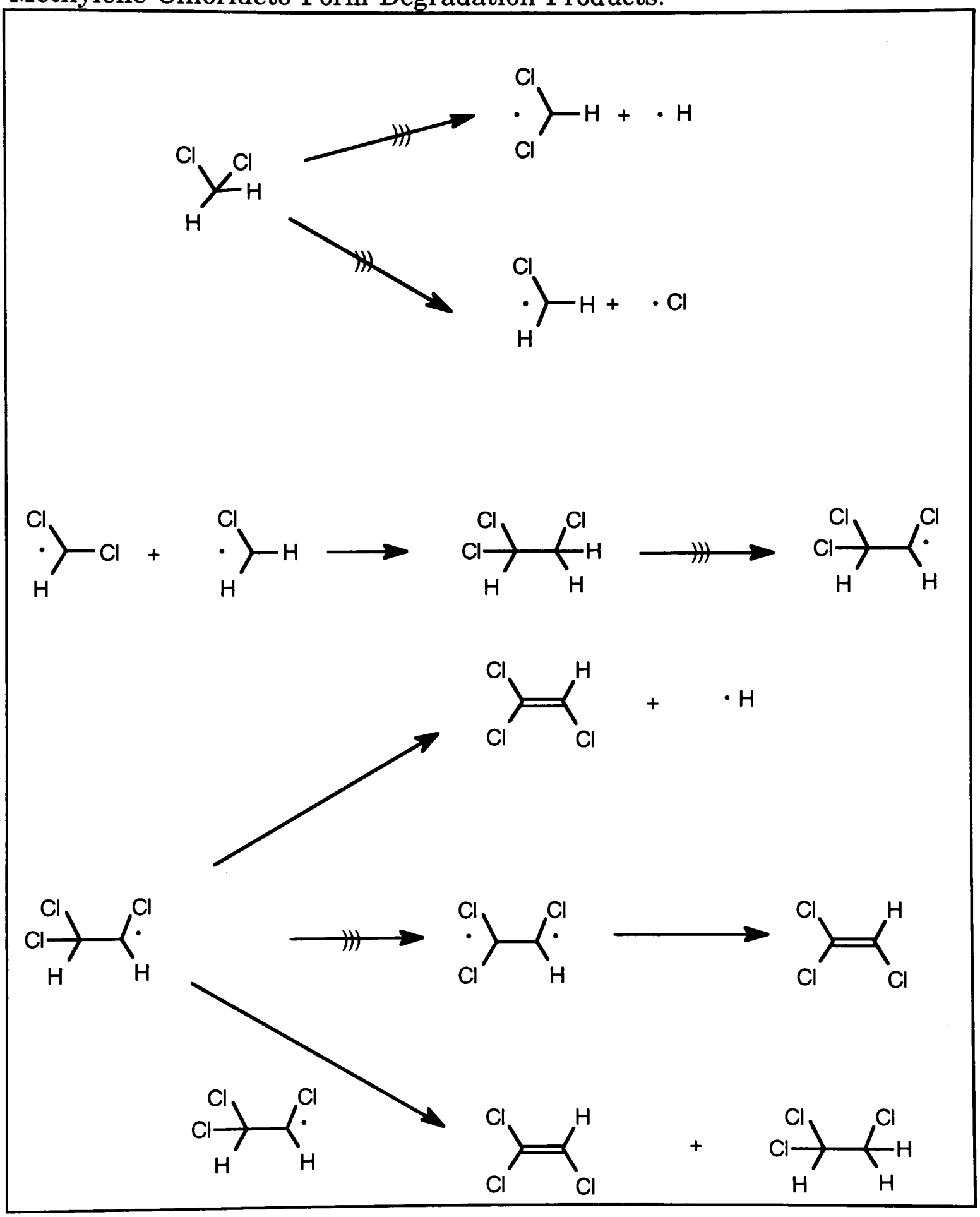
Figure 7. Degradation of Various Concentrations of Methylene Chloride.

minutes (m)), trans-1,2-dichloroethylene (2.58 m), cis-1,2-dichloroethylene (3.00 m), chloroform (3.12 m), 1,2-dichloroethane (3.59 m), trichloroethylene (4.67 m) and 1,1,2-trichloroethane (7.56 m). Figure 8 shows the gas chromatogram for this experiment. Sonicating a 5000 ppm aqueous solution of methylene chloride for the same amount of time did not give any additional degradation products, as seen in Figure 9. The peak at 6.84 minutes is an air peak.

At a methylene chloride concentration of 6000 ppm, which is near the saturation limit of methylene chloride in water, the degradation was only 25% complete at 30 minutes. After 120 minutes of sonication time, it was still only 35% complete (see Figure 10). For both 5000 ppm and 6000 ppm of methylene chloride, the first of the degradation products, cis-1,2-dichloroethylene, was seen after as little as 30 seconds of sonication time

(see Figure 11). The degradation products detected by the GC-MS after 120 minutes of sonication time were 1,1-dichloroethylene (2.45 m),

Scheme 1. Radical Formation and Recombination During Sonication of Methylene Chlorideto Form Degradation Products.



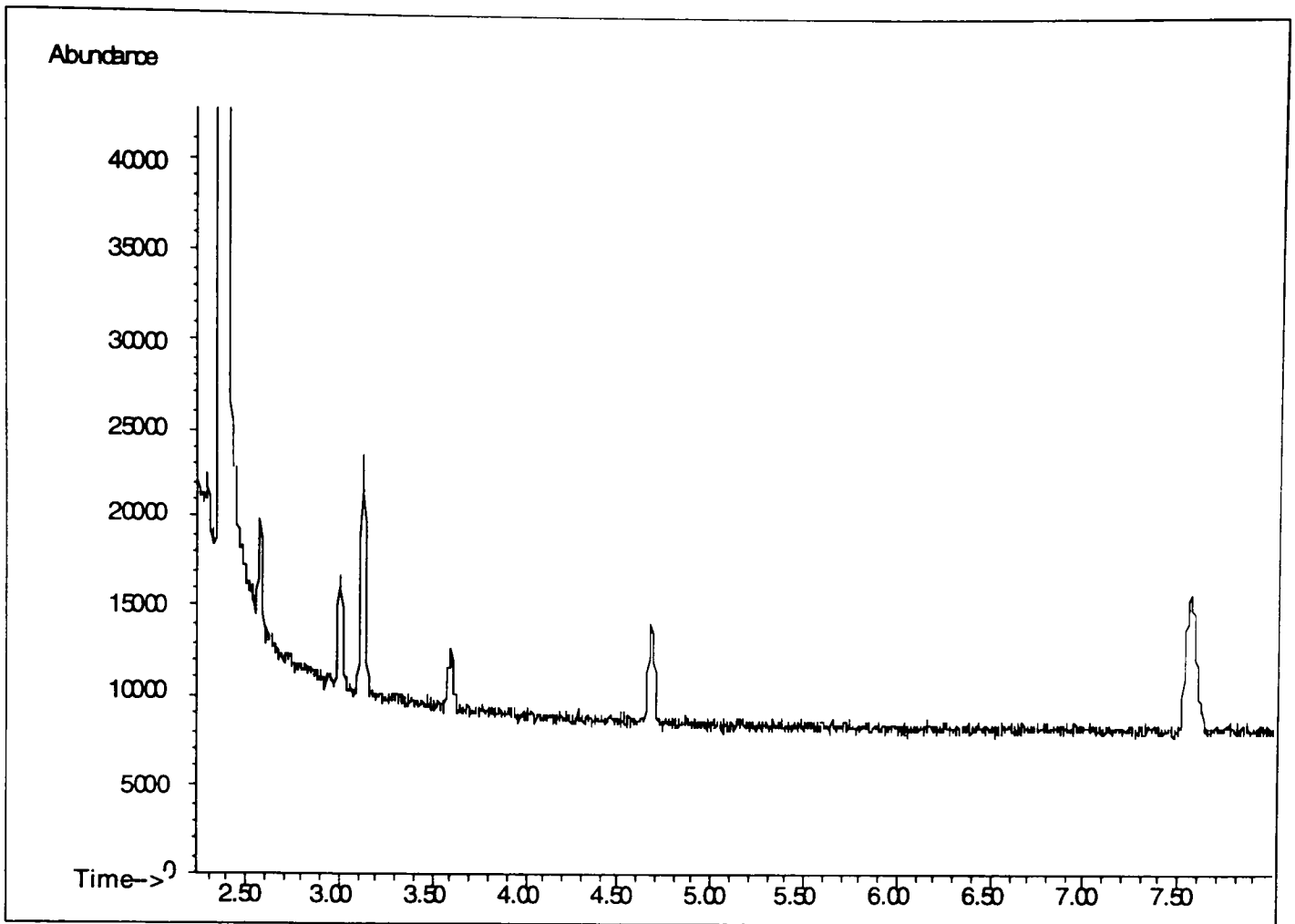


Figure 8. Gas Chromatogram of 2500 ppm Methylene Chloride Sonicated for 10 Minutes.

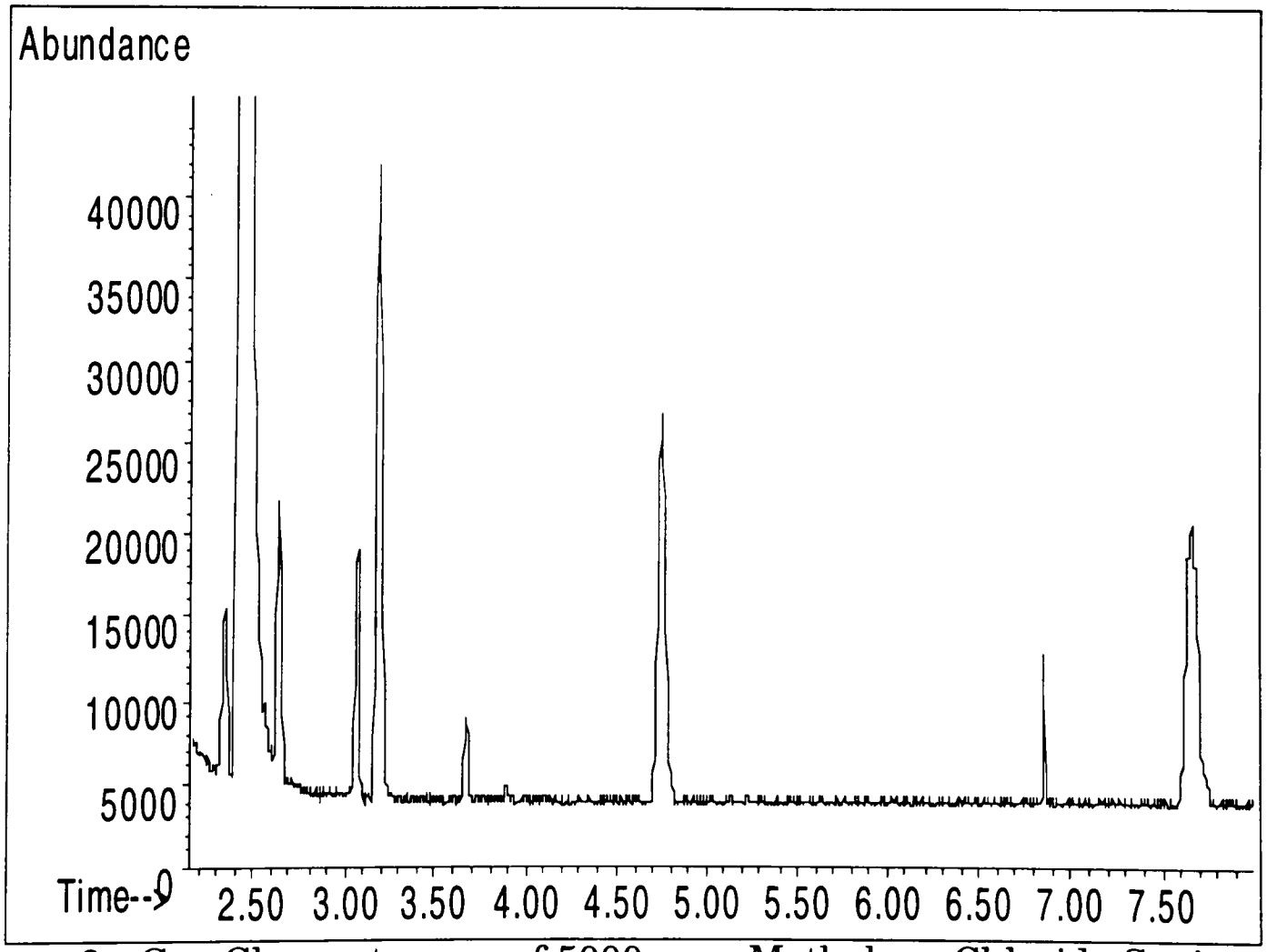


Figure 9. Gas Chromatogram of 5000 ppm Methylene Chloride Sonicated for 10 Minutes.

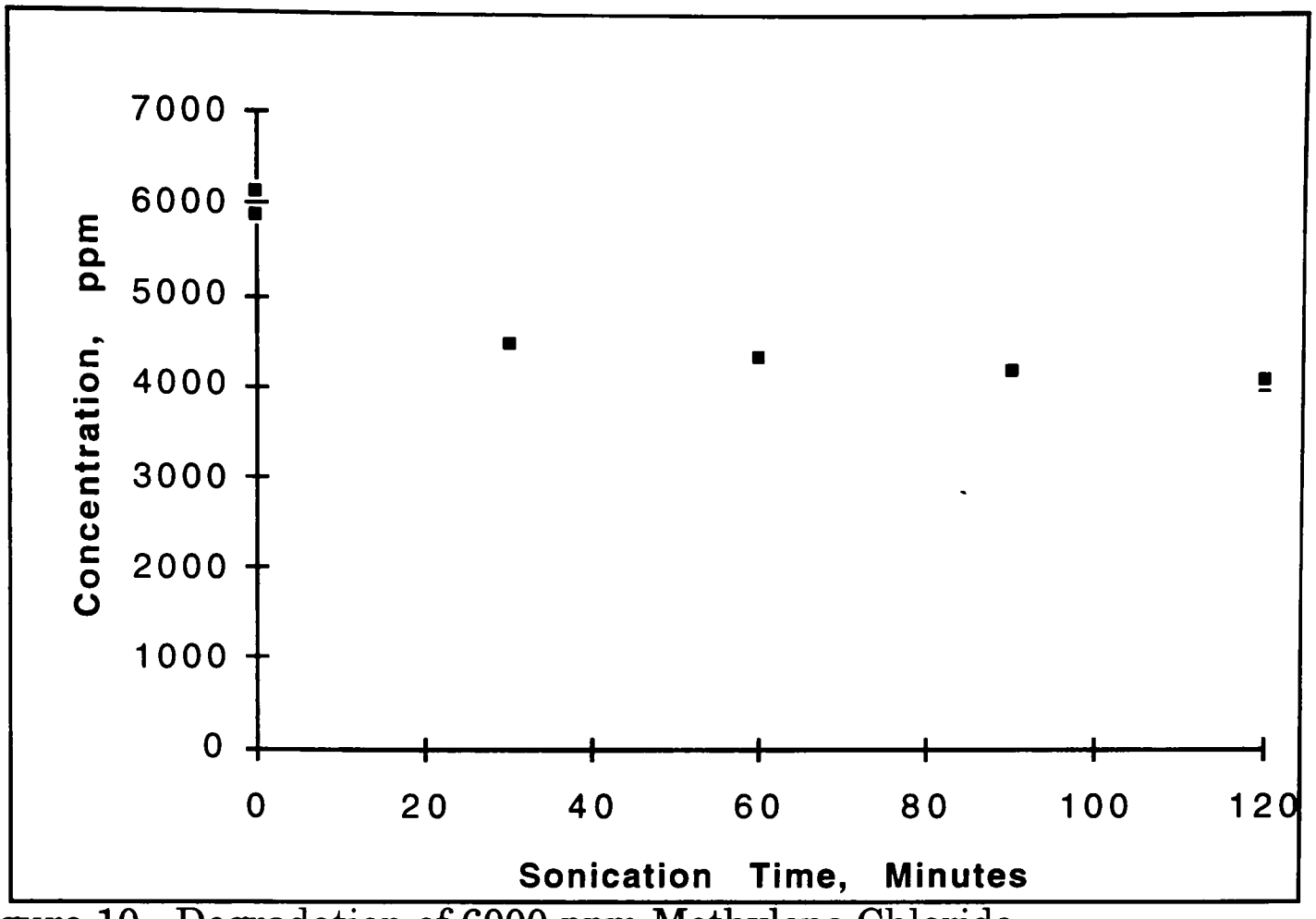


Figure 10. Degradation of 6000 ppm Methylene Chloride.

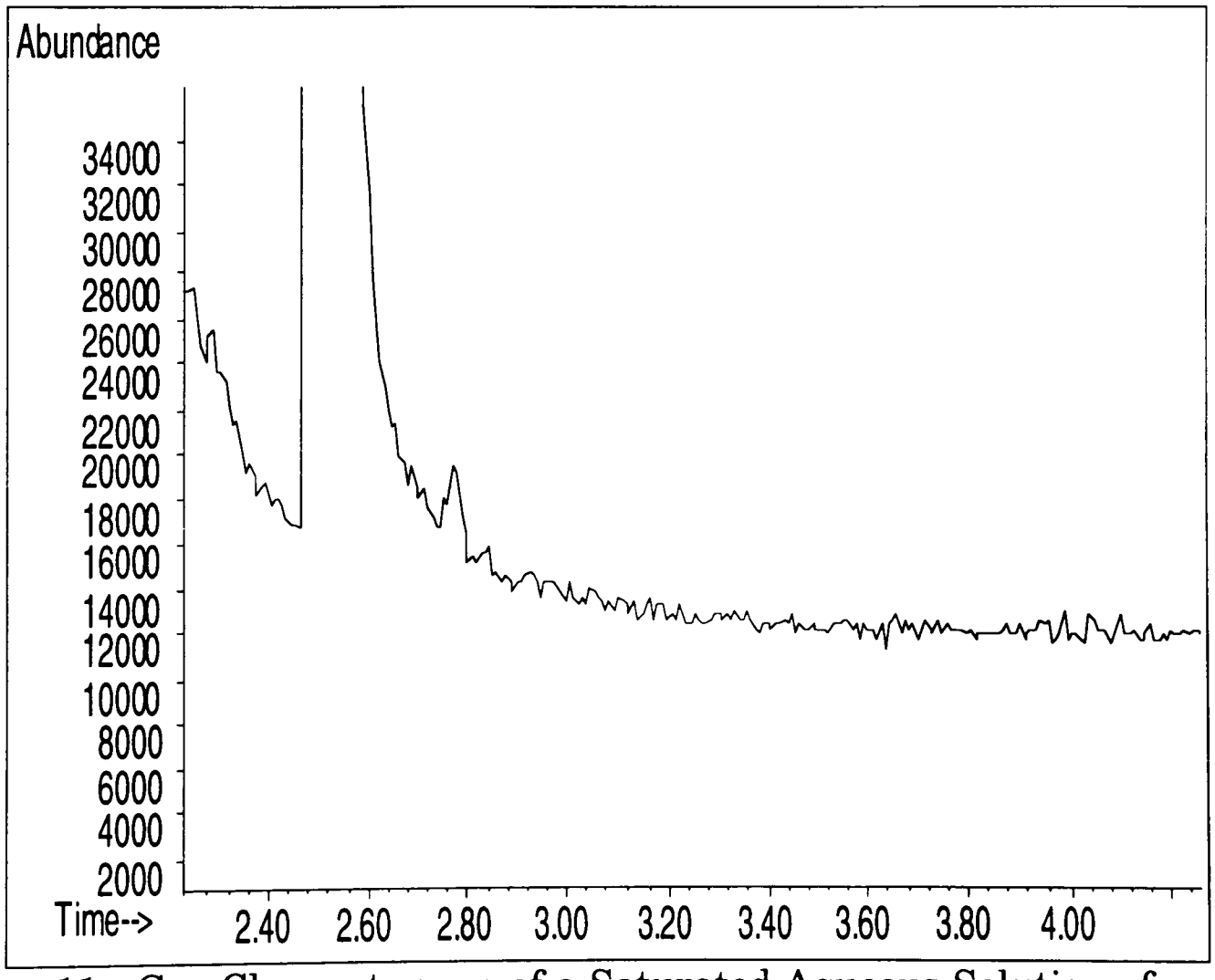


Figure 11. Gas Chromatogram of a Saturated Aqueous Solution of Methylene Chloride Sonicated for 30 Seconds.

trans-1,2-dichloroethylene (2.63 m), cis-1,2-dichloroethylene (2.89 m), chloroform (2.95 m), 1,2-dichloroethane (3.20 m), trichloroethylene (3.63 m), 1,1,2-trichloroethane (4.31 m) and 1,1,2,2-tetrachloroethane (5.61 m) (see Figure 12). 1,2-Dichloroethane, and 1,1,2,2-tetrachloroethane were not observed upon sonication of neither 2500 ppm nor 5000 ppm methylene chloride, as they were with the 6000 ppm solution. However, after 120 minutes of sonication time, the concentrations of chloroform and 1,1,2,2-trichloroethane were about 40 ppm; the other products formed were not quite 15 ppm (see Figure 13).

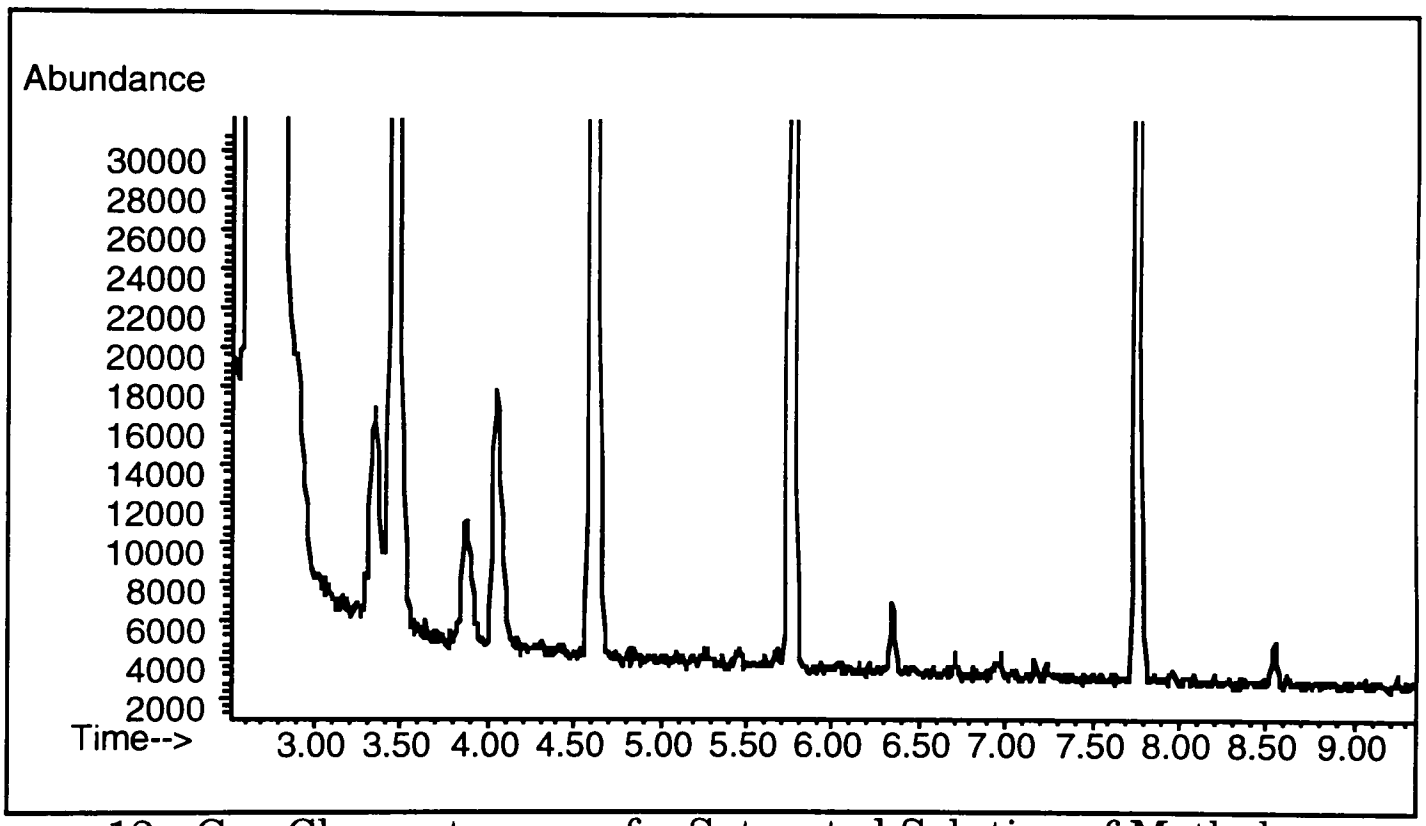


Figure 12. Gas Chromatogram of a Saturated Solution of Methylene Chloride Sonicated for 120 Minutes.

Neat methylene chloride was sonicated, to determine whether water was necessary for sonication, and to see what products formed if it did occur. The injection sample size used for the GC-MS was doubled to 2 μL. Along with a multitude of other products, some of the same degradation products that formed in the aqueous solution were found in

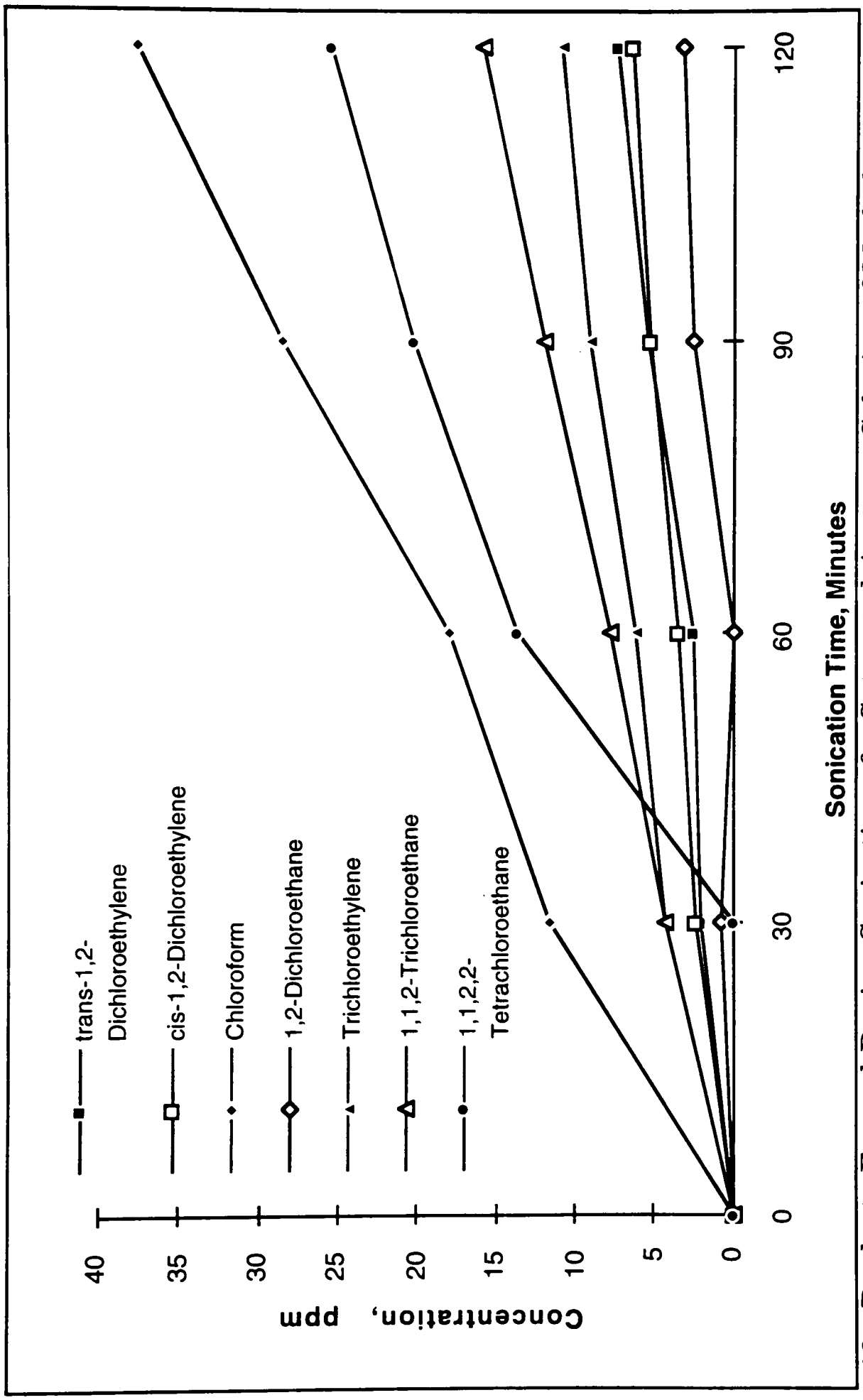


Figure 13. Products Formed During Sonication of a Saturated Aqueous Solution of Methylene Chloride.

the sonicated neat solution, which are shown in Figure 14 and are cis-1,2-dichloroethylene (3.10 m), chloroform (3.19 m), trichloroethylene (4.19 m), 1,1,2-trichloroethane (5.30 m) and 1,1,2,2-tetrachloroethane (7.62 m). It is possible that these many unidentified products are also present in the aqueous samples, just below detection levels. It is also possible that the presence of water causes other products such as HCl to be formed in larger quantities and cause a smaller number of degradation products to form in the aqueous solutions.

The role of oxygen in the reaction was examined by sonicating a 50 ppm solution under an atmosphere of argon instead of air. The degradation of methylene chloride under argon was similar, as shown in Figure 15, which compares the degradation of methylene chloride in both

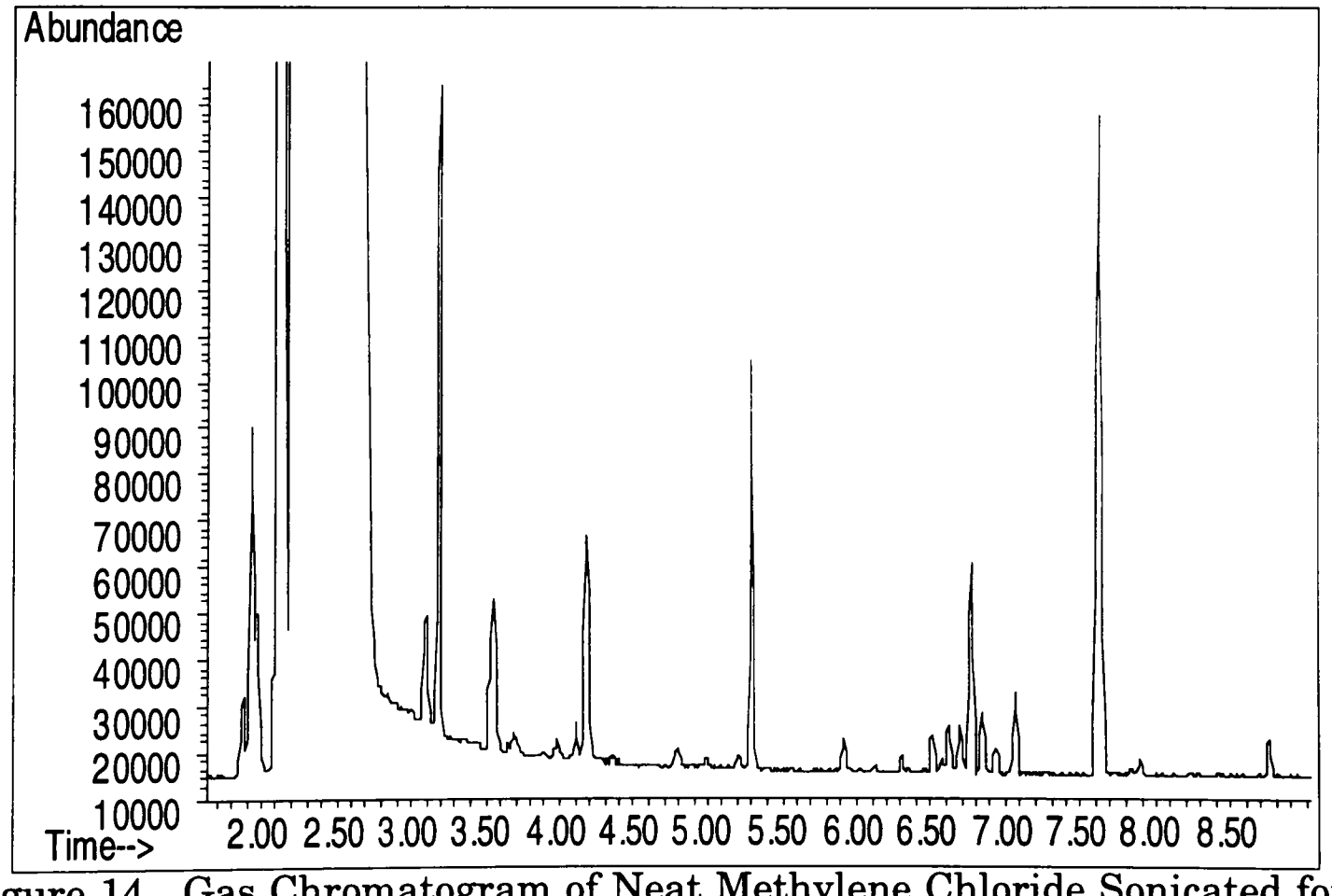


Figure 14. Gas Chromatogram of Neat Methylene Chloride Sonicated for 120 Minutes, and With a GC Injection Sample Size of 2 μL.

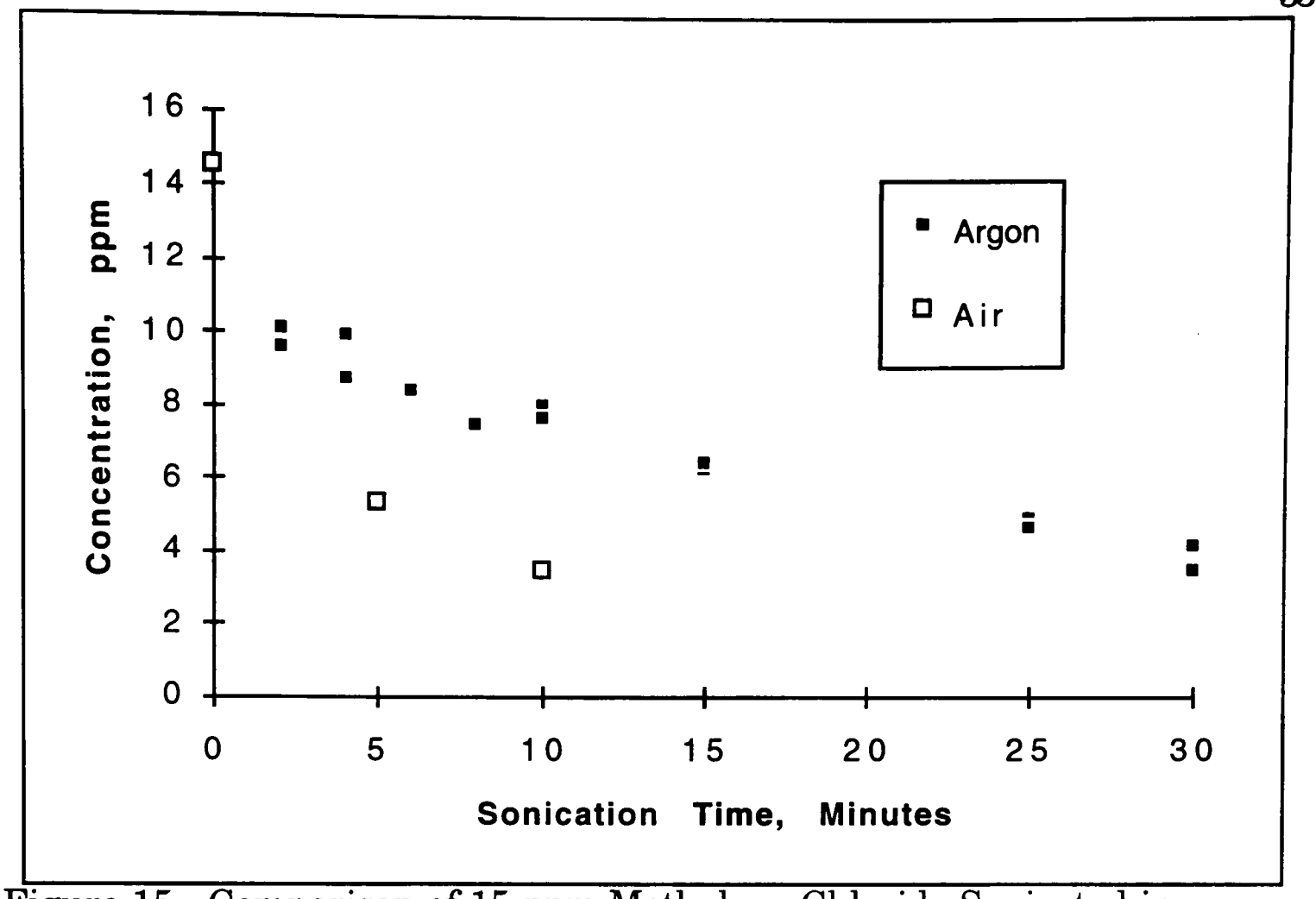


Figure 15. Comparison of 15 ppm Methylene Chloride Sonicated in Atmospheres of Air and Argon.

air and argon atmospheres. Sonication at this concentration level in neither atmosphere had degradation products that were detected.

The formation of ethylenes brought about some questions concerning the reaction mechanism. Was the reaction mechanism a one radical, two-step process, or instead a diradical process? In order to determine whether or not a diradical process was occurring, a carbene trap study was done. A carbene reacting with a cyclic alkene yields a fused bicyclic alkane, due to carbene insertion. Methylene chloride and cyclooctene were added in a large excess to water and sonicated. There was no evidence for a bicyclononane of any variety, indicating the lack of carbenes during sonication. The ethylenes seem to be formed via a one radical, two-step process.

Chloroform

Chloroform, in aqueous solutions as well as neat, was sonicated to see whether concentration had any effect on both the degradation and the subsequent formation of degradation products. The aqueous samples ranged in concentration from as low as 15 ppm to as high as 3500 ppm. At all aqueous concentrations, the pH dropped, which has been attributed to the formation of HCl, and possibly HOCl which would come from the hydrolysis of Cl_2.[86] The degradation products were not detected in solutions with initial chloroform concentrations of less than 500 ppm. At a relatively low concentration of chloroform, 15 ppm, the degradation was rapid and nearly complete, with 89% degradation in 10 minutes (see Figure 16). Figure 17 shows the degradation of chloroform at concentrations of about 60 ppm. The degradation was also rapid, with 95% degradation in just 10 minutes. There were no degradation products detected. Although the degradation at 60 ppm concentration is as fast as that at 15 ppm it is slightly less complete.

At a concentration of 500 ppm, detectable degradation products were present after 30 minutes of sonication time. At this concentration, the chloroform degradation was 99% complete in 120 minutes, as seen in Figure 18. The products that formed after 30 minutes of sonication were identified by the mass spectrometer as carbon tetrachloride, trichloroethylene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, pentachloroethane and hexachloroethane, with hexachloroethane having the highest concentration. The formation of these products as a function of time is shown in Figure 19. These products are presumably formed by the recombination of the radicals formed during sonication, as depicted in Scheme 2. After 90 minutes of sonication time, the concentrations

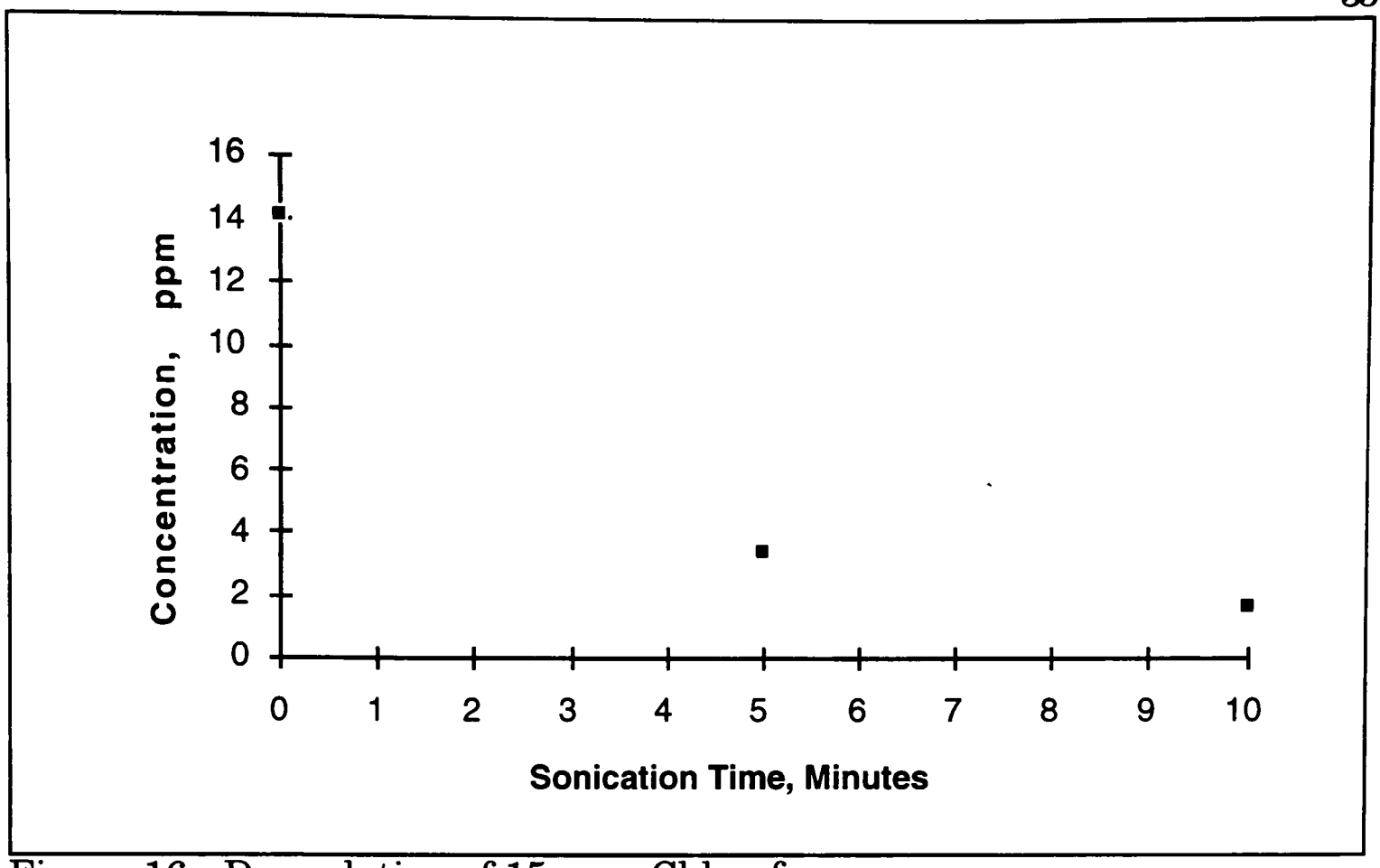


Figure 16. Degradation of 15 ppm Chloroform.

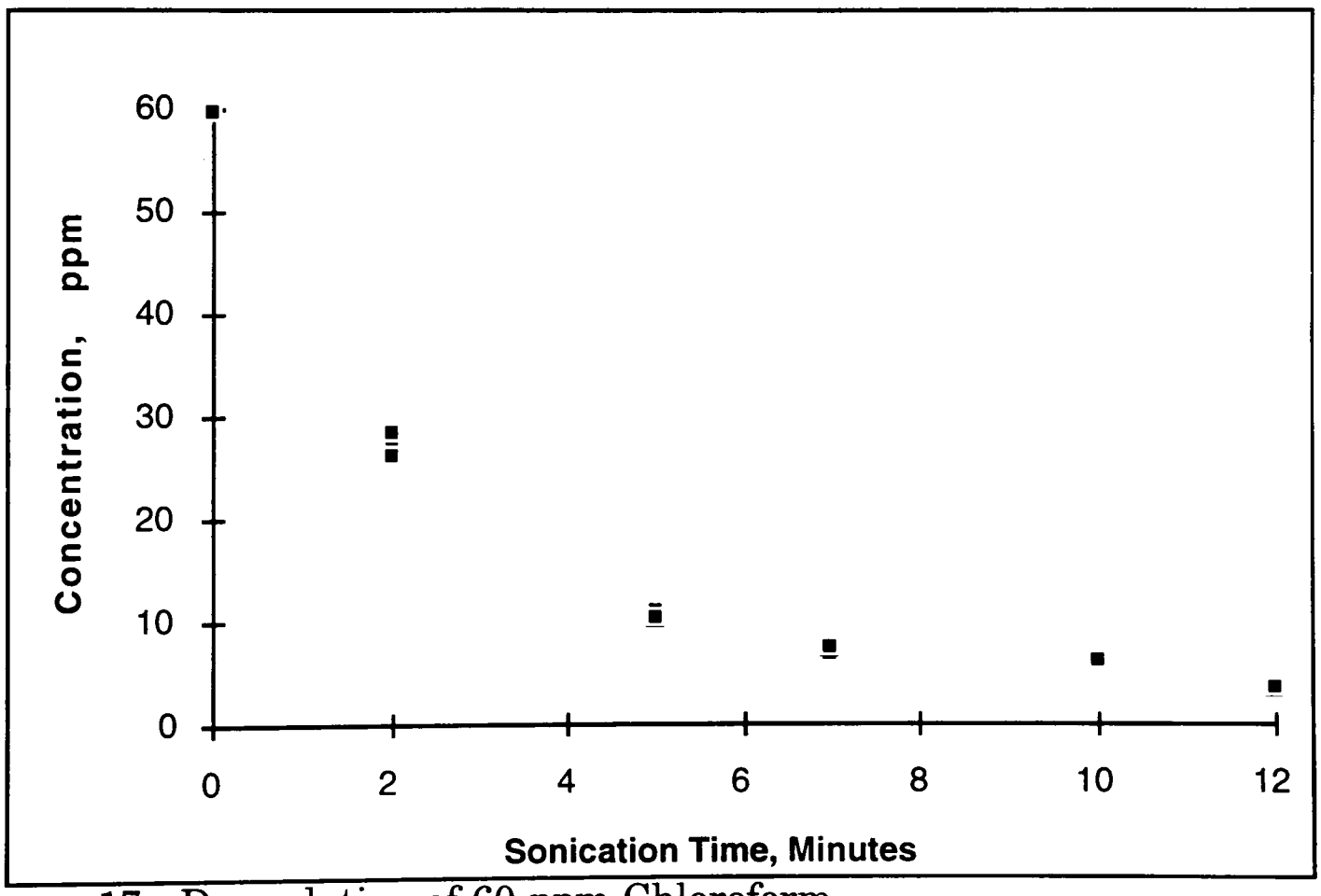


Figure 17. Degradation of 60 ppm Chloroform.

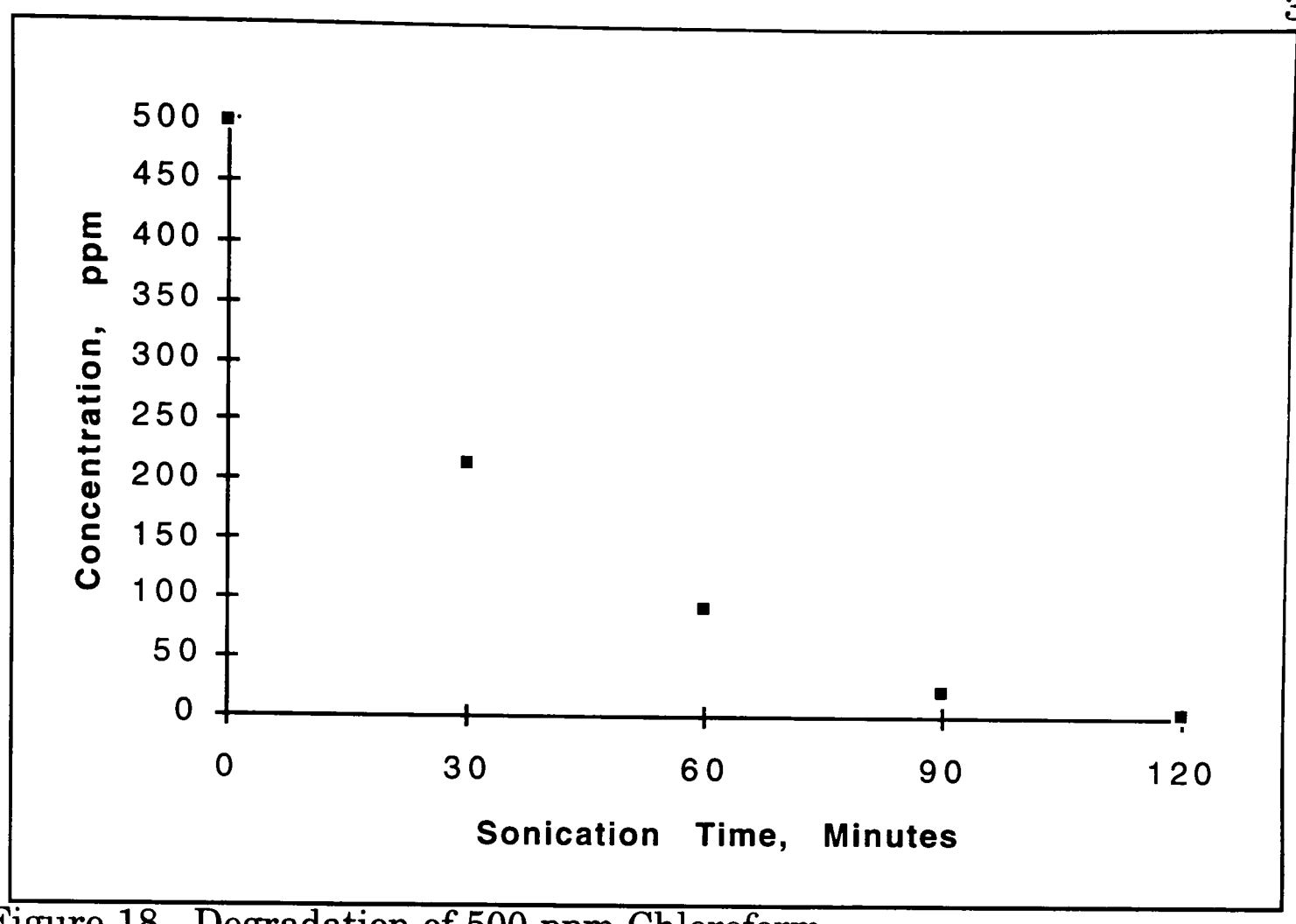


Figure 18. Degradation of 500 ppm Chloroform.

of all the products began to decrease, while after 6 hours, all but the tetrachloroethylene and carbon tetrachloride were reduced to below the detection level, which was between 500 ppb and 1 ppm. By 10 hours, all chloroform and products were not detected, as seen in Figure 20.

A saturated solution of chloroform, at a concentration level of approximately 2300 ppm, was sonicated to investigate degradation and degradation product formation. In as little as 30 seconds, the most prevalent of these products, carbon tetrachloride (3.4 m) and tetrachloroethylene (5.0 m), began to appear (see Figure 21) and in 2 minutes all the major degradation products, carbon tetrachloride (3.4 m), trichloroethylene (3.6 m), tetrachloroethylene (5.0 m), 1,1,2,2-tetra-chloroethane (5.6 m), pentachloroethane (6.2 m) and hexachloroethane (7.0 m) had formed (see Figure 22). After 30 minutes, 5

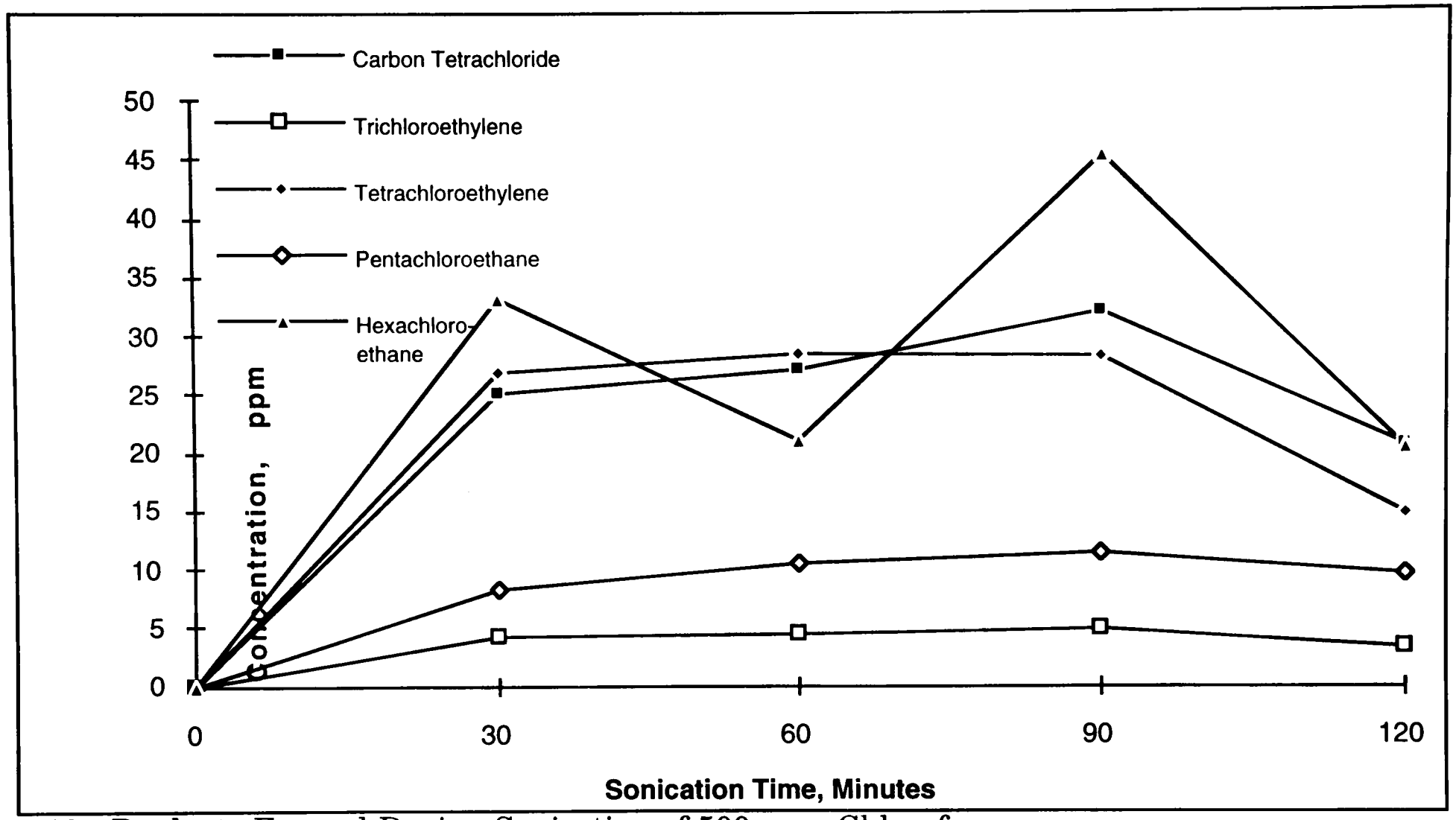
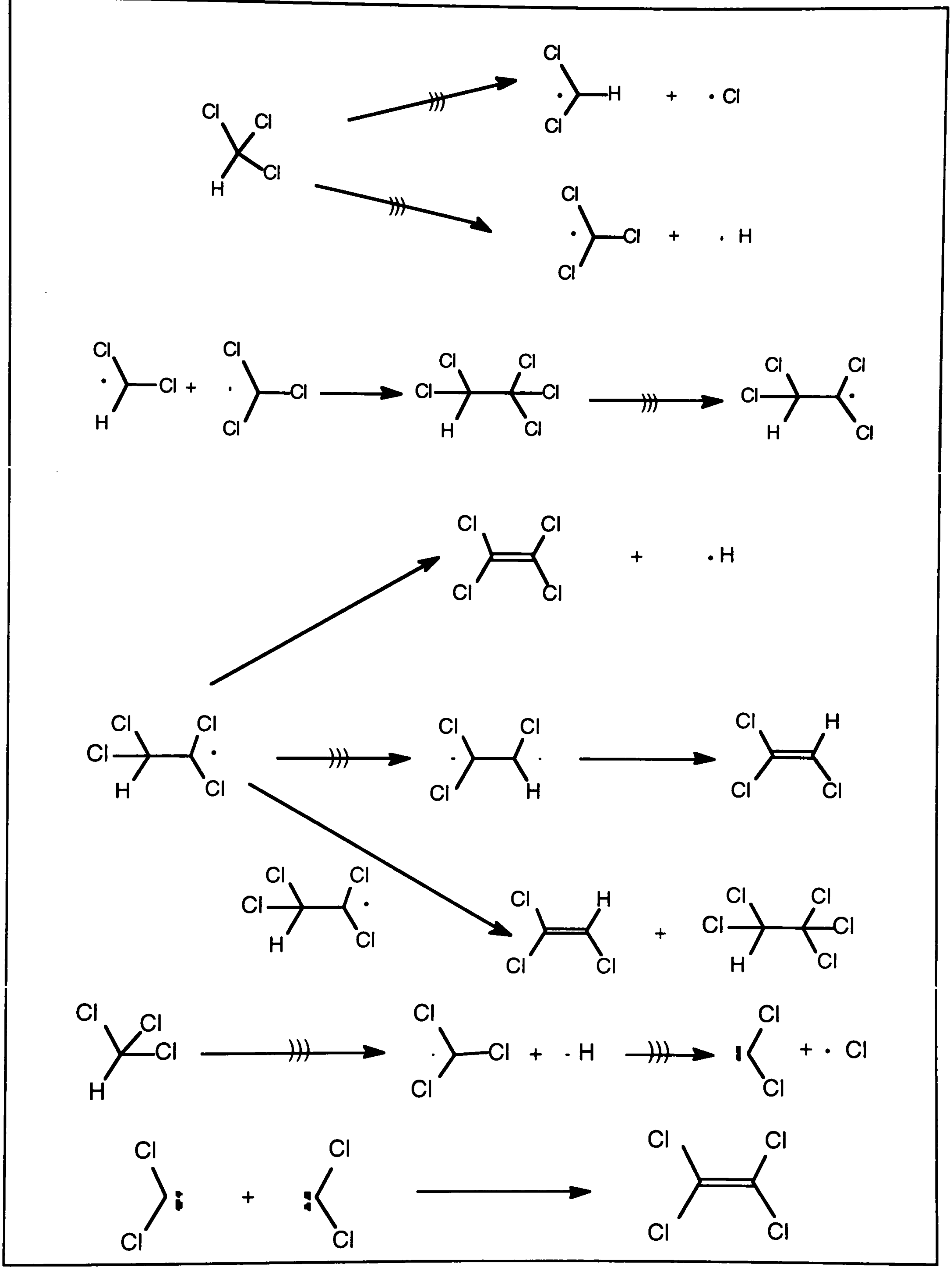


Figure 19. Products Formed During Sonication of 500 ppm Chloroform.

Scheme 2. Radical Formation and Recombination During Sonication to Form Degradation Products.



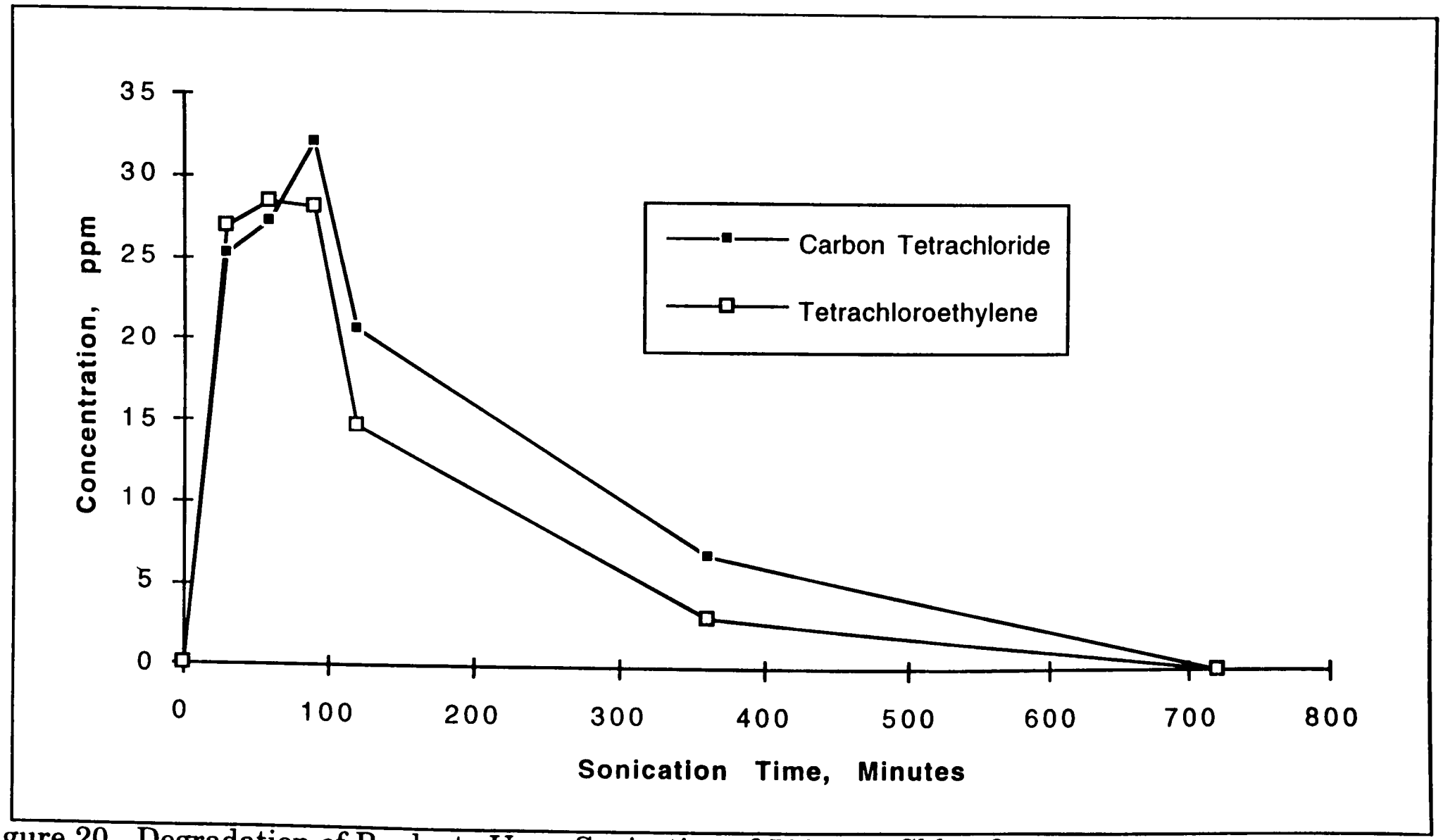


Figure 20. Degradation of Products Upon Sonication of 500 ppm Chloroform.

minor products that were not identified appeared at 5.35 m, 6.70 m, 8.10m, 8.15 m, and 10.35 m, as shown in Figure 23. Computer analysis of the isotopic ratios in the mass chromatogram suggests that these minor products are possibly chlorinated propanes or larger chlorinated hydrocarbons. After 120 minutes of sonication, over 70% of the chloroform degraded, as shown in Figure 24. As was seen with high concentrations of methylene chloride, the degradation to levels below the instrument detection level was very slow, but after 12 hours of sonication time, there was no detectable chloroform, as shown in Figure 25.

Neat chloroform was sonicated to observe which, if any, degradation products formed in the absence of water. Indeed, several were formed, among them phosgene, methylene chloride,

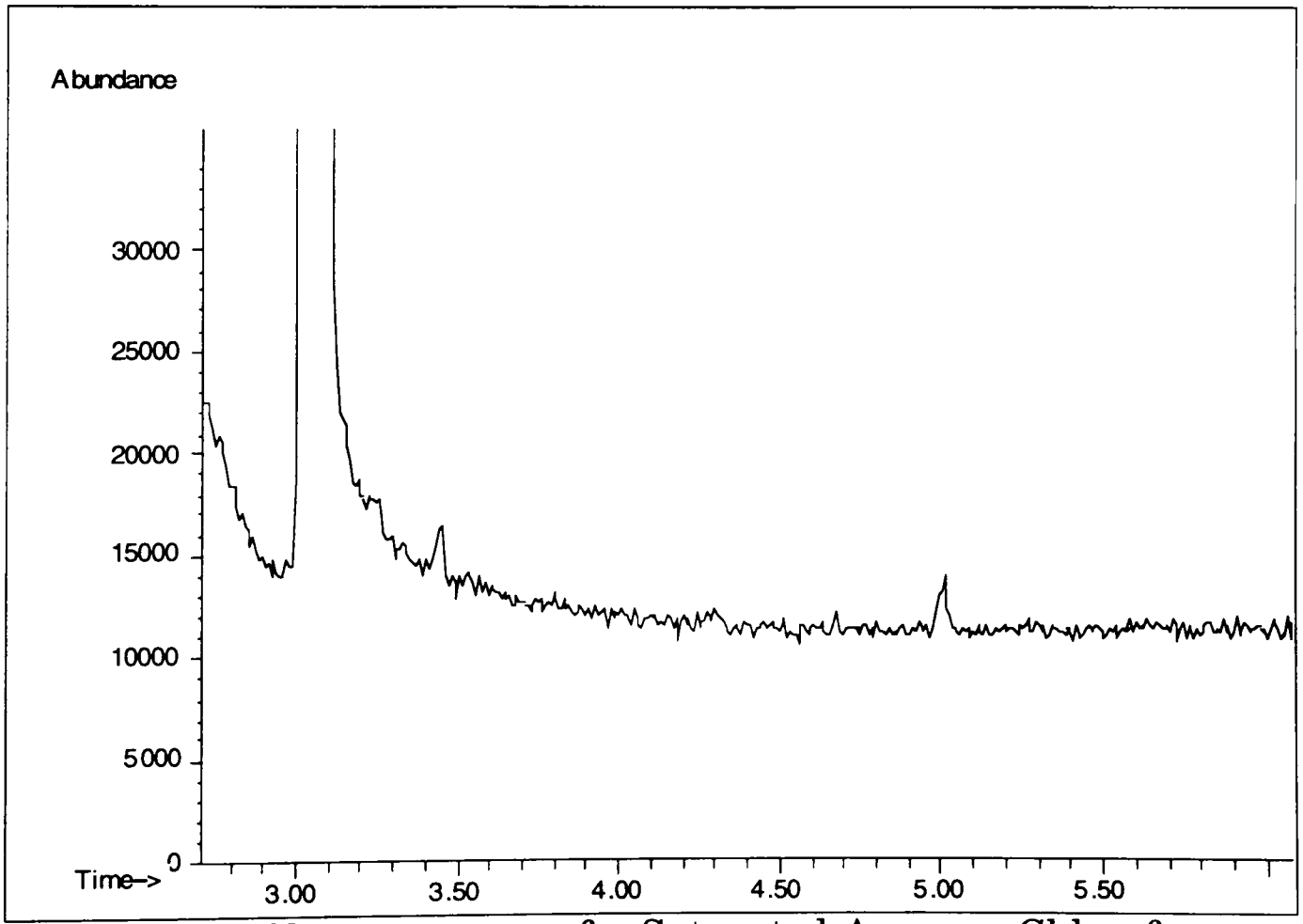


Figure 21. Gas Chromatogram of a Saturated Aqueous Chloroform Solution Sonicated for 30 Seconds.

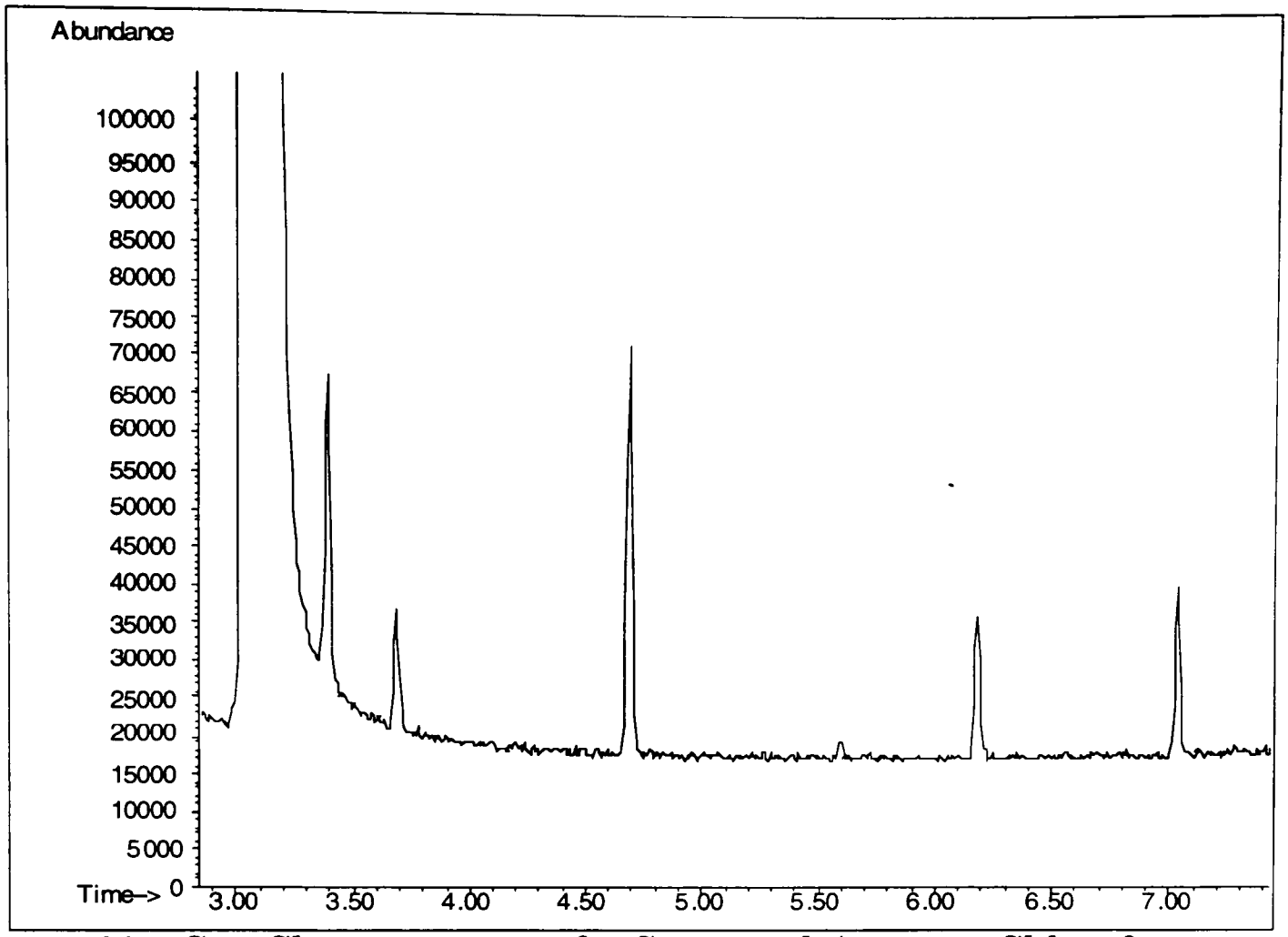


Figure 22. Gas Chromatogram of a Saturated Aqueous Chloroform Solution Sonicated for 2 Minutes.

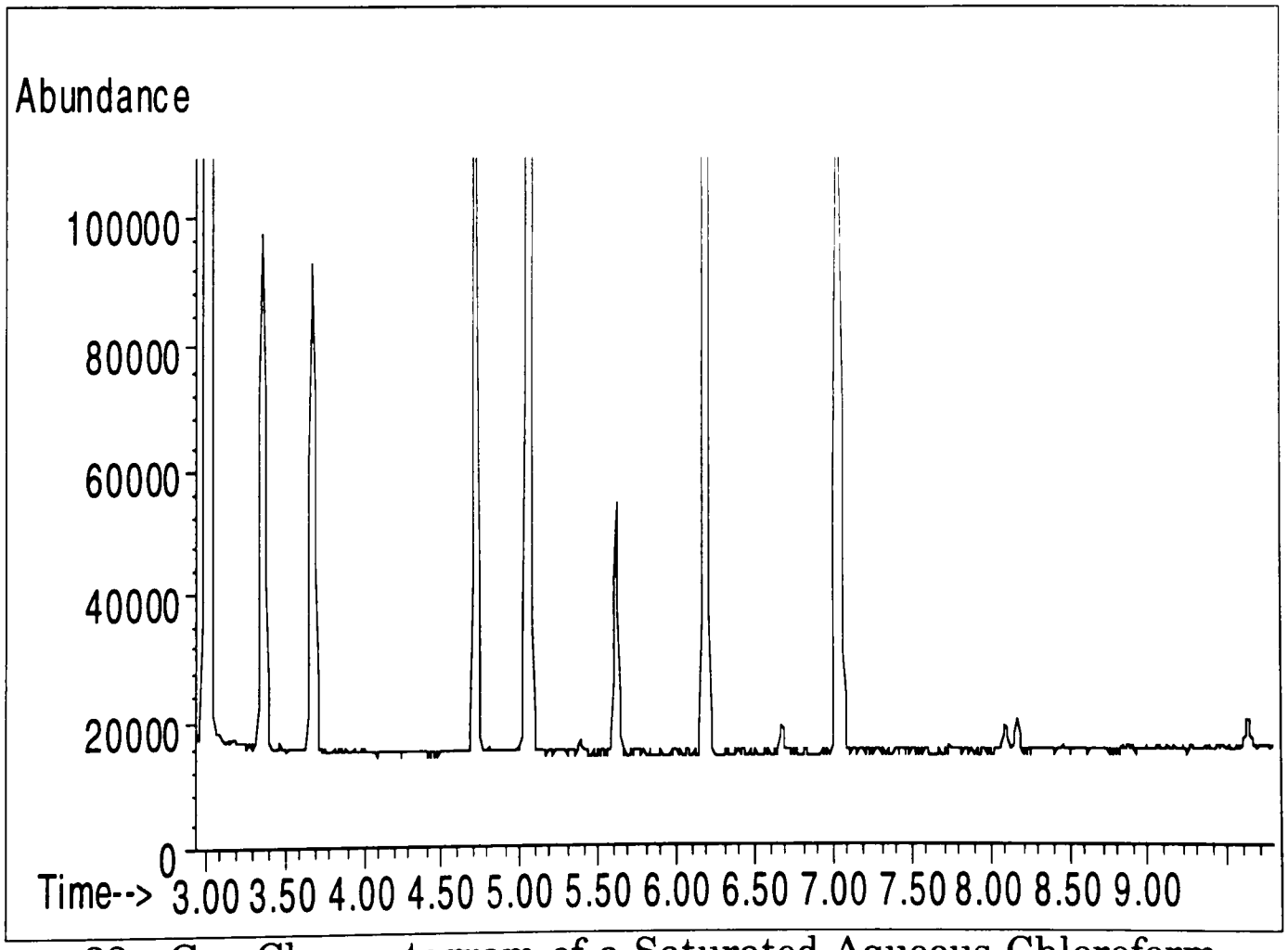


Figure 23. Gas Chromatogram of a Saturated Aqueous Chloroform Solution Sonicated for 30 Minutes.

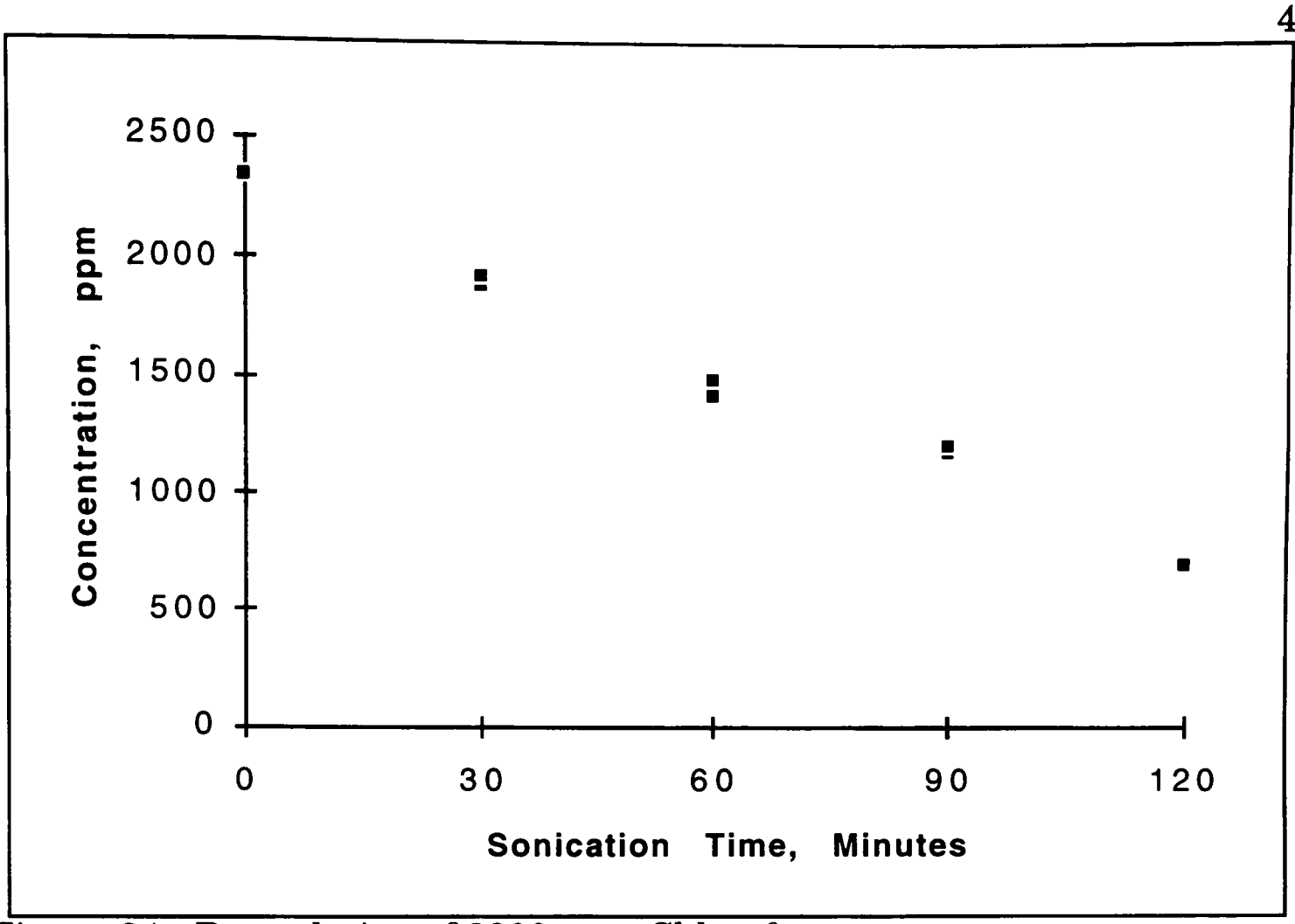


Figure 24. Degradation of 2300 ppm Chloroform.

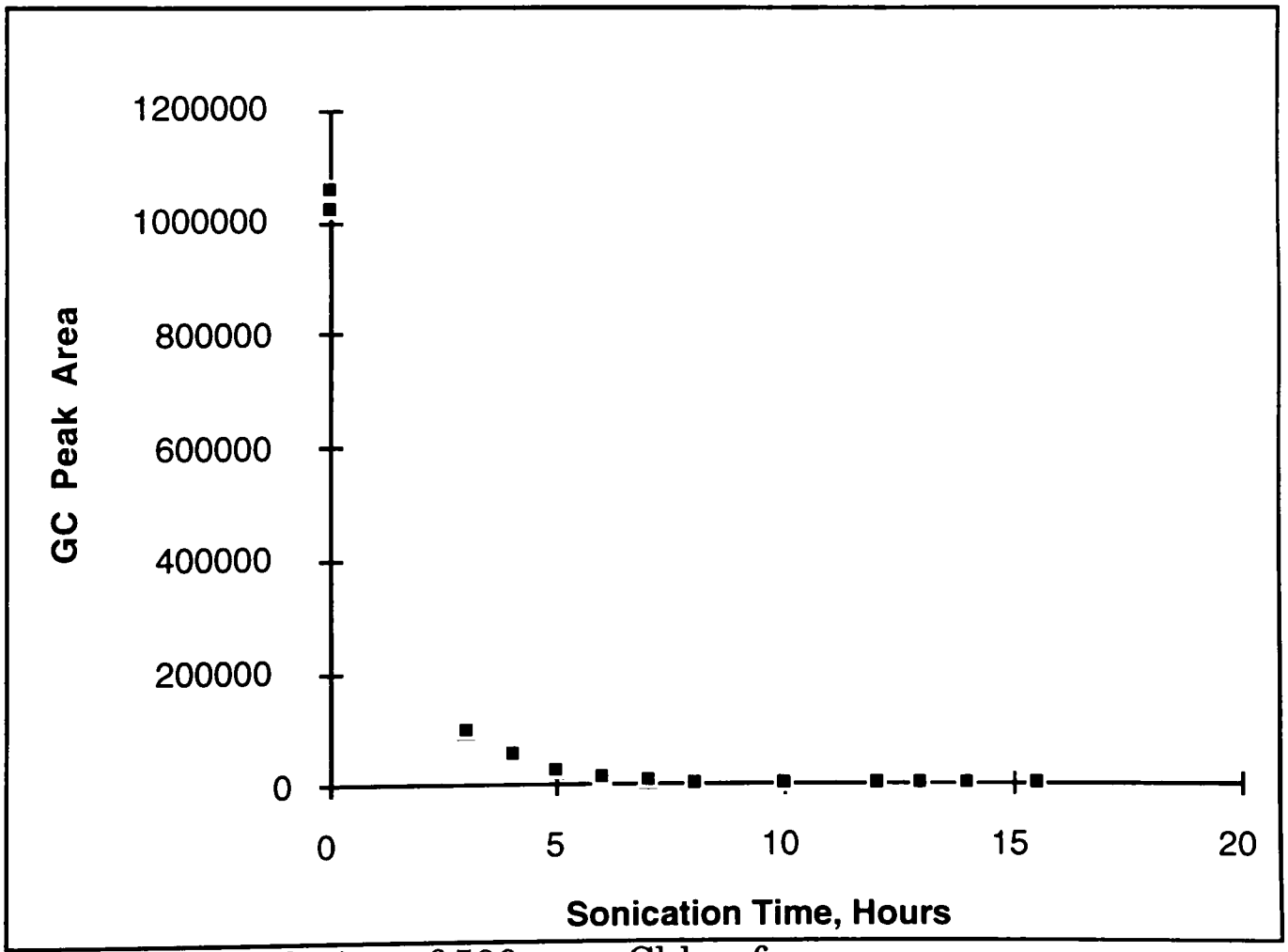


Figure 25. Degradation of 500 ppm Chloroform.

cis-1,2-dichloroethylene, carbon tetrachloride, trichloroethylene, tetrachloroethylene, pentachloroethane and hexachloroethane. This is shown in Figure 26. There were also numerous products that did not

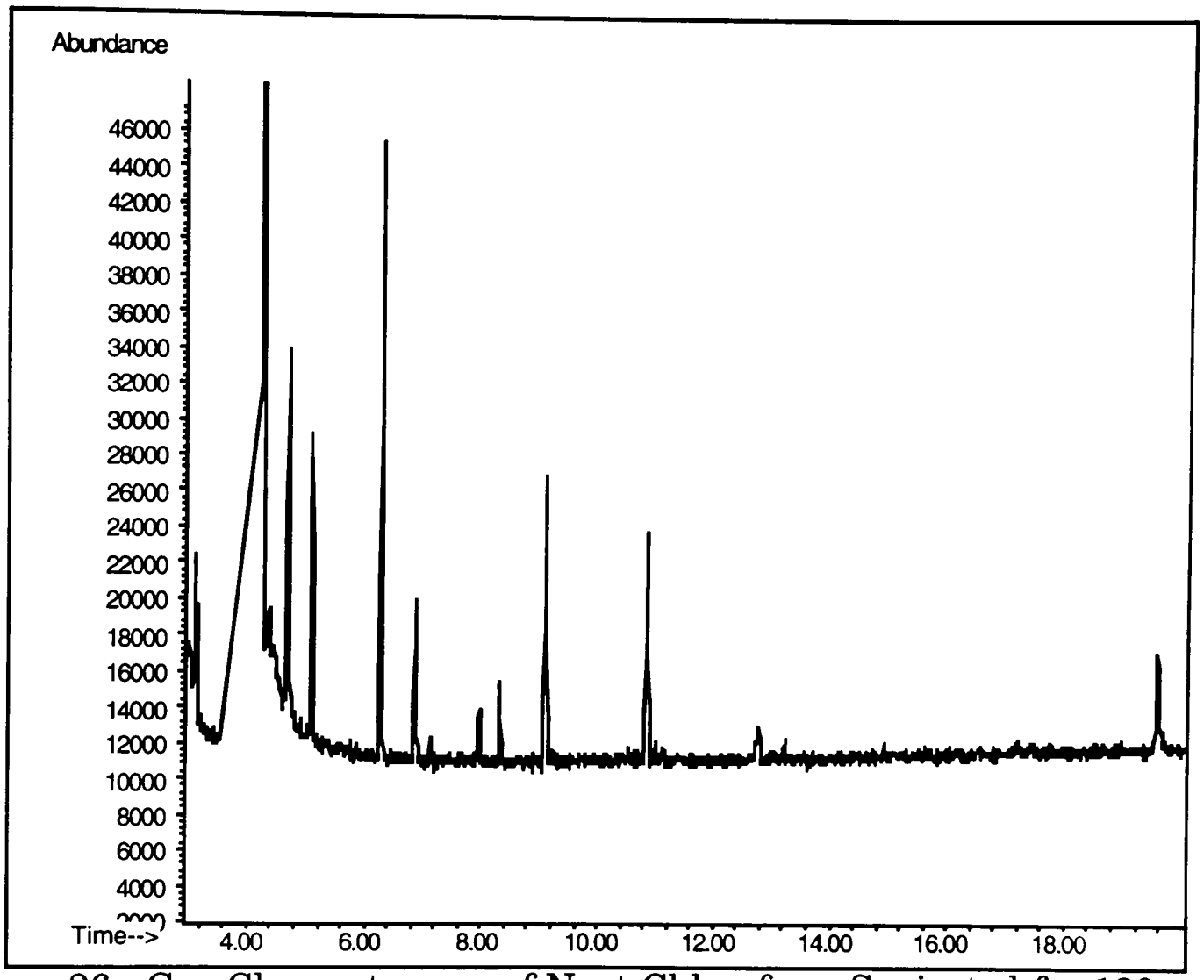


Figure 26. Gas Chromatogram of Neat Chloroform Sonicated for 120 Minutes.

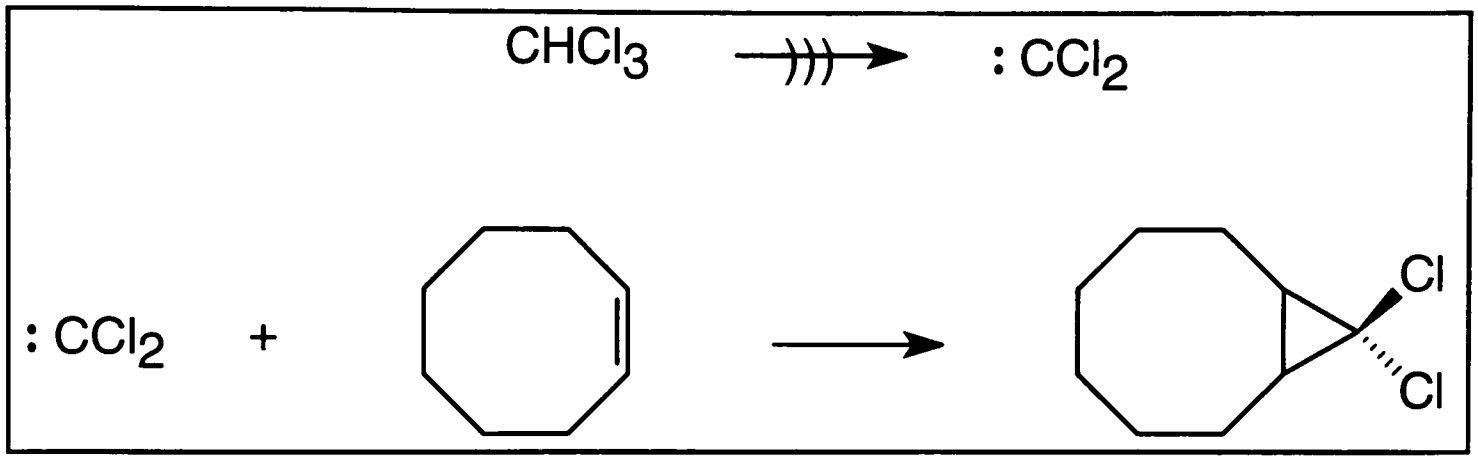
match any in the mass spectrometer's library. It is possible that these products may be present in the aqueous solutions of chloroform as well, but present below the detection limit, which was between 500 ppb and 1 ppm.

The production of ethylenes upon sonication led to the idea that carbenes might have been formed in solution. In the high temperatures of thermal degradation of chloroform, around 600°C, dichlorocarbenes were observed in the decomposition pathway of chloroform,[102] so it

seemed possible that carbenes were being formed upon sonication, and indeed Henglein and Fischer[99] found that carbenes were present when neat chloroform was sonicated.

Dichlorocarbene was produced from chloroform utilizing a standard base-induced method[103] and cyclooctene was used to trap the dichlorocarbene. See Scheme 3. Once it was determined that the product,

Scheme 3. Formation Of 9,9-Dichlorobicyclo[6.1.0]Nonane In Presence Of Carbenes.



9,9-dichlorobicyclo[6.1.0]nonane, was detectable using the headspace-GC/MS procedure, as shown in Figure 27 (8.28 m), attention was turned to aqueous chloroform. Since cyclooctene was not soluble in water, it was mixed with chloroform, and this was added in large excess to water. During sonication, an emulsion was formed which turned the solution milky white. After 20 minutes of sonication, the solution was allowed to settle until the layers separated. The organic layer was analyzed, and 9,9-dichlorobicyclo[6.1.0]nonane was detected in small quantities (see Figure 28). This suggests that carbenes are formed during sonication of halocarbons in aqueous solutions, and are one possible pathway in the degradation product formation.

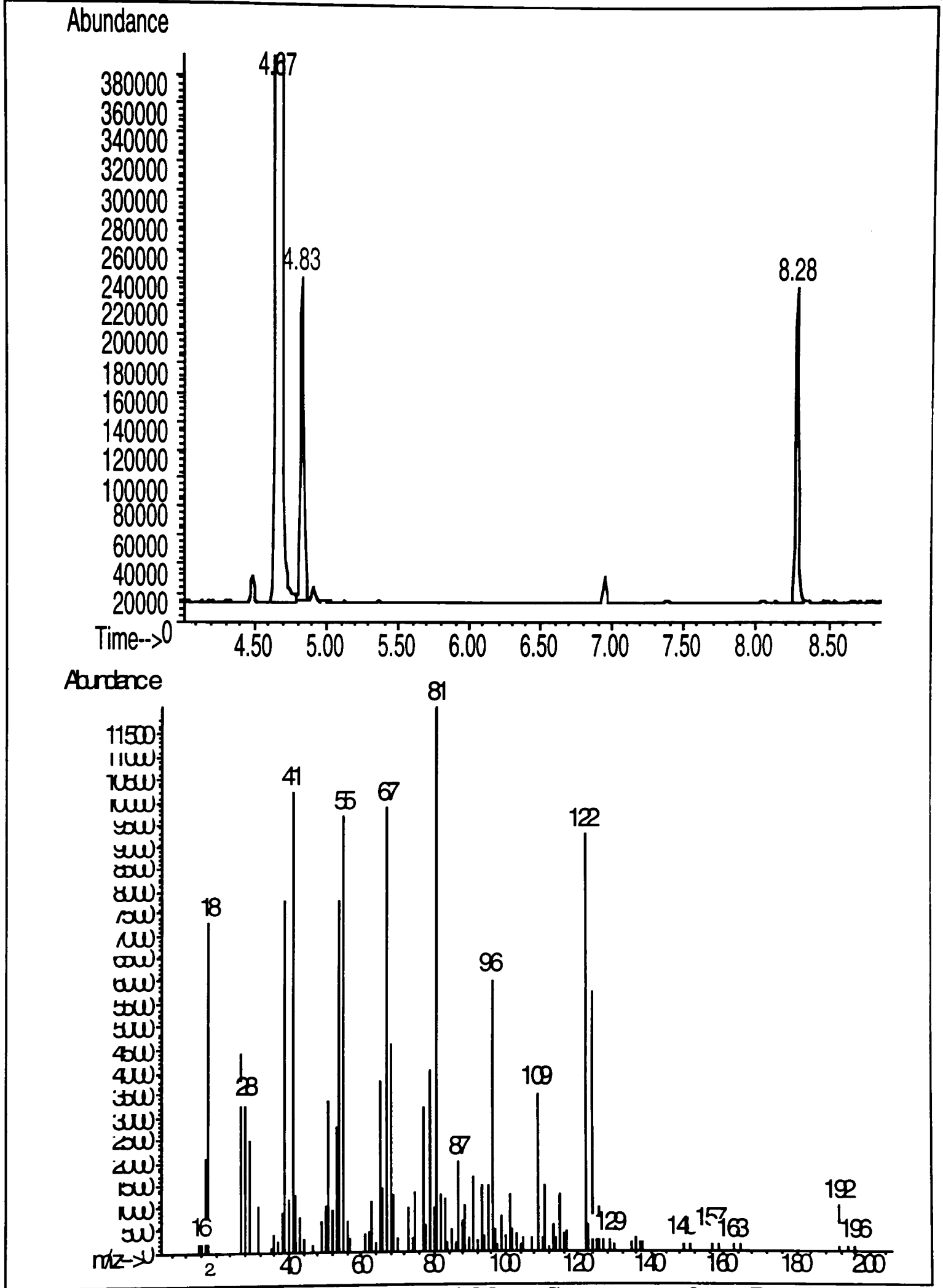


Figure 27. Gas Chromatogram and Mass Spectrum of 9,9-Dichloro-bicyclo[6.1.0]Nonane Formed Via Sodium Hydroxide.

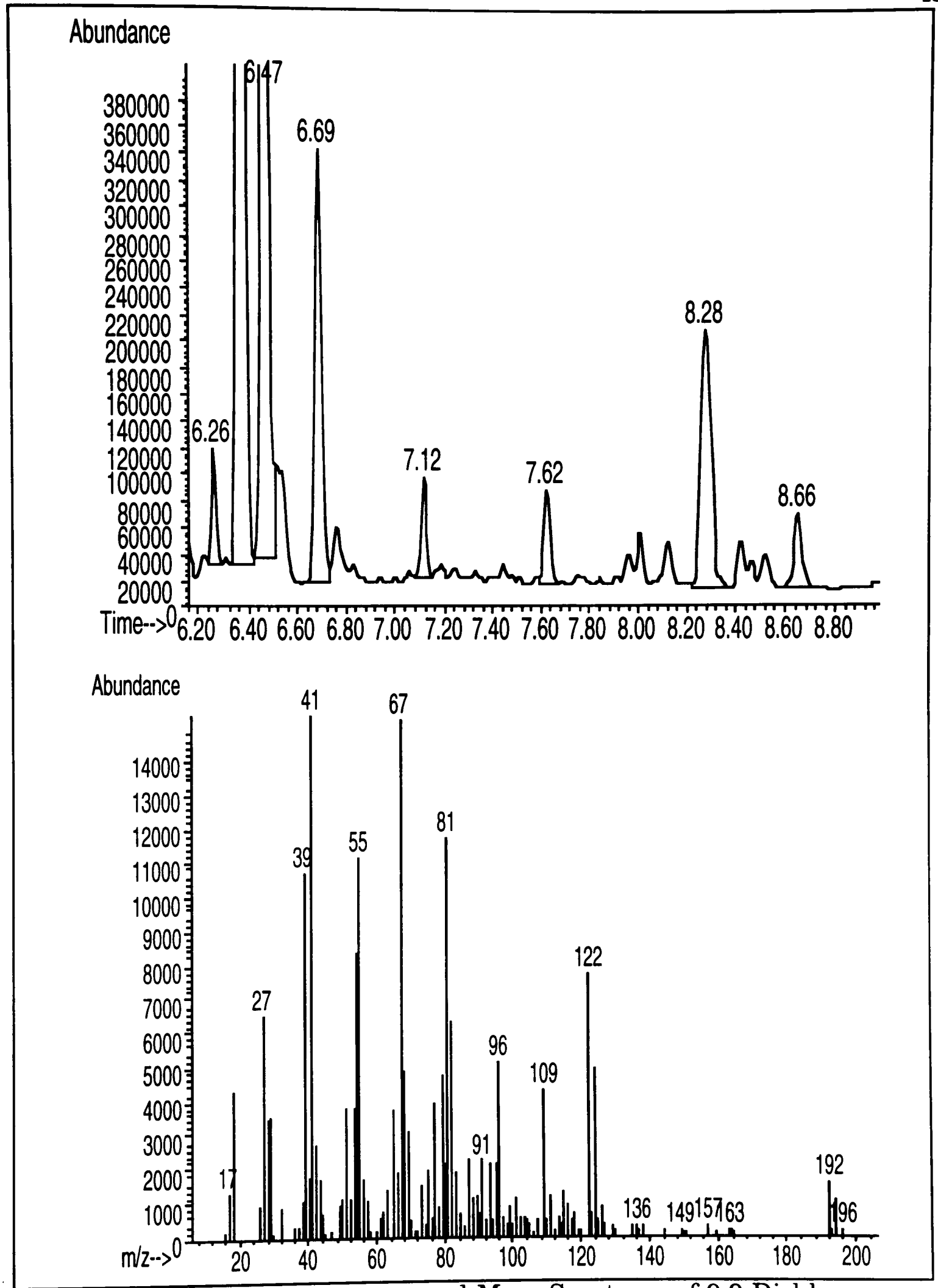


Figure 28. Gas Chromatogram and Mass Spectrum of 9,9-Dichlorobicyclo[6.1.0]Nonane Formed Via Sonication.

Carbon Tetrachloride

Various concentrations of carbon tetrachloride were sonicated to determine the degradation and the effect that concentration would have on both the rate of degradation and the products formed upon sonication. These aqueous solutions ranged in concentration from 20 ppm to 250 ppm. At all aqueous concentrations, the pH dropped, which has been attributed to the formation of HCl and possibly HOCl which would come from the hydrolysis of Cl_2.[86] Neat carbon tetrachloride was also sonicated to see if water plays a part in the degradation and the products formed.

At low concentrations, such as 20 ppm of carbon tetrachloride, sonication gave rapid and nearly complete degradation. Greater than 96% of the carbon tetrachloride was degraded in the first 20 minutes (see Figure 29). When the carbon tetrachloride initial concentration was

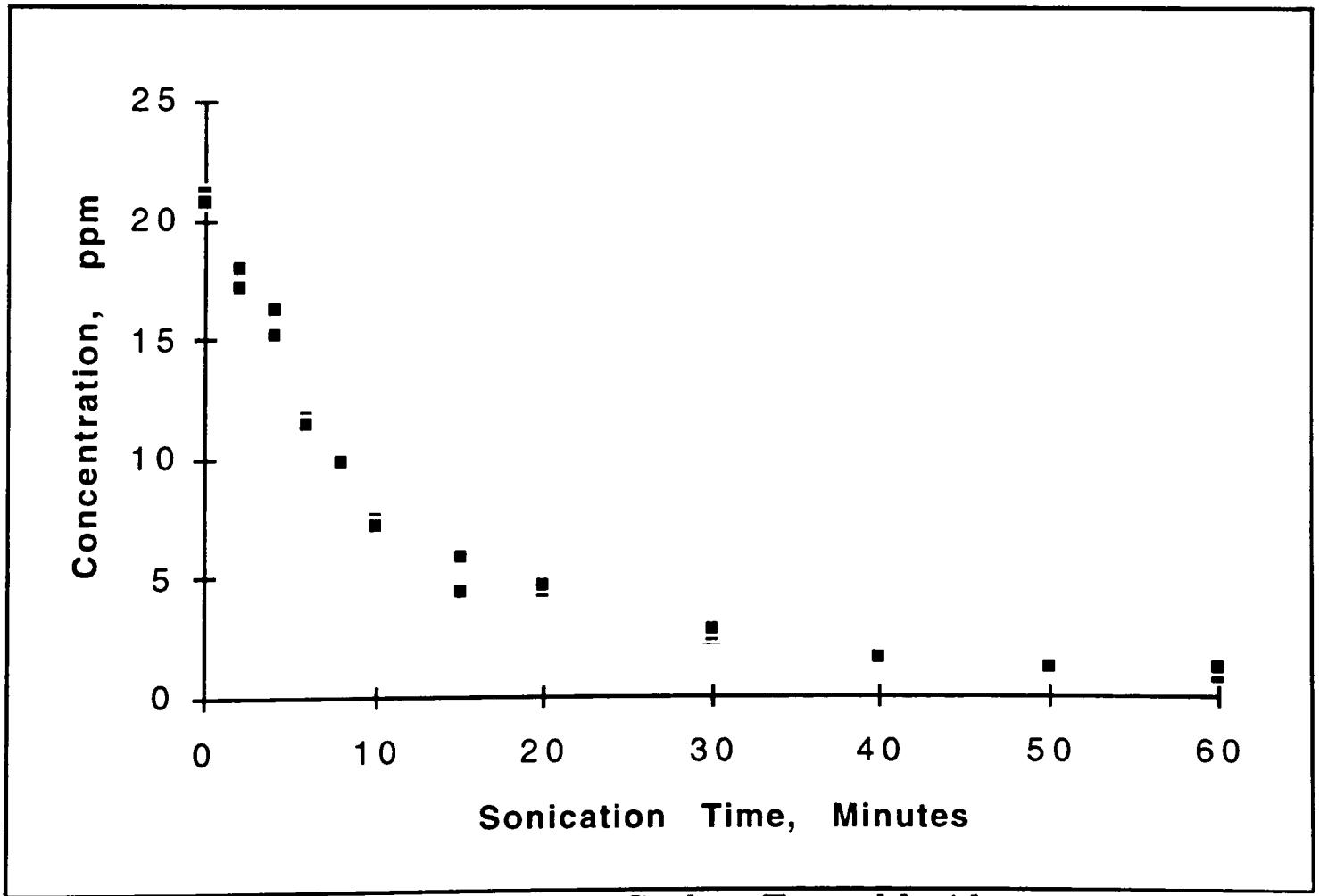


Figure 29. Degradation of 20 ppm Carbon Tetrachloride.

increased to 50 ppm, the result was similar, as shown in Figure 30 with 90% degradation of the carbon tetrachloride in 10 minutes of sonication time. Sonication of slightly higher concentrations of carbon tetrachloride, such as 100 ppm, once again gave similar results. There was 90% degradation in 10 minutes of sonication time (see Figure 31).

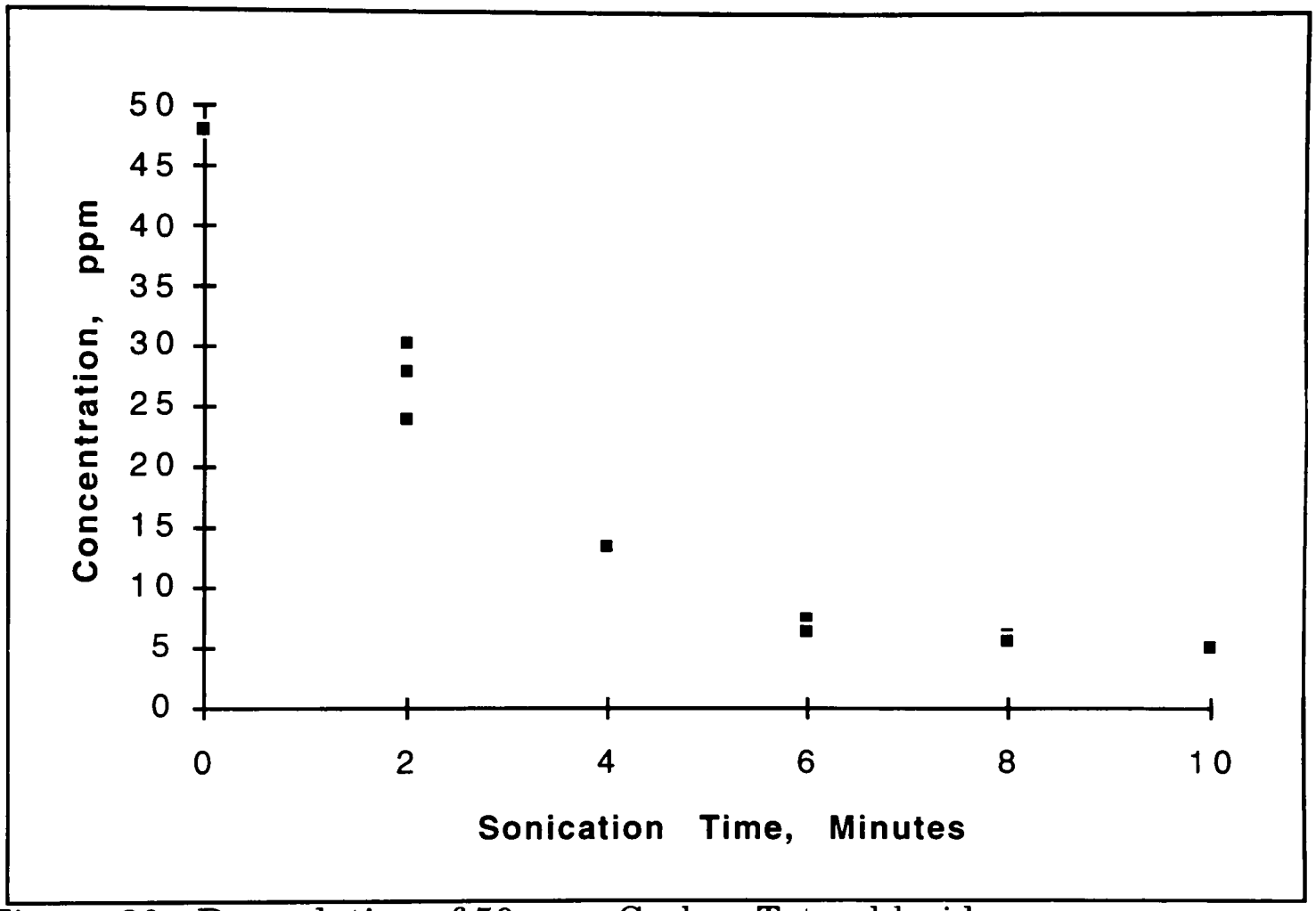


Figure 30. Degradation of 50 ppm Carbon Tetrachloride.

At higher carbon tetrachloride concentrations, those close to the saturation limit in water, almost 250 ppm, it took 120 minutes of sonication to achieve greater than 99% degradation (see Figure 32). Like methylene chloride and chloroform at comparable concentrations, a variety of detectable degradation product emerged upon sonication as shown in Figure 33. They are methylene chloride (3.32 m), chloroform (3.45 m), tetrachloroethylene (6.35 m) and hexachloroethane (9.62 m), with

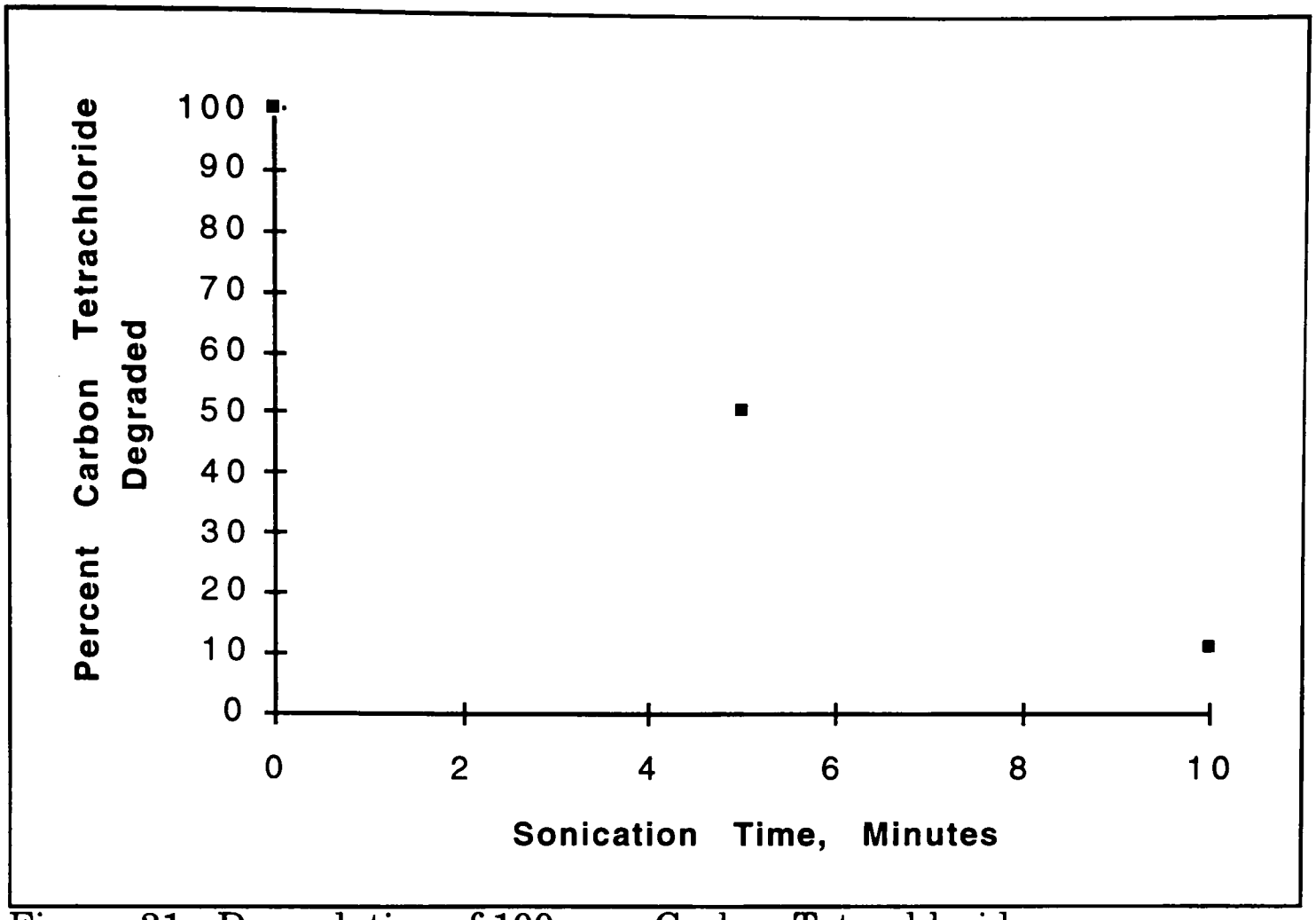


Figure 31. Degradation of 100 ppm Carbon Tetrachloride.

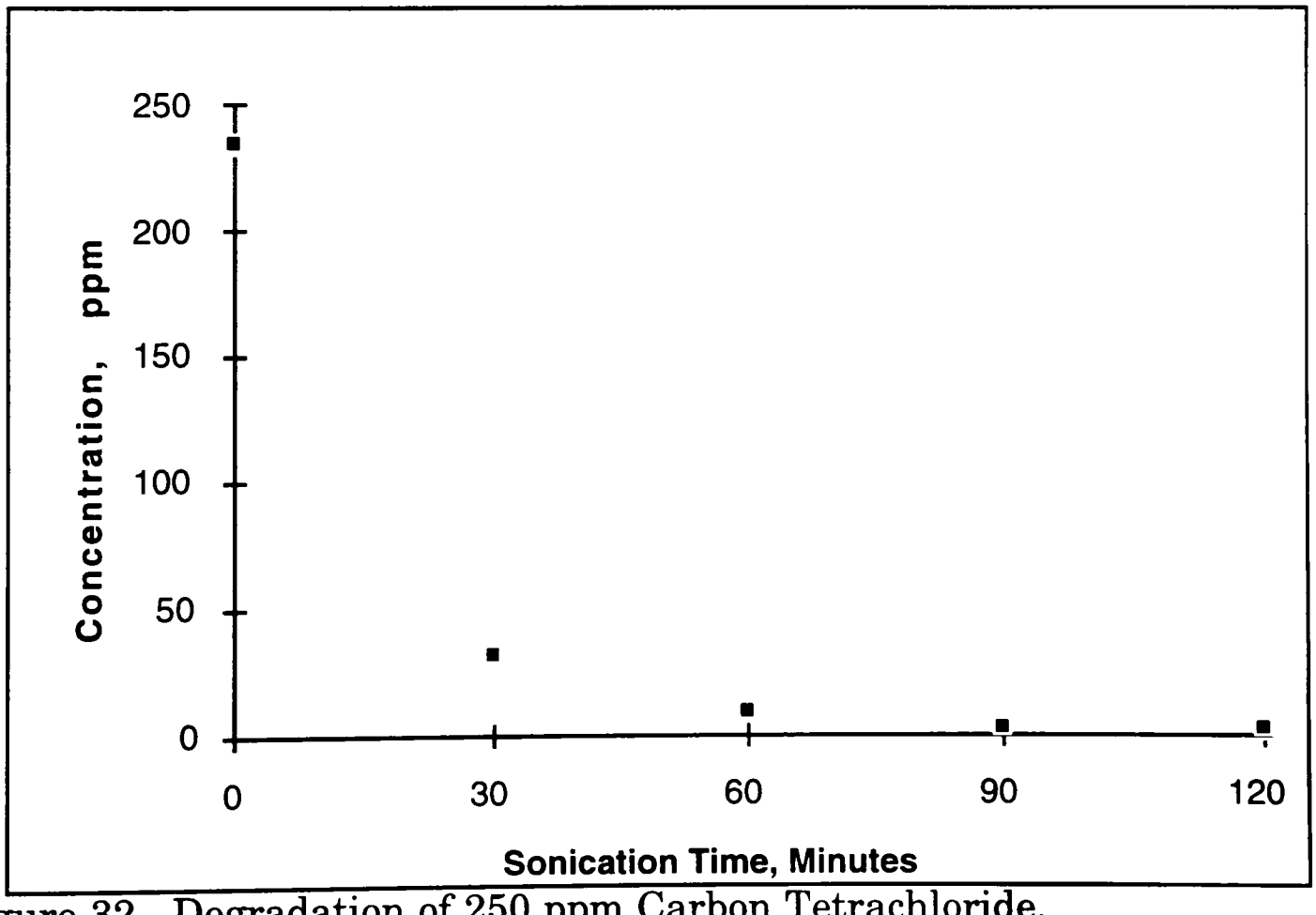


Figure 32. Degradation of 250 ppm Carbon Tetrachloride.

an unidentified peat at 10.13 minutes. The formation of these products over time is shown in Figures 34 and 35.

A solution of 50 ppm carbon tetrachloride was sonicated under an atmosphere of argon, instead of air, to see if the absence of oxygen altered the degradation results. However, the results were quite similar. It took 20 minutes of sonication time to degrade greater than 99% of the carbon tetrachloride (see Figure 36).

Neat carbon tetrachloride was sonicated, to see if there were any degradation products formed without water present. Indeed, several were formed, among them the expected tetrachloroethylene and hexachloroethane. Unexpectedly, chloroform, phosgene and methylene chloride were also present. This is shown in Figure 37. The incorporation of protons indicates that the carbon tetrachloride was not completely free of water. So these products may be present in the aqueous solutions of carbon tetrachloride as well, but present below the detection limit, which is between 500 ppb and 1 ppm.

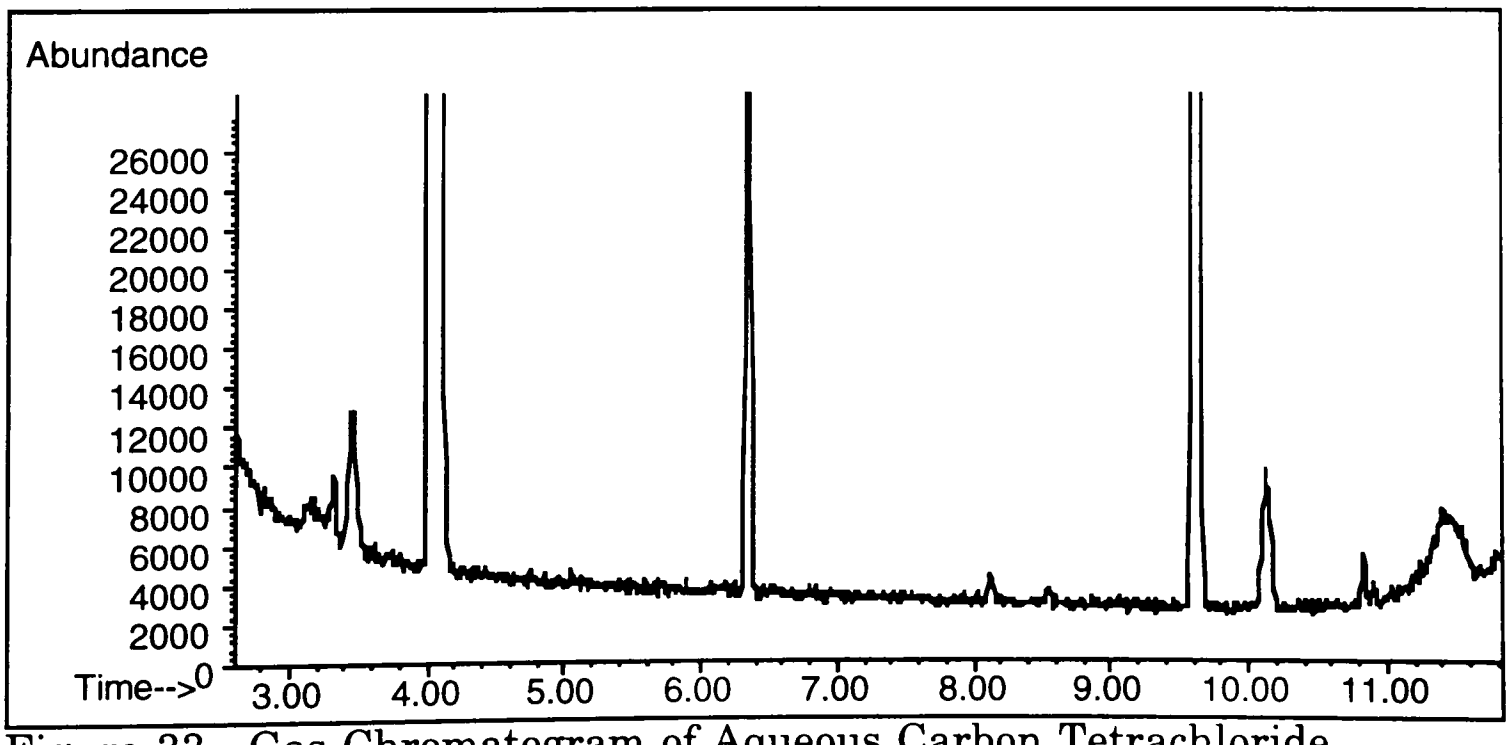


Figure 33. Gas Chromatogram of Aqueous Carbon Tetrachloride Sonicated for 120 Minutes.

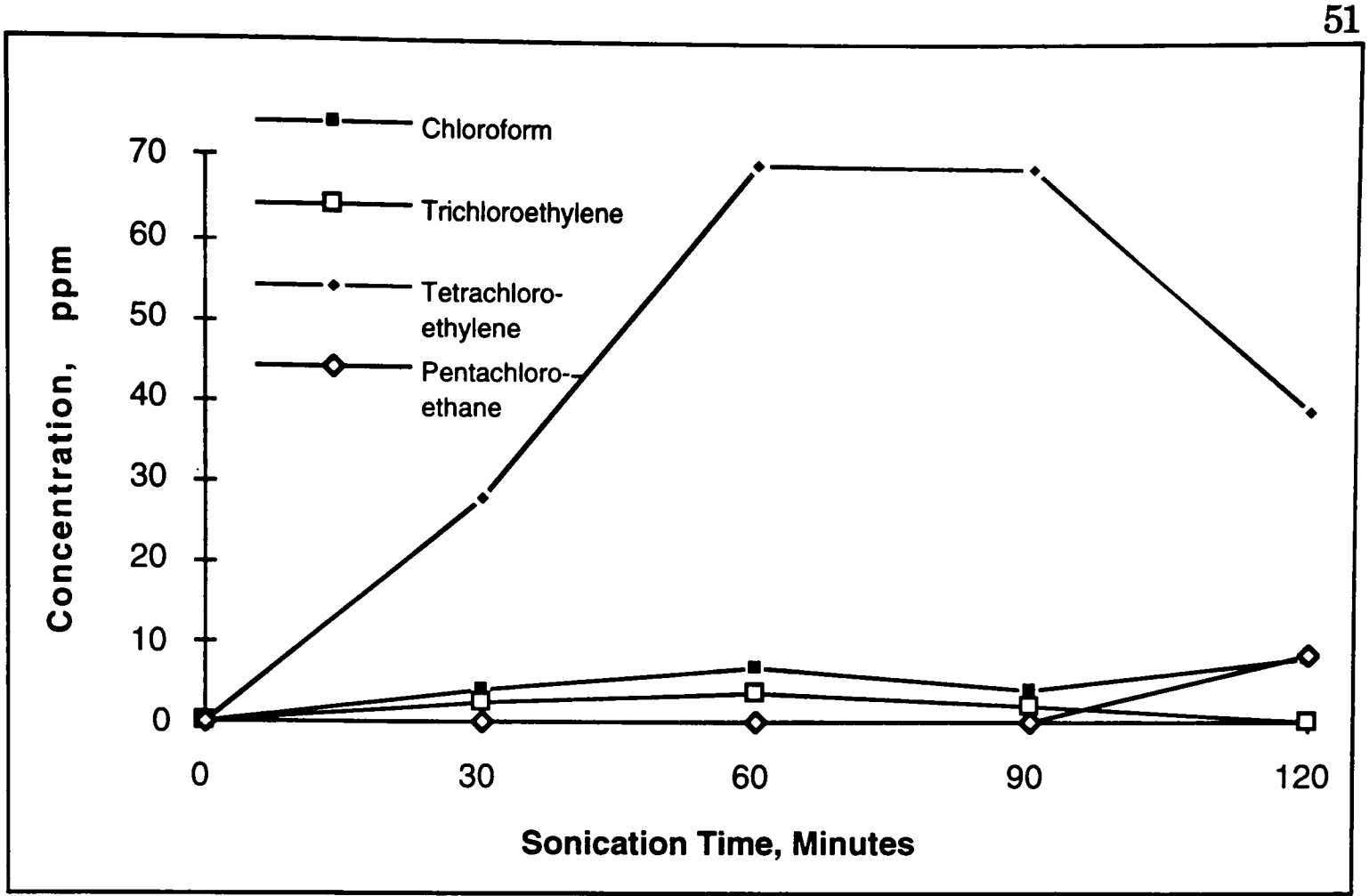


Figure 34. Products, Except Hexachloroethane, Formed During the Soncation of Aqueous Carbon Tetrachloride.

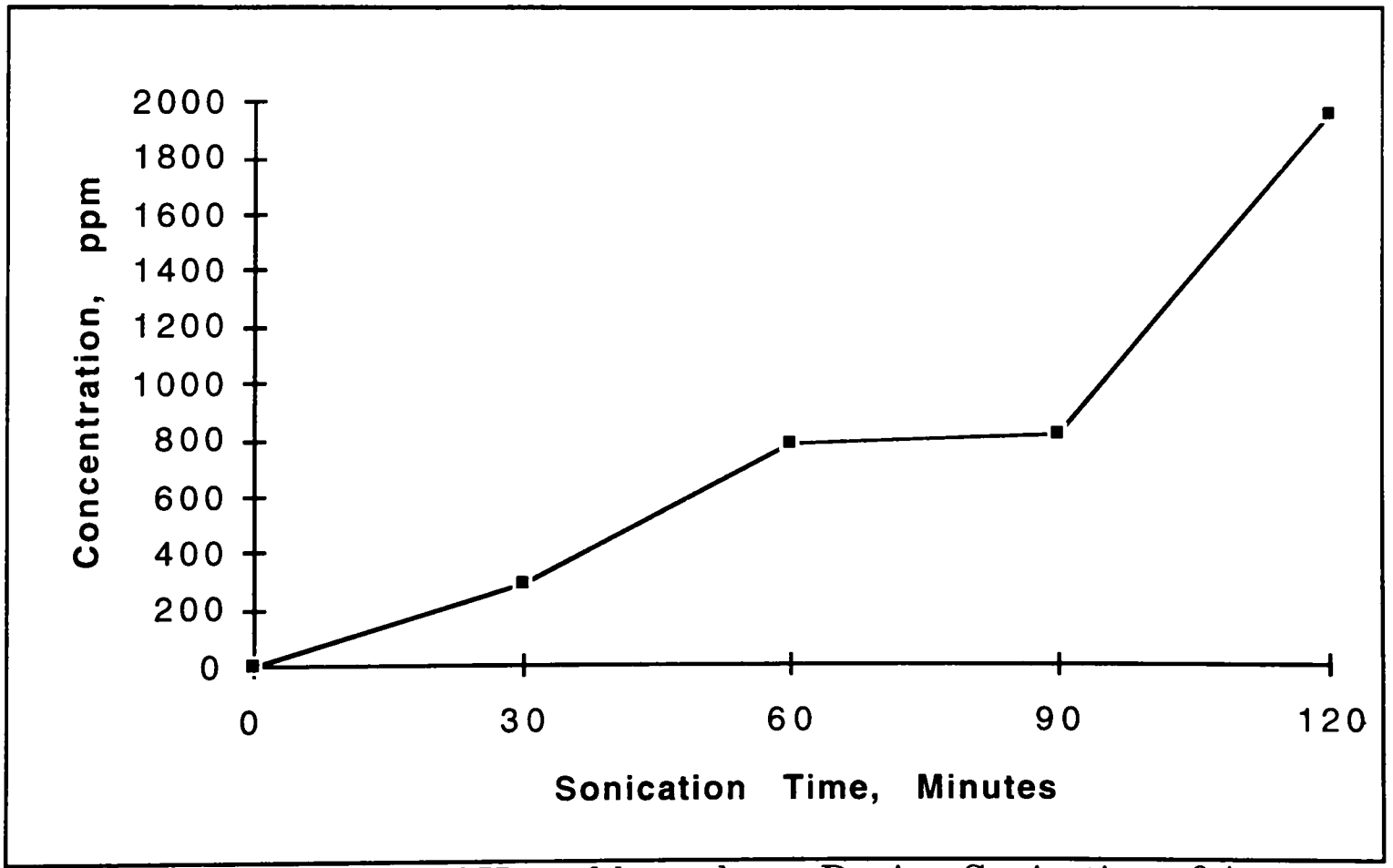


Figure 35. Formation of Hexachloroethane During Sonication of Aqueous Carbon Tetrachloride.

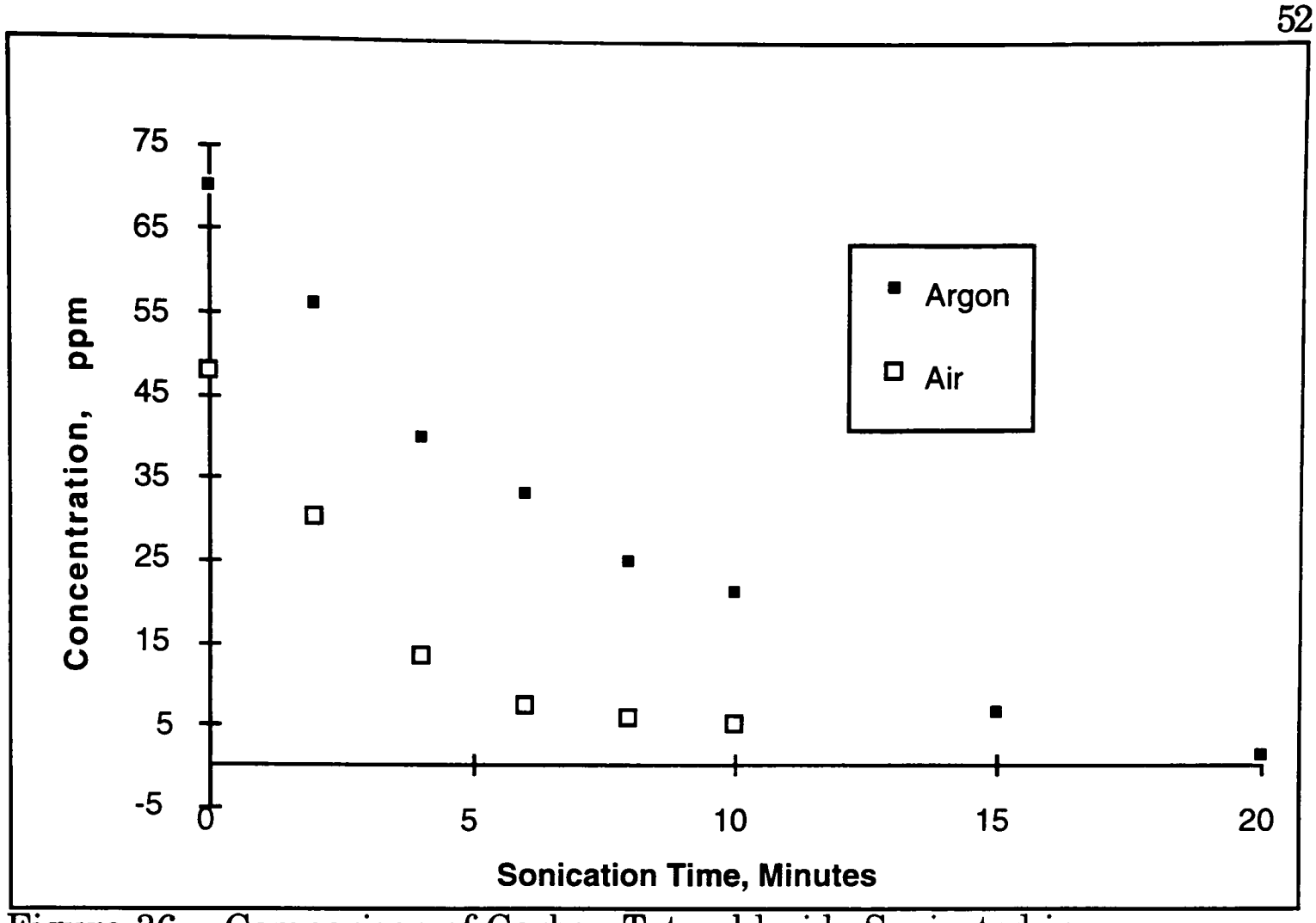


Figure 36. Comparison of Carbon Tetrachloride Sonicated in Atmospheres of Air and Argon.

Trichloroethylene

Various concentrations of aqueous trichloroethylene (TCE) were sonicated to determine the rate of degradation and the effect that concentration would have on both the degradation and the products formed upon sonication. These solutions ranged in concentration from 50 ppm to 3000 ppm. At all aqueous concentrations, the pH dropped, which has been attributed to the formation of HCl and possibly HOCl which would come from the hydrolysis of Cl_2.[86]

Figure 38 shows the sonication of 50 ppm TCE, which had almost 95% degradation in as little as 10 minutes. Intermediate concentrations, such as 200 ppm, achieved degradation of 80% in 2 hours, as shown in

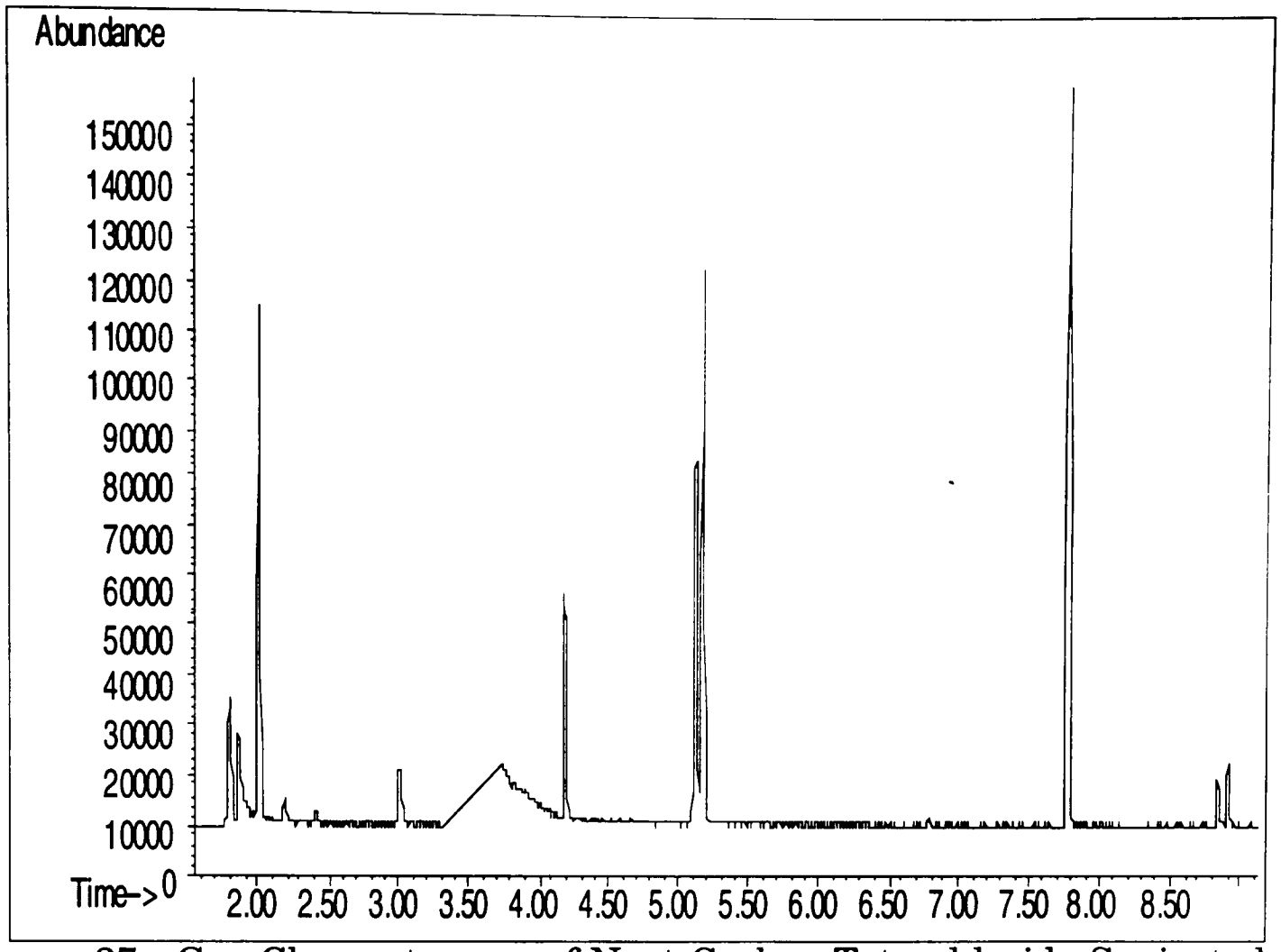


Figure 37. Gas Chromatogram of Neat Carbon Tetrachloride Sonicated for 120 Minutes.

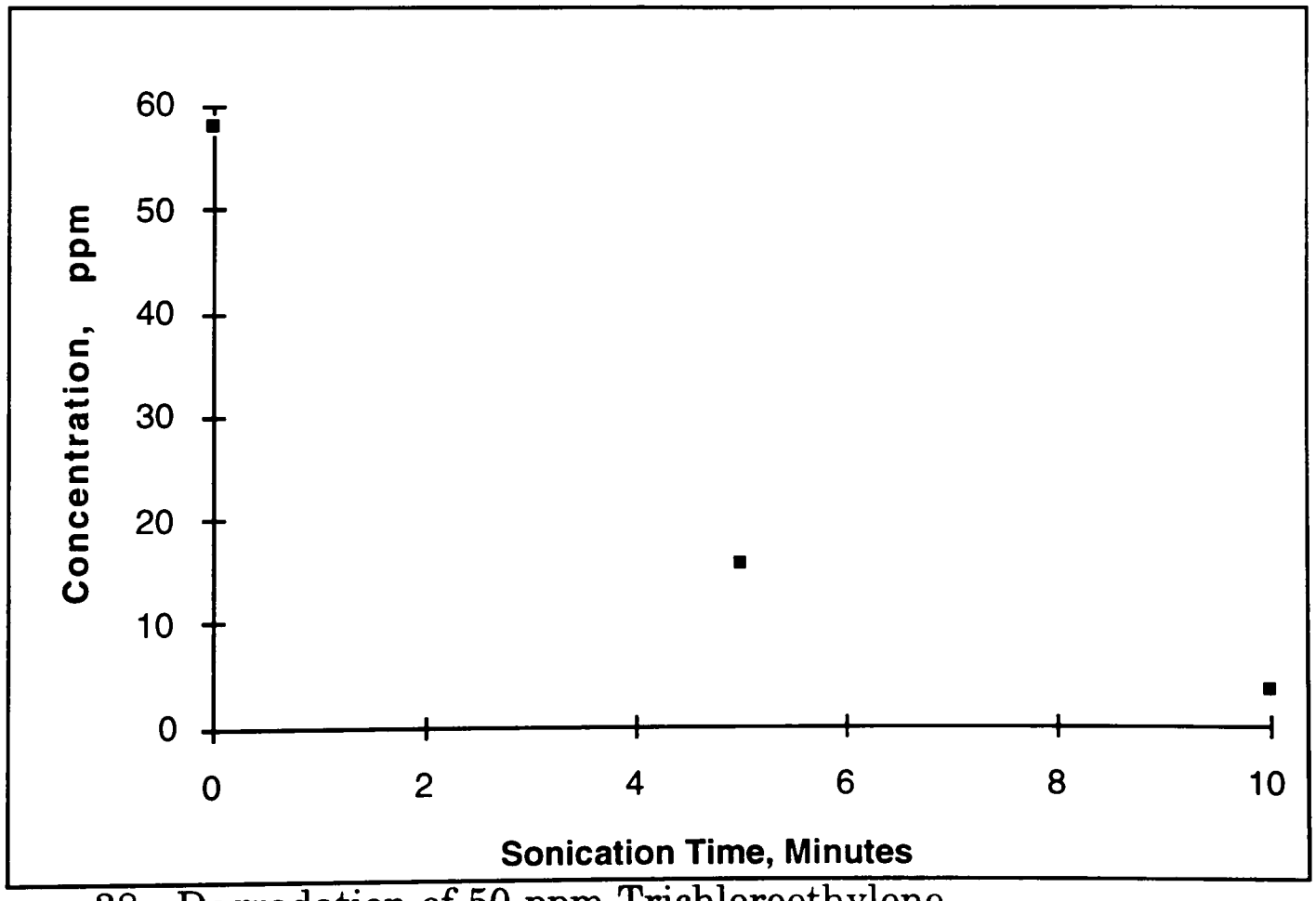


Figure 38. Degradation of 50 ppm Trichloroethylene.

Figure 39. Like the other chlorohydrocarbons investigated, there were several degradation products detectable, dichloroethyne (2.58 m), methylene chloride (3.30 m), cis-1,2-dichloroethylene (3.40 m), chloroform (3.45 m), carbon tetrachloride (4.05 m), tetrachloroethylene (6.35 m), 1,1,2,2-tetrachloroethane (7.80 m) and hexachloroethane (9.62 m) as shown in Figure 40. The formation of methylene chloride, cis-1,2-dichloroethylene, chloroform, tetrachloroethylene and 1,1,2,2-tetrachloroethane over sonication time is shown in Figure 41. At higher concentrations, near 3000 ppm, about 50% of the TCE was degraded in 2 hours (see Figure 42).

Conclusions

Various concentrations of methylene chloride, chloroform, carbon tetrachloride and trichloroethylene were sonicated to study degradation

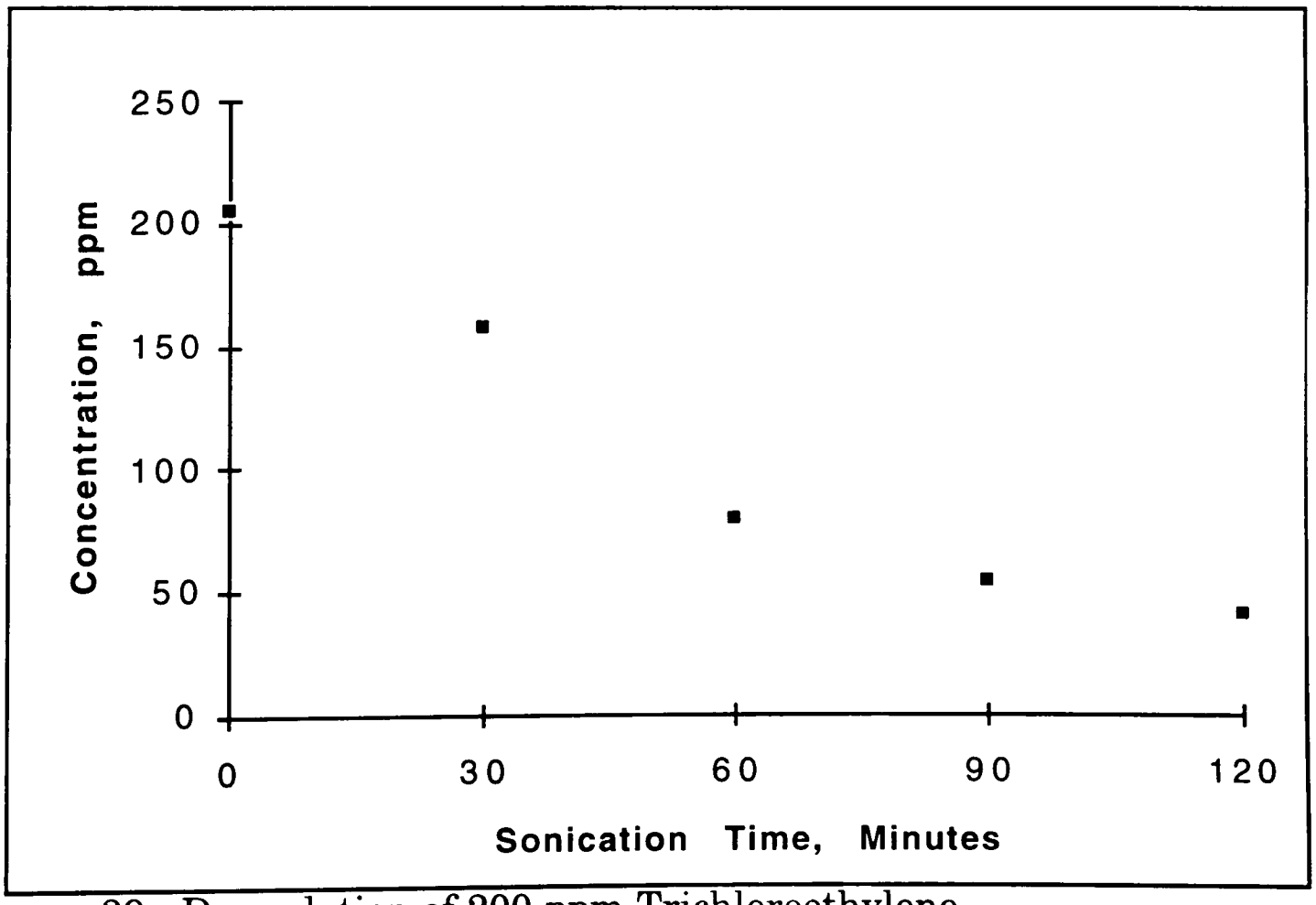


Figure 39. Degradation of 200 ppm Trichloroethylene.

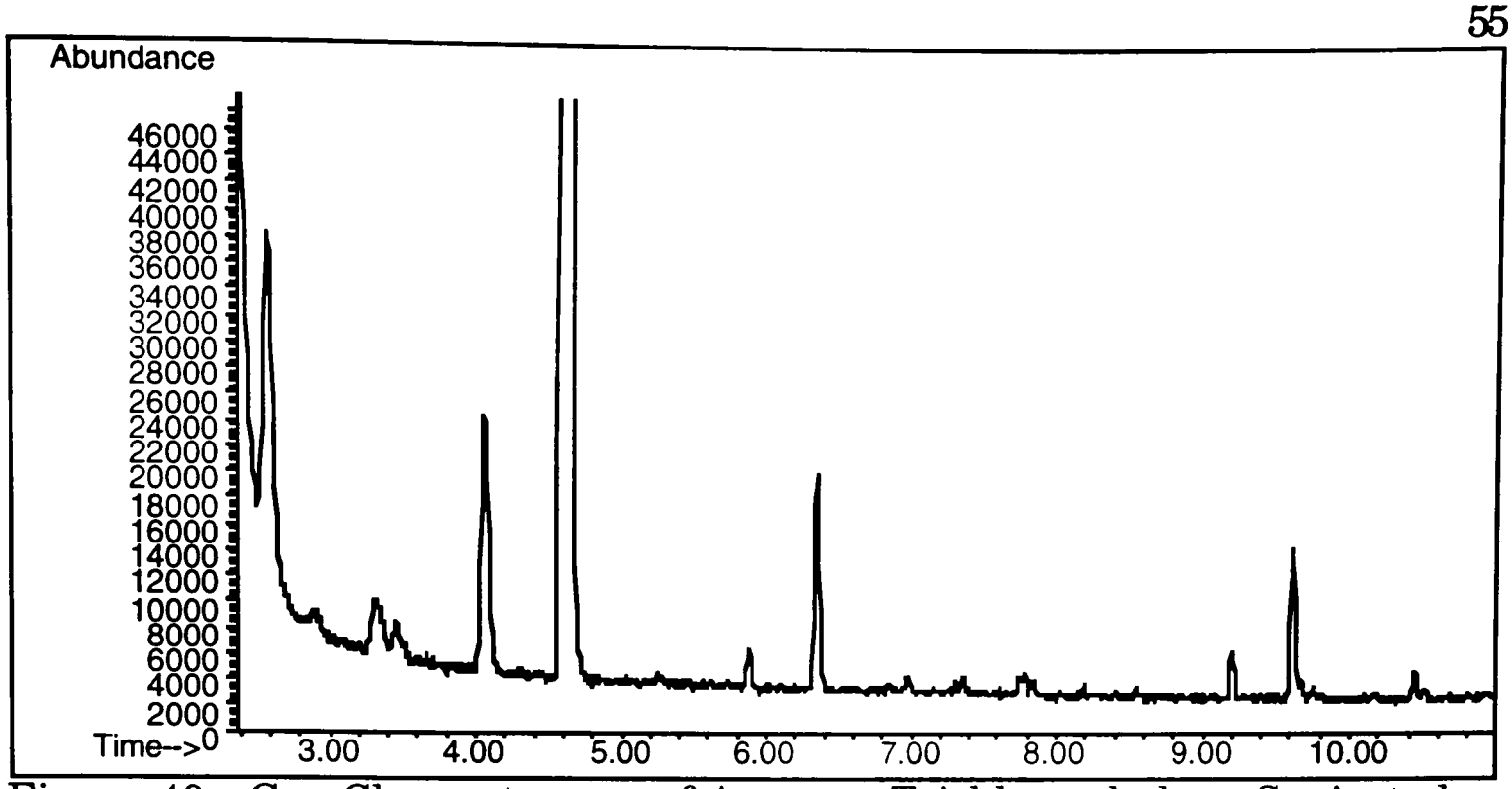


Figure 40. Gas Chromatogram of Aqueous Trichloroethylene Sonicated for 120 Minutes.

and product formation. Each of the chlorinated solvents was degraded, and each had several products form upon sonication. Methylene chloride had products such as 1,1-dichloroethylene, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, chloroform, 1,2-dichloroethane, trichloroethylene, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane form upon sonication. Chloroform had some of the same products form, with a few additional products: methylene chloride, carbon tetrachloride, tetrachloroethylene, pentachloroethane and hexachloroethane. Chloroform also had five products form just above the detection limit of the GC-MS which could not be unambiguously identified. However, they appear to be chlorinated hydrocarbons such as chlorinated propanes and butanes. Carbon tetrachloride had several of the same detectable products form. Methylene chloride, chloroform, TCE, tetrachloroethane, pentachloroethane and hexachloroethane were present. Trichloro-ethylene also had only one new product form, dichloroethyne, as well as methylene chloride, chloroform, carbon tetrachloride,

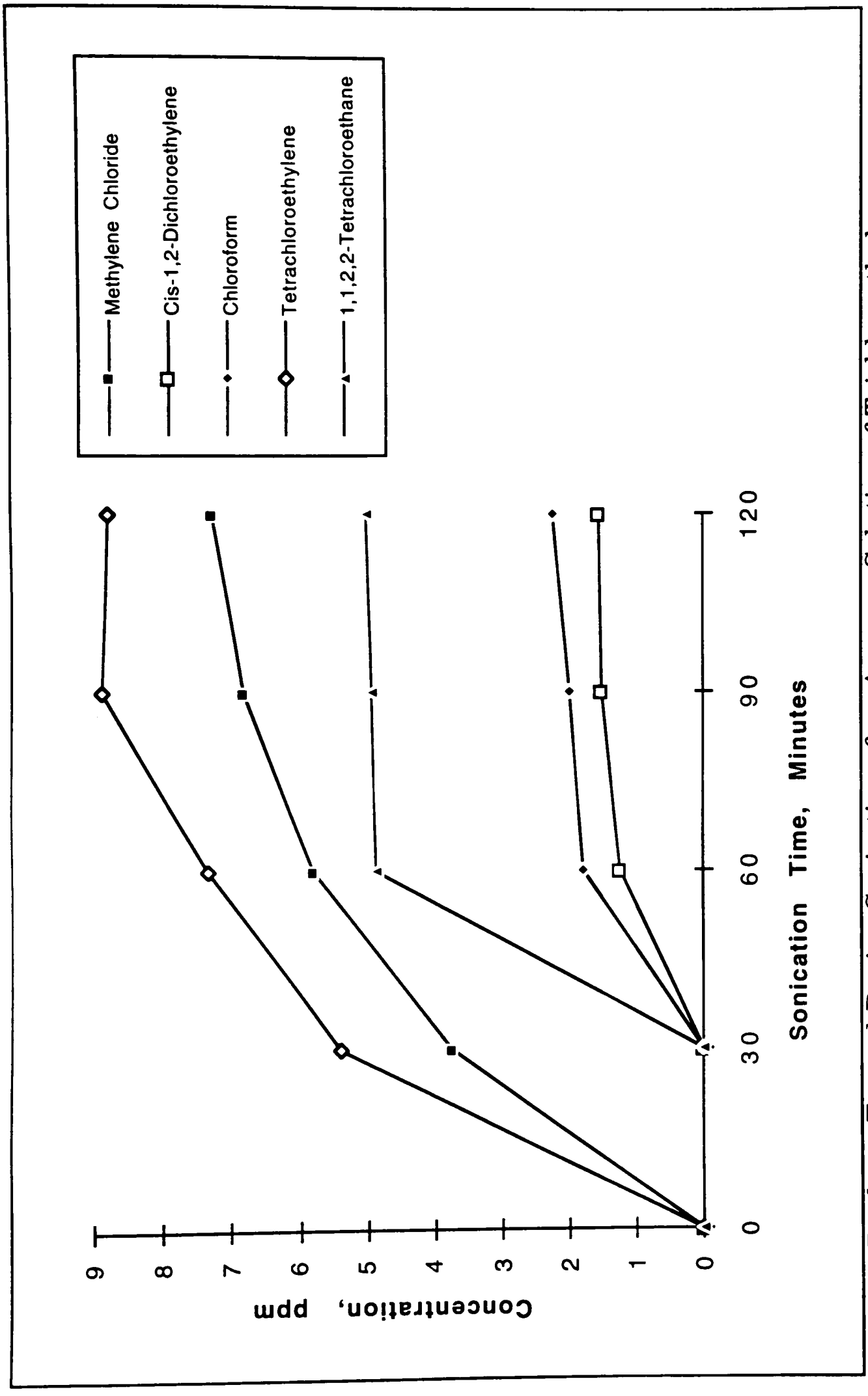


Figure 41. Products Formed During Sonication of an Aqueous Solution of Trichloroethylene.

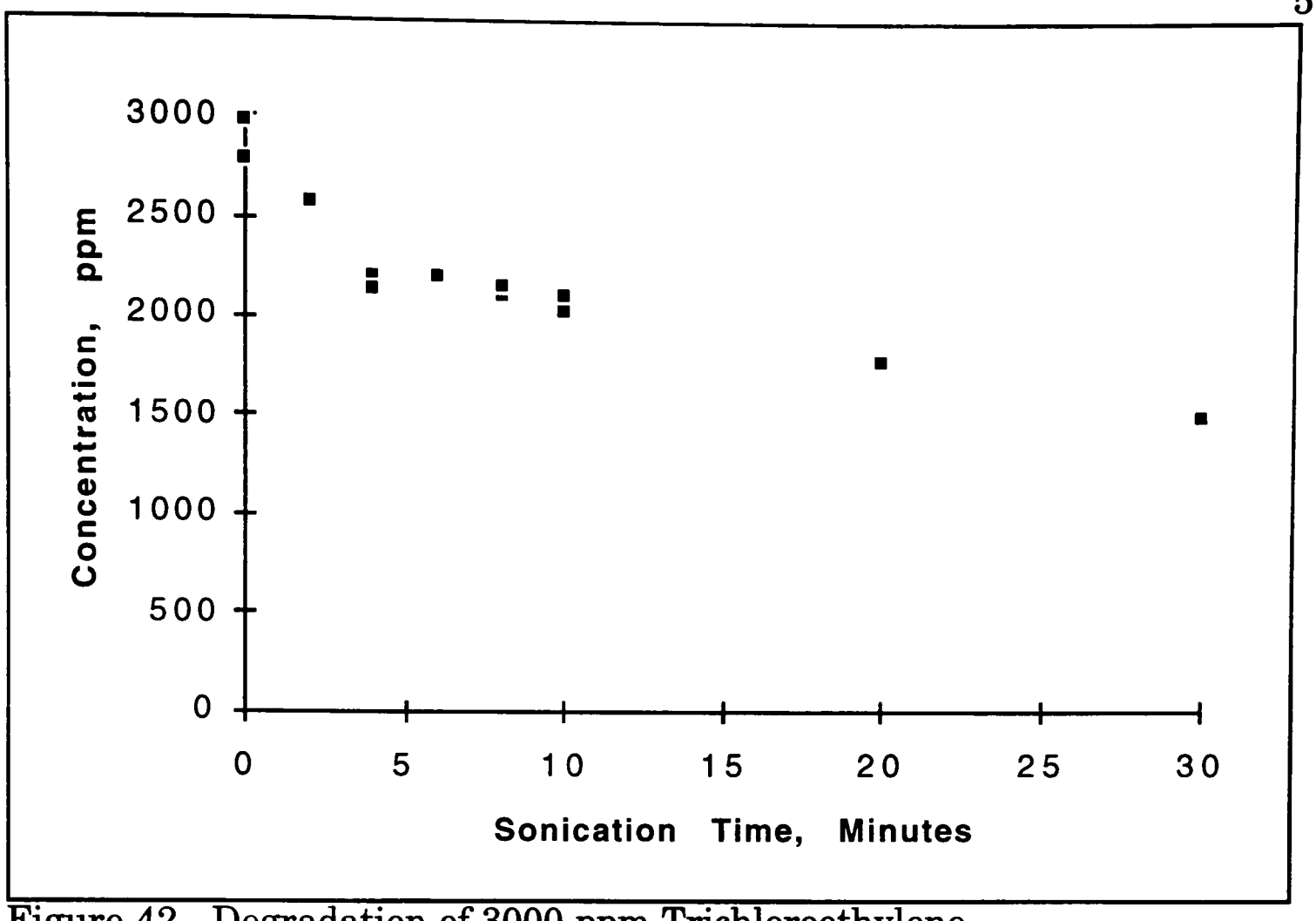


Figure 42. Degradation of 3000 ppm Trichloroethylene.

tetrachloroethylene, 1,1,2,2-tetrachloroethane and hexachloroethane. All of these products were formed in rather small quantities, and after more sonication time, they also began to degrade. Hydrochloric acid is formed in large quantities, and this is shown in Figure 43, which shows the pH over sonication time of the higher concentrations of all four organics.

The rate of degradation for all four solvents was similar. The degradation of roughly 60 ppm aqueous solutions as a function of time is shown in Figure 44. As the concentration increases, the relative rates of degradation for all four stay similar, as seen in Figure 45. Ultimately, ultrasound as a method of degradation of chlorinated hydrocarbons appears to be a viable process.

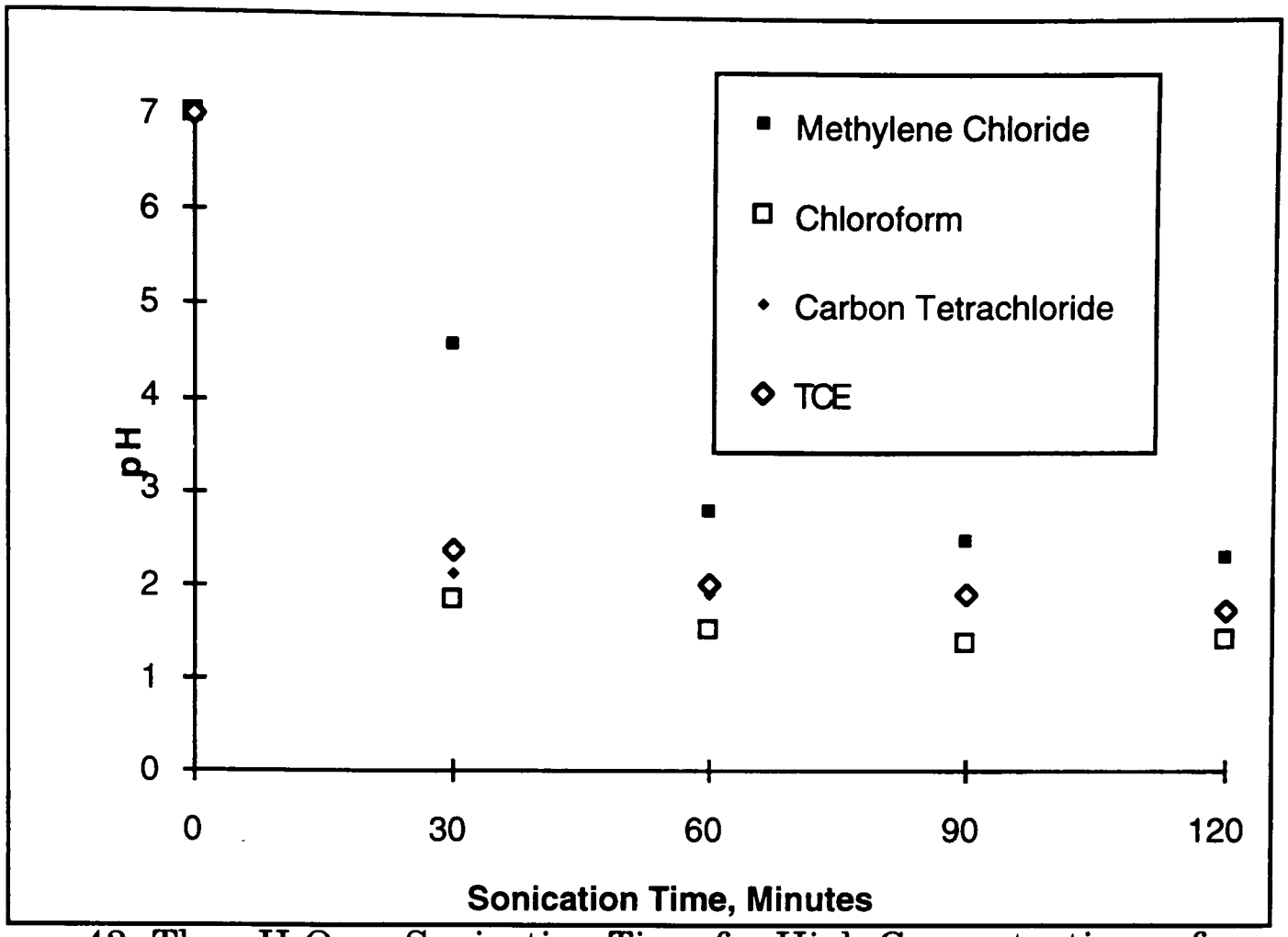


Figure 43. The pH Over Sonication Time for High Concentrations of Methylene Chloride, Chloroform, Carbon Tetrachloride and TCE.

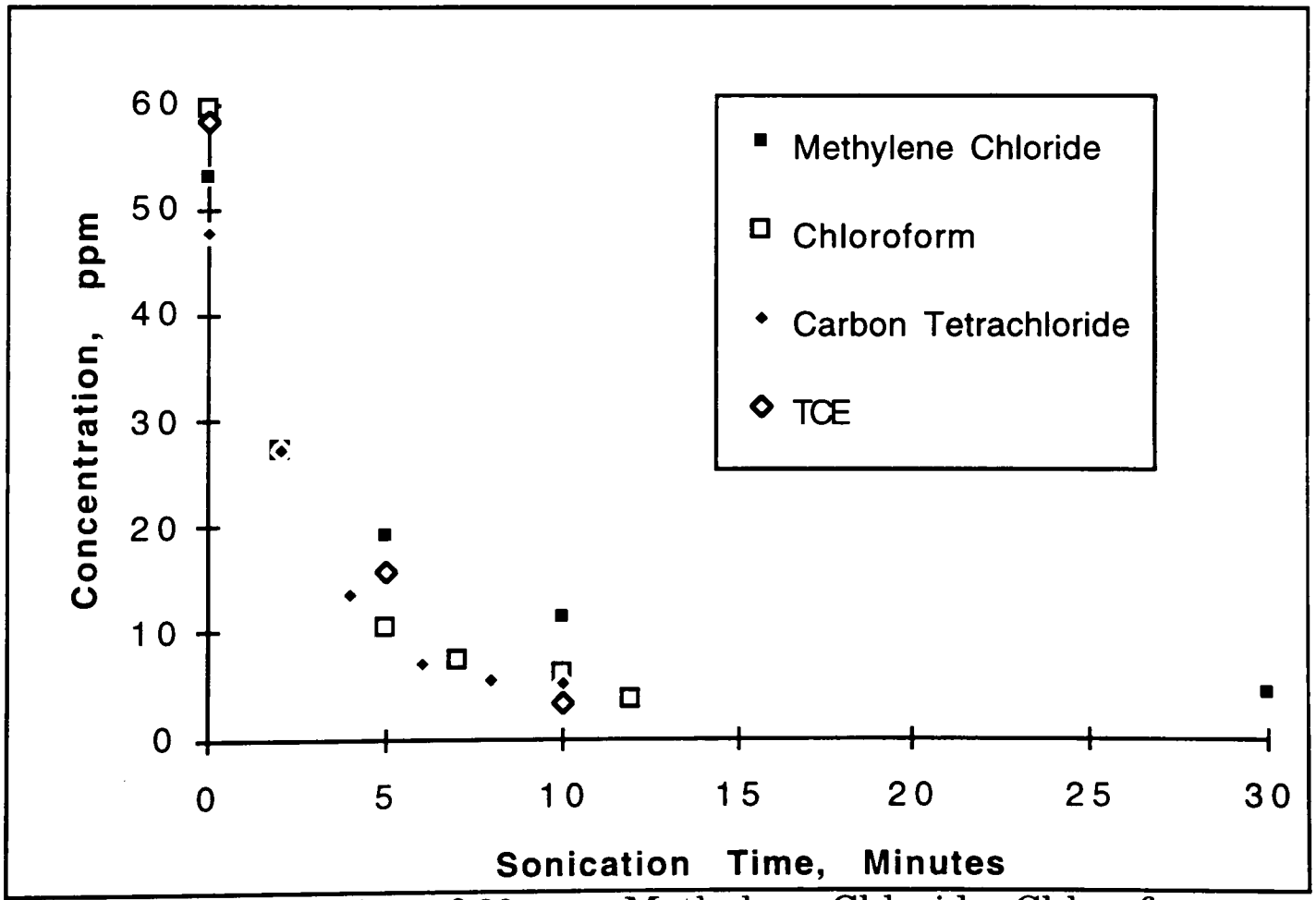


Figure 44. Degradation of 60 ppm Methylene Chloride, Chloroform, Carbon Tetrachloride and TCE.

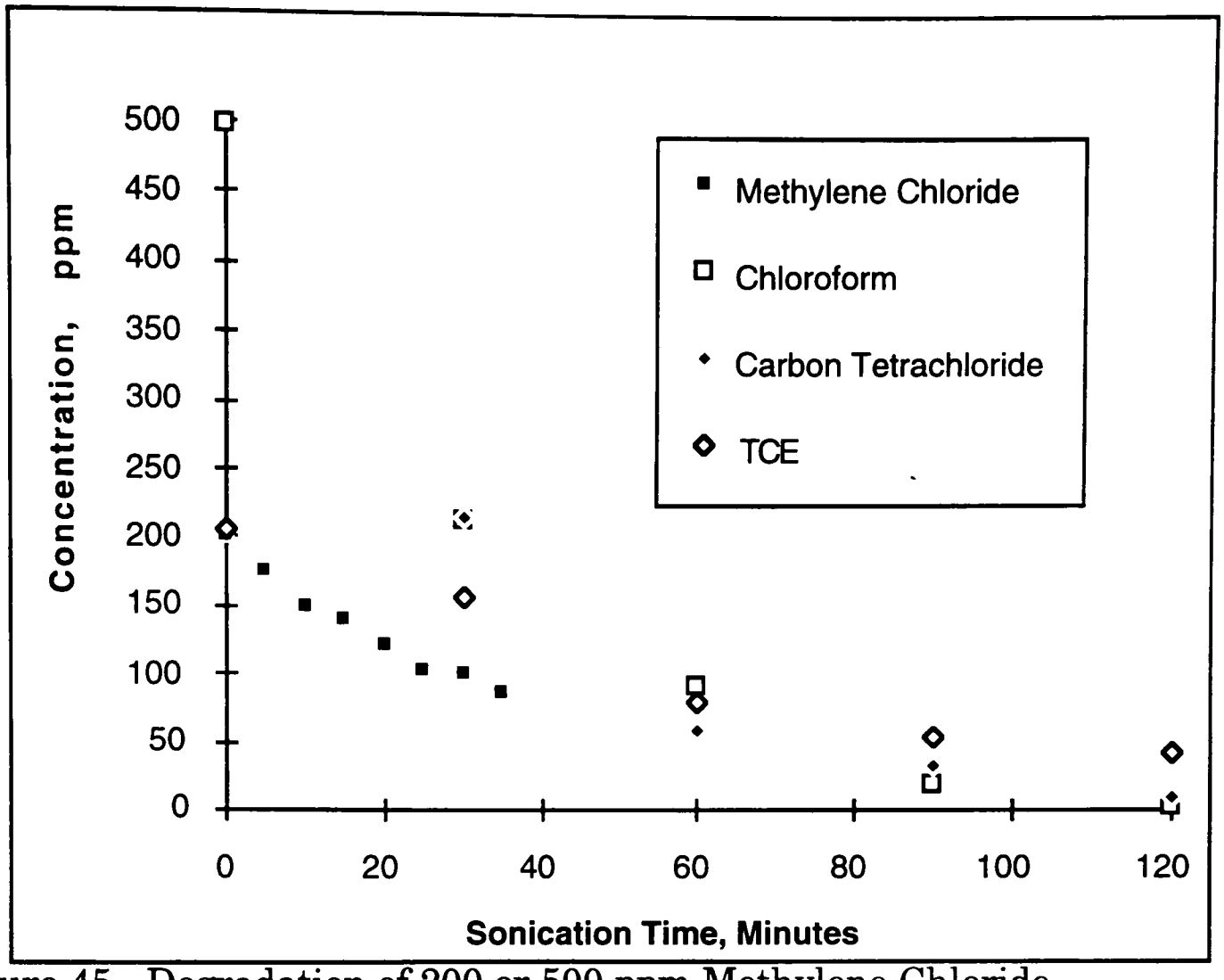


Figure 45. Degradation of 200 or 500 ppm Methylene Chloride, Chloroform, Carbon Tetrachloride and TCE.

CHAPTER III

EXPERIMENTAL

General

The methylene chloride, chloroform, carbon tetrachloride and trichloroethylene were HPLC grade, and used as received from Fischer.

The 250 mL sonication cell was a 3-necked conical shaped cell that was jacketed, so that a cooling bath, set to 1°C, could be used to keep the sample at temperatures less than 20°C during sonication. The 25 mL sonication cell was a 2-necked conical shaped cell that also was jacketed, so that the cooling bath could be used.

An Ace Glass 9810 600 W Ultrasonic Generator operating at 20 kHz provided the high energy ultrasound. The gas chromatograph (GC) used was a Hewlett-Packard 5890A Series II. The detector used was a Hewlett-Packard mass spectrometer (MS) 5972. The GC-MS method was carefully developed to get good separation of the products within a reasonable run time. A headspace autosampler, a Tekmar 7000, was utilized; the aqueous sample is heated at a predetermined temperature for a predetermined amount of time to equilibrate the amount of the volatile components in the headspace with what is still in the water. Then the vapors from the vial are sampled and sent to the GC-MS. When the Tekmar was not used, an autosampler directly injected 1 μL of the sample into the GC.

Sonication of a 15 ppm Aqueous Methylene Chloride Solution

A stock solution of aqueous methylene chloride was prepared by adding 500 μL of methylene chloride to water to give a total of 500 mL. This gave a concentration of 1325 ppm. Dilutions of this stock were made for a calibration curve (see Table 1). The equation of the line for this curve is y = 200574.4x -119897.2, with an R squared value of 0.990. A 10 mL aliquot of the 14.5 ppm solution was taken to be analyzed for the 0 minute timepoint. A 10 mL aliquot of the 14.5 ppm solution was placed in the 25 mL sonication cell, and sonicated for 5 minutes. Once the sonication was finished, the sample was taken out and analyzed. Another 10 mL sample was placed in the cleaned and dried sonicator cell and sonicated for 10 minutes. The whole sample was analyzed.

Table 1. Dilutions Used in the Calibration Curve for Sonication of a 15 ppm Aqueous Methylene Chloride Solution.

Stock solution (μL)	Total Volume (mL)	ppm
300.00	100.00	3.97
500.00	100.00	6.62
700.00	100.00	9.27
1100.00	100.00	14.57
1500.00	100.00	19.87

Sonication of Another 15 ppm Aqueous Methylene Chloride Solution

An aqueous solution of methylene chloride was prepared by adding 378 μL of methylene chloride to water to give a total of 100 mL. This gave a concentration of 5008.5 ppm. The dilutions used for the standard curve for this experiment are shown in Table 2. The equation of the line for this curve is y = 20924.2x + 11893727, with an R squared value of 0.9999. A 10

mL aliquot of this solution was placed in the 25 mL sonication cell, and sonicated for 10 minutes. Once the sonication was finished, the sample was taken out and analyzed. Another 10 mL sample was placed in the cleaned and dried sonicator cell and sonicated for 20 minutes. The whole sample was analyzed. Another 10 mL sample was sonicated for 30 minutes, and the whole sample was analyzed.

Table 2. Dilutions Made for the Calibration Curve for Sonication of a 15 ppm Aqueous Methylene Chloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
10	10	5008.5
7.5	25	1502.6
5	25	1001.7
2.5	25	500.9

Sonication of a 50 ppm Aqueous Methylene Chloride Solution

An aqueous solution of methylene chloride was prepared by adding 8 μL of methylene chloride to water to give a total of 200 mL. This gave a concentration of 53.00 ppm. The dilutions used for the standard curve for this experiment are shown in Table 3. The equation of the line for this curve is $y = 185978.5x + 385962.6$, with an R squared value of 0.988. A 10 mL aliquot of this solution was placed in the 25 mL sonication cell, and sonicated for 5 minutes. Once the sonication was finished, the sample was taken out and analyzed. Another 10 mL sample was placed in the cleaned and dried sonicator cell and sonicated for 10 minutes. The whole sample was analyzed. Another 10 mL sample was sonicated for 30 minutes, and the whole sample was analyzed.

Table 3. Dilutions Made for the Calibration Curve for Sonication of a 50 ppm Aqueous Methylene Chloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
10	10	53.0
5	10	26.5
0.566	10	2.9

Sonication of a 50 ppm Aqueous Methylene Chloride Solution to Determine Time For Total Degradation

An aqueous solution of methylene chloride was prepared by adding 4 μL of methylene chloride to water to give a total of 100 mL. This gave a concentration of 53.00 ppm. 10 mL of this solution was placed in the 25 mL sonication cell, and sonicated for 45 minutes. Once the sonication was finished, the sample was taken out and analyzed. Another 10 mL sample was placed in the cleaned and dried sonicator cell and sonicated for 60 minutes. The whole sample was analyzed.

Sonication of Another 50 ppm Aqueous Methylene Chloride Solution

An aqueous solution of methylene chloride was prepared by adding 8 μL of methylene chloride to water to give a total of 200 mL. This gave a concentration of 53.00 ppm. The dilutions used for the standard curve for this experiment are shown in Table 4. The equation of the line for this curve is $y = 509.3x - 1689.5$, with an R squared value of 0.987. 10 mL of this solution was placed in the 25 mL sonication cell, and sonicated for 2 minutes. Once the sonication was finished, the sample was taken out and analyzed. Another 10 mL sample was placed in the cleaned and dried

sonicator cell and sonicated for 5 minutes. This was repeated for timepoints of 7, 10 and 12 minutes.

Table 4. Dilutions Made for the Calibration Curve for Sonication of Another 50 ppm Aqueous Methylene Chloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
25	25	53.0
10	25	21.2
1.415	25	3.0

Sonication of a 200 ppm Aqueous Methylene Chloride Solution

An aqueous solution of methylene chloride was prepared by adding 38 μL of methylene chloride to water to give a total of 250 mL. This gave a concentration of 201.4 ppm. A 200 mL sample of the methylene chloride solution was placed in the 250 mL sonication cell, and sonicated for 5 minutes. Once the sonication was finished, duplicate 2 mL samples were analyzed. Sonication was continued for another 5 minutes and then stopped. Again, duplicate 2 mL samples were analyzed. This continued for the additional timepoints of 15, 20, 25, 30 and 35 minutes. The dilutions used for the standard curve are shown in Table 5. The equation of the line for this curve is $y = 226.7x - 640.1$, with an R squared value of 0.999.

Table 5. Dilutions Made for the Calibration Curve for Sonication of a 200 ppm Aqueous Methylene Chloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
10	10	201.4
4	10	80.5
2	10	40.2

Sonication of a 2500 ppm Aqueous Methylene Chloride Solution

An aqueous solution of methylene chloride was prepared by adding 378 μL of methylene chloride to water to give a total of 200 mL. This gave a concentration of 2504.25 ppm. A 10 mL aliquot of the methylene chloride solution was placed in the 25 mL sonication cell, and sonicated for 10 minutes. Once the sonication was finished, the whole sample was analyzed. The dilutions used for the standard curve are shown in Table 6. The equation of the line for this curve is y = 671.8x - 54695.4, with an R squared value of 0.990.

Table 6. Dilutions Made for the Calibration Curve for Sonication of a 2500 ppm Aqueous Methylene Chloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
6	10	1502.5
4	10	1001.7
2	10	500.8

Sonication of a 90 ppm Aqueous Methylene Chloride Solution

An aqueous solution of methylene chloride was prepared by adding 40 μL of methylene chloride to water to give a total of 250 mL. This gave a concentration of 212.0 ppm. From the methylene chloride standard solution, 200 mL were taken and sonicated in the 250 mL sonication cell. Duplicate 2 mL samples of the methylene chloride standard solution were taken for analysis before sonication for the 0 minute timepoint. After 2 minutes of sonication time, duplicate 12 mL aliquots were taken for analysis. This was repeated for the 4, 6, 8, 10, 15 and 20 minute timepoints. The dilutions used for the calibration curve are shown in Table 7.

Table 7. Dilutions Made for the Calibration Curve for Sonication of a 90 ppm Aqueous Methylene Chloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
1.000	1.000	212.0
0.750	1.000	159.0
0.500	1.000	185.5
0.250	1.000	53.0

Sonication of a Saturated Aqueous Methylene Chloride Solution to Determine Product Formation

A mixture of water and excess methylene chloride was shaken for 10 minutes, and then sat for several hours to obtain a maximum concentration of aqueous methylene chloride. Calibration curves for each of the products formed were made. A solution was made with 2 μL each of cis-1,2-dichloroethylene, chloroform, carbon tetrachloride, tetrachloroethylene, trichloroethylene (TCE), 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and pentachloroethane added to water to give 50 mL. Also added was 3.0 mg of hexachloroethane. The initial concentrations this gave, as well as the dilutions for theses are shown in Table 8, and the slopes, intercepts and R squared values for each curve are shown in Table 9. A 2 mL aliquot was taken for analysis. A 200 mL aliquot of the saturated aqueous methylene chloride was placed in the 250 mL sonication cell and sonicated for 30 minutes, after which, a 2 mL aliquot taken for analysis. This was repeated for timepoints of 60, 90 and 120 minutes of sonication time.

Table 8. Concentrations Used for the Calibration Curves for the Products.

Product	Concentrations used for curve			
cis-1,2-Dichloroethylene	51.36	38.52	25.68	12.84
Chloroform	59.68	44.76	29.84	14.92
Carbon Tetrachloride	63.76	47.82	31.88	15.94
TCE	58.60	43.95	29.30	14.65
1,2-Dichloroethane	50.24	37.68	25.12	12.56
1,1,2-Trichloroethane	57.60	43.02	28.80	14.40
1,1,2,2-Tetrachloroethane	63.44	47.58	31.72	15.86
Tetrachloroethylene	64.92	48.69	32.46	16.23
Pentachloroethane	66.84	50.13	33.42	16.71
Hexachloroethane	60.34	45.25	30.17	15.08

Table 9. Slopes, Intercepts and R Squared Values From the Calibration Curves for the Products.

Product	Slope	Intercept	R Squared Value
cis-1,2-Dichloroethylene	10688	-11799	0.998
Chloroform	5638	-8101	0.996
Carbon Tetrachloride	5277.5	-8101.6	0.996
TCE	8686	-11170	0.996
1,2-Dichloroethane	9112	-5711.6	0.999
1,1,2-Trichloroethane	10013.7	-11250	0.998
1,1,2,2-Tetrachloroethane	6864	-32291.6	0.976
Tetrachloroethylene	2942	-977	0.999
Pentachloroethane	4889	-36471	0.908
Hexachloroethane	715	1463.2	0.981

Sonication of a Saturated Aqueous Methylene Chloride Solution to Determine Which Products are Present After 30 Seconds of Sonication

This experiment was performed to see how quickly degradation products form upon sonication. A saturated solution of methylene chloride that had been prepared by adding excess methylene chloride to water and left sitting for several days was used. A 200 mL portion of the

saturated solution was placed in the 250 mL sonication cell, and sonicated for 30 seconds. A 2 mL sample was pulled for analysis.

Sonication of Neat Methylene Chloride Utilizing a Larger Sample Injection Size for the GC-MS to Determine Product Formation

Approximately 15 mL of neat methylene chloride was placed in the 25 mL sonication cell and sonicated for 120 minutes. A sample was analyzed. It was directly injected into the GC, and the injection sample size was increased from 1 μL to 2 μL.

Attempt to Form a Carbene Utilizing Sonication

A solution of approximately 50 mL methylene chloride and 50 mL cyclooctene was mixed with approximately 100 mL of water and placed in the 250 mL sonicator cell and sonicated for 50 minutes. After the layers separated, the organic layer was analyzed. A portion was directly injected into the GC-MS.

Sonication of a 45 ppm Aqueous Chloroform Solution

A 45.36 ppm solution of aqueous chloroform was prepared by adding 7.6 μL of chloroform to water to give a total volume of 250 mL. Duplicate 2 mL samples of this were analyzed for the 0 minute timepoint. Two hundred mL of this solution was placed in a 250 mL sonication cell, and sonicated for 2 minutes. Once the sonication was finished, duplicate

2 mL samples were removed and analyzed. Sonication was continued for another two minutes and then stopped. Again, duplicate 2 mL samples were analyzed. This continued for the timepoints of 4, 6, 8, 10, 15, 20, 30, 45 and 60 minutes. The dilutions used for the standard curve for this experiment are shown in Table 10. The equation of the line for this curve is y = 10478.7x + 59791, with an R squared value of 0.988. The 0 timepoint did not give a concentration of 45.36 ppm as expected, but rather 20.41 ppm.

Table 10. Dilutions Made for the Calibration Curve for Sonication of a 45 ppm Aqueous Chloroform Solution.

Stock solution (mL)	Total Volume (mL)	ppm
2.000	2.000	45.4
1.500	2.000	34.0
1.000	2.000	22.7
0.500	2.000	11.3

Sonication of a 60 ppm Aqueous Chloroform Solution

A 59.68 ppm aqueous solution of chloroform was made by adding 4 μL of chloroform to water to give a total volume of 100 mL. A 10 mL aliquot was placed in the 25 mL sonication cell and sonicated for 2 minutes. Triplicate 2 mL aliquots were removed for analysis. Another 10 mL aliquot was placed in the clean, dried cell and sonicated for another 2 minutes. Once again, triplicate 2 mL aliquots were removed for analysis. This was repeated for timepoints of 6, 8 and 10 minutes. The dilutions used for the standard curve for this experiment are shown in Table 11. The equation of the line for this curve is y = 4685.2x + 18927.2, with an R squared value of 0.988.

Table 11. Dilutions Made for the Calibration Curve for Sonication of a 60 ppm Aqueous Chloroform Solution.

Stock solution (mL)	Total Volume (mL)	ppm
10.0	10.0	59.7
2.0	10.0	11.4
0.575	10.0	3.4

Sonication of a 100 ppm Aqueous Chloroform Solution Under Argon

An aqueous solution of chloroform was made by placing 200 mL Millipore water in the 250 mL sonicator cell, and sonicating while being flushed with argon for 2 minutes to degas. Then the system was closed under a static argon atmosphere, and 13.2 mL of chloroform was added via a syringe to give a concentration of 98.5 ppm. This solution was sonicated for 2 minutes and duplicate 2 mL samples were removed via syringe for analysis. This continued for the timepoints of 4, 6, 8, 10, 15, 20, 30, 45, and 60 minutes. A standard solution of chloroform was prepared for the calibration curve, using a Rainin electronic pipette, instead of syringes. An aqueous solution of chloroform was prepared by adding 1.2 μL of chloroform to water to give a total volume of 25 mL for a concentration of 71.6 ppm. The dilutions used for the standard curve for this experiment are shown in Table 12. The equation of the line for this curve is $y = 2217.9x - 5106.5$, with an R squared value of 0.997.

Table 12. Dilutions Made for the Calibration Curve for Sonication of a 100 ppm Aqueous Chloroform Solution Under Argon.

Stock solution (mL)	Total Volume (mL)	ppm
2.000	2.000	71.6
1.500	2.000	53.7
1.000	2.000	35.8
0.500	2.000	17.9

Sonication of a 500 ppm Aqueous Chloroform Solution to Determine Product Formation and Degradation

An aqueous solution of chloroform was prepared by adding 167.0 μL of chloroform to water to give a total volume of 500 mL. This gave a concentration of 498.3 ppm. Duplicate 2 mL samples of this were analyzed for the 0 minute timepoint. Two hundred mL of the chloroform solution was placed in the 250 mL sonication cell, and sonicated for 30 minutes. Once the sonication was finished, duplicate 2 mL samples were analyzed. Sonication was continued for another 30 minutes and then stopped. Again, duplicate 2 mL samples were analyzed. This continued for the additional timepoints of 90 and 120 minutes. This experiment was to show the degradation products forming and then being degraded. However, at the 120 minute timepoint, there were still products present. So approximately 100 mL of the solution that had been sonicated for 120 minutes was taken and diluted to approximately 200 mL. A 2 mL aliquot was taken for the new 120 minute timepoint, and the rest of the 200 mL diluted sample was sonicated for 30 minutes. At this time, a 2 mL sample was analyzed, and the solution was sonicated for another 30 minutes. A 2 mL sample was analyzed. This continued for additional timepoints of 210, 240, 270 and 300 minutes. The calibration curve information shown in Tables 8 and 9 was used.

Sonication of a Saturated Aqueous Chloroform Solution to Determine Product Formation After 2 Minutes

This experiment was to see if degradation products form upon 2 minutes of sonication. A saturated solution of chloroform that had been

prepared by adding excess chloroform to water and left sitting for several days was used. A 200 mL portion of the saturated aqueous solution was placed in the 250 mL sonication cell, and sonicated for 2 minutes. A 2 mL sample was pulled for analysis.

Sonication of a Saturated Aqueous Chloroform Solution to Determine Product Formation After 30 Seconds

This was done to see how quickly degradation products form upon sonication. A saturated solution of chloroform that had been prepared by adding excess chloroform to water and left sitting for several days was used. 200 mL of the aqueous portion of the saturated solution was placed in the 250 mL sonication cell, and sonicated for 30 seconds. A 2 mL sample was pulled for analysis.

Sonication of a Saturated Aqueous Chloroform Solution to Determine Total Degradation Time

This was done to see how long it took to completely degrade a high concentration chloroform solution. 200 mL of the saturated aqueous chloroform solution was placed in the 250 mL sonication cell and sonicated for 3 hours. At that time, a 2 mL aliquot was analyzed. This continued for timepoints of 4, 5, 6, 7, 8, 10, 12, 13, 14 and 15.5 hours. A standard solution used for a calibration curve was prepared using 65 μL of chloroform in a total volume of 200 mL, giving a concentration of 484.90 ppm. The dilutions made for the calibration curve of chloroform are

shown in Table 13. The equation of the line for this curve is y = 713.2x + 35182.5, with an R squared value of 0.999.

Table 13. Dilutions Made for the Calibration Curve for Sonication of a Saturated Aqueous Chloroform Solution to Determine Total Degradation Time.

Stock solution (mL)	Total Volume (mL)	ppm
2.000	2.000	484.9
1.500	2.000	363.7
1.000	2.000	242.4
0.500	2.000	121.2

Sonication of Neat Chloroform

Approximately 15 mL of neat chloroform was sonicated in the 25 mL sonication cell. After 30 minutes of sonication time, a 2 mL aliquot was analyzed. The sample was directly injected into the GC, bypassing the headspace analyzer. This was repeated for timepoints of 60, 90 and 120 minutes of sonication time. To avoid overloading the MS detector, it was turned off for the period of time that the chloroform was coming off. The chloroform had ethanol in it as a stabilizer.

Formation of Dichlorocarbene Utilizing NaOH

To produce the 9,9-dichlorobicyclo[6.1.0]nonane that will be used to detect carbenes during sonication, the procedure from Regen and Singh[103] was followed. NaOH (0.8 g, 20.0 mmol) was powdered and added to 20 mL chloroform in a 100 mL round bottomed flask. Cyclooctene (260 mL) was also added to the flask. The flask was hand held in a sonication cleaning bath and swirled during the 5 minutes of sonication. The bath

temperature was kept at 34°C. This was filtered and the organic layer was directly injected into the GC-MS.

Formation of Dichlorocarbene Utilizing Sonication

A mixture of chloroform and cyclooctene was added in excess to water, to give 200 mL total volume. After shaking for 10 minutes, and standing for about an hour, the solution was added to the 250 mL sonication cell and sonicated for approximately 20 minutes. During sonication, the solution turned a milky white color, and an emulsion formed. After sonication, the solution was capped and sat for two days. The solution separated and the organic layer was analyzed. It was directly injected into the GC-MS, bypassing the headspace analyzer.

Sonication of a 50 ppm Aqueous Carbon Tetrachloride Solution

An aqueous solution of carbon tetrachloride was prepared by adding 3.0 μL of carbon tetrachloride to water to give a total volume of 100 mL. This gave a concentration of 47.8 ppm. A 10 mL aliquot of this was placed in the 25 mL sonication cell, and sonicated for 2 minutes. Once the sonication was finished, triplicate 2 mL samples were analyzed. Another 10 mL sample was placed in the cleaned and dried sonicator cell and sonicated for 4 minutes. Again, triplicate 2 mL samples were analyzed. This continued for timepoints of 6, 8 and 10 minutes. The dilutions used for the standard curve for this experiment are shown in Table 14. The

equation of the line for this curve is y = 2497.342x - 9340.513, with an R squared value of 0.988.

Table 14. Dilutions Made for the Calibration Curve for Sonication of a 50 ppm Aqueous Carbon Tetrachloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
10	10	47.8
4	10	19.1
0.627	10	2.9

Sonication of a Saturated Aqueous Carbon Tetrachloride Solution to Determine Degradation and Product Formation

A 200 mL portion of the saturated aqueous carbon tetrachloride solution was placed in the 250 mL sonication cell and sonicated for 30 minutes. After 30 minutes of sonication time, a 2 mL aliquot was removed for analysis. This was repeated for timepoints of 60, 90 and 120 minutes of sonication time. The calibration curve information in Tables 8 and 9 was used.

Sonication of Another Saturated Aqueous Carbon Tetrachloride Solution to Determine Degradation and Product Formation

A 200 mL portion of the saturated aqueous carbon tetrachloride solution was placed in the 250 mL sonication cell and sonicated. A single 2 mL sample of the carbon tetrachloride standard solution was taken for analysis before sonication for the 0 minute timepoint. After 30 minutes of sonication time, a 2 mL aliquot was removed for analysis. This was repeated for timepoints of 60, 90 and 120 minutes of sonication time. The calibration curve information in Tables 8 and 9 was used.

Sonication of Neat Carbon Tetrachloride

Approximately 15 mL of neat carbon tetrachloride was sonicated in the 25 mL sonication cell. A single 2 mL sample of the carbon tetrachloride was taken before sonication for the 0 minute timepoint. After 2 minutes of sonication time, a 2 mL aliquot was taken for analysis. The sample was directly injected into the GC, bypassing the headspace analyzer. This was repeated for timepoints of 4, 6, 8, 10, 15, 20, 25 and 30 minutes of sonication time. To avoid overloading the MS detector, it was turned off for the period of time that the carbon tetrachloride was coming off. The carbon tetrachloride had a small amount of chloroform in it.

Sonication of Another 50 ppm Aqueous Carbon Tetrachloride Solution

An aqueous solution of carbon tetrachloride was prepared by adding 7.5 μL of carbon tetrachloride to water to give a total volume of 250 mL. This gave a concentration of 47.8 ppm. Duplicate 2 mL samples of this were analyzed for the 0 minute timepoint. Two hundred mL of this solution was placed in the 250 mL sonication cell, and sonicated for 2 minutes. Once the sonication was finished, duplicate 2 mL samples were analyzed. Sonication was continued for another two minutes and then stopped. Again, duplicate 2 mL samples were analyzed. This continued for the timepoints of 4, 6, 8, 10, 15, 20, 30, 40 and 60 minutes. The dilutions used for the standard curve for this experiment are shown in Table 15. The equation of the line for this curve is $y = 4569.6x + 351.0$, with an R squared value of 0.998. The 0 timepoint did not give a concentration of 47.82 ppm as expected, but rather 21.15 ppm.

Table 15. Dilutions Made for the Calibration Curve for Sonication of Another 50 ppm Aqueous Carbon Tetrachloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
2.000	2.000	47.8
1.500	2.000	35.9
1.000	2.000	23.9
0.500	2.000	12.0

Sonication of a 70 ppm Aqueous Carbon Tetrachloride Solution Under an Argon Atmosphere

An aqueous solution of carbon tetrachloride was prepared by placing 200 mL Millipore water in the 250 mL sonicator cell and sonicating while being flushed with argon for 3 minutes to degas. Then the system was closed under a static argon atmosphere, and 8.8 μL of carbon tetrachloride was added via a syringe to give a concentration of 70 ppm. This solution was sonicated for 2 minutes and duplicate 2 mL samples were removed via syringe for analysis. This continued for the timepoints of 4, 6, 8, 10, 15 and 20 minutes. A standard solution of carbon tetrachloride was prepared for the calibration curve, using a Rainin electronic pipette, instead of syringes. 2.0 μL of carbon tetrachloride was added to water to give a total volume of 10 mL for a concentration of 334.74 ppm. The dilutions used for the standard curve for this experiment are shown in Table 16. The equation of the line for this curve is $y = 1743.0x + 13858.5$, with an R squared value of 0.996.

Table 16. Dilutions Made for the Calibration Curve for Sonication of a 70 ppm Aqueous Carbon Tetrachloride Solution Under an Argon Atmosphere.

Stock solution (mL)	Total Volume (mL)	ppm
2.000	2.000	334.7
1.500	2.000	251.1
1.000	2.000	167.4
0.500	2.000	83.7

Sonication of a 95 ppm Aqueous Carbon Tetrachloride Solution

An aqueous solution of carbon tetrachloride was prepared by adding 3.0 μL of carbon tetrachloride to water to give a total volume of 100 mL. This gave a concentration of 47.8 ppm. A 10 mL aliquot of this was placed in the 25 mL sonication cell, and sonicated for 5 minutes. Once the sonication was finished, the whole sample was analyzed. Another 10 mL sample was placed in the cleaned and dried sonicator cell and sonicated for 10 minutes. Again, the whole sample was analyzed. The dilutions used for the standard curve for this experiment are shown in Table 17. The equation of the line for this curve is y = 128060.8x - 287668.0, with an R squared value of 0.996.

Table 17. Dilutions Made for the Calibration Curve for Sonication of a 95 ppm Aqueous Carbon Tetrachloride Solution.

Stock solution (mL)	Total Volume (mL)	ppm
10	10	47.8
5	10	23.9
0.627	10	3.0

Sonication of Neat Carbon Tetrachloride

Approximately 15 mL of neat carbon tetrachloride was sonicated in the 25 mL sonication cell. After 30 minutes of sonication time, an aliquot was analyzed. The sample was directly injected into the GC, bypassing the headspace analyzer. This was repeated for timepoints of 60, 90 and 120 minutes of sonication time. To keep from overloading the MS detector, it was turned off for the period of time that the carbon tetrachloride was coming off. The carbon tetrachloride had a small amount of chloroform in it.

Sonication of a Saturated Aqueous TCE Solution to Determine Degradation and Product Formation

An aqueous solution of TCE was prepared by adding TCE in large excess to Millipore water and letting the solution sit for several hours. From this solution, 25 mL of the aqueous layer were taken to be sonicated. Before sonication, duplicate 2 mL aliquots were taken from the TCE solution for analysis. After sonicating for 30 minutes, duplicate 2 mL aliquots were taken for analysis. This was repeated for timepoints of 60, 90 and 120 minutes. The calibration curve information from Tables 8 and 9 was used.

Sonication of a 60 ppm Aqueous TCE Solution

An aqueous solution of TCE was prepared by adding 4.0 μL of TCE to water to give a total volume of 100 mL. This gave a concentration of 58.24 ppm. A 10 mL aliquot of this was placed in the 25 mL sonication cell, and sonicated for 5 minutes. Once the sonication was finished, the whole

sample was analyzed. Another 10 mL sample was placed in the cleaned and dried sonicator cell and sonicated for 10 minutes. Again, the whole sample was analyzed. The dilutions used for the standard curve for this experiment are shown in Table 18. The equation of the line for this curve is y = 556588.1x + 1505457.9, with an R squared value of 0.983.

Table 18. Dilutions Made for the Calibration Curve for Sonication of a 60 ppm Aqueous TCE Solution.

Stock solution (mL)	Total Volume (mL)	ppm
10	10	47.8
4	10	19.1
0.627	10	3.0

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