REACTIONS OF HYDROGEN TUNGSTEN BRONZE AND CHLOROCARBONS

By

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REACTIONS OF HYDROGEN TUNGSTEN

BRONZE AND CHLOROCARBONS

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NOMENCLATURE

amu	atomic units
APCD	air pollution control device
C_1	one carbon
C_2	two carbons
CCl_4	carbon tetrachloride
CFC	chlorofluorocarbon
cm	centimeters
HCl	hydrochloric acid (aq)
$H_{0.5}WO_3$	hydrogen tungsten bronze
H_2O	water
H_3O^+	hydronium ion
M	molarity
M'	other metal
M''	transition metal
M''_yO_z	highest binary oxidation state
M_xWO_3	alkali metal tungsten trioxide
$NaWO_3$	sodium tungsten bronze
O	oxygen
SO_2	sulfur dioxide
SO_3	sulfur trioxide

LITERATURE REVIEW

Introduction

Wastes have continually been dumped over the centuries into landfills and chemical burial sites. Prior to the industrial revolution most of the items being placed in these sites were leather scraps, wood byproducts, and limited common chemicals like lye soap.[26] The discovery of petroleum in the 1880's caused an increase in organic chemical and organic wastes.[26] With the coming of the industrial revolution and later, World War I and II, even larger surges of organic chemicals were produced.[26] Vast uses for various chemicals already discovered led to an increase in new products and new wastes. Plastics, pesticides and the nuclear compounds were a few of the immense array of chemicals starting to be produced.[26] But during all this time of great discovery, the wastes from the research and consumer use still landed in burial sites. For example, Dr. Tom Burgoyne obtained information on a chemical burial site eight miles southwest of Oklahoma State University's main campus. Dr. Burgoyne gathered that the University buried 3469 gallons of chemical waste prior to 1980.[32] The waste includes: hydraulic fluid, chloranil, various organophosphates, and trichloropropane.[32] In addition to the chemicals that were actually buried in this site, the degradation of those chemicals with other unknown chemicals present and reactions between the wastes allows for various new products yet to be determined. Industries did not only deposit chemicals in other burial sites across the United States, other industries dumped their hazardous wastes into rivers, lakes, and the ocean. The EPA estimated in 1984 that there is 300 million metric tons of hazardous waste generated through the years.[26] To observe specific chemicals buried in the sites, EPA places monitoring wells to gain knowledge on the levels of hazardous waste leeching into ground water and remaining on the soil.

Prior to the early twentieth century's idea of proper waste disposal, incineration facilities were nonexistent. The first waste-to-energy plant was operating in New York City in 1905. Even though the people had thought of ideas better than the dumping of hazardous chemicals into our environment, a long time was to follow till regulations were set up to monitor the disposal of wastes. So, until the 1960's, hazardous wastes, including halogenated compounds were disposed in standard practice at burial sites or incinerators.[27]

Hazardous wastes are defined by the Environmental Protection Agency under the Resource Conservation and Recovery Act as "a waste material that can be classified as potentially dangerous to human health or the environment, based on certain criteria."[27] One out of five criteria can be met in order to achieve the status of hazardous wastes. First, the compound might ignite easily, posing a fire hazard. Second, the compound might be corrosive, capable of damaging materials or injuring people. Third, the compound might be reactive. Reactivity is within the reach of the likelihood of explosion, flammability, or noxious fume release when in contact with water or other materials. The capacity for toxicity, enabling the compound to cause illness or other health problems if precaution is not taken is a fourth criteria.[27] Solvent wastes are classified as hazardous wastes from nonspecific source. A list of the halogenated solvent wastes includes: carbon tetrachloride, chlorofluorocarbons, methylene chloride, tetrachloroethylene, and chlorobenzene.[26] Not only are these compounds used as solvents, certain pesticides and other products contain these compounds.

Chlorocarbons

Halogenated organic compounds are an intricate part of nature's life cycles, which includes naturally occurring and manufactured halomethanes. Naturally, more than 3000 halogenated organic compounds are produced in the processes of living organisms. Approximately 1800 of these 3000 compounds contain chlorine.[3] For example, polyphore fungi in rotting wood are a highly researched source of methyl chloride in the environment.[4] Table 1 shows a list of man-made chlorocarbons with respect to methyl chloride, a natural halomethane, and their estimated emissions and atmospheric residency times.

Table 1. Man-made and natural chlorocarbons and their estimated emissions, atmospheric residency time, and atmospheric concentration

	Estimated emissions for 1990[a] (10^3 t y^{-1})	Atmospheric concentration[b] (parts per 10^{12} by volume) [c]	Atmospheric residence time[b] (y)
Man-made			
CCl_4	100	103	42
CH_3CCl_3	730	109	5
Natural			
CH_3Cl	4000	606	1.4

[a] based on data from Prather and Watson[6] and Khalil and Rasmussen.[7] [b] Montzka *et al.*[8] and Khalil and Rasmussen.[7] (adapted from reference 4)

As shown, methyl chloride is the chlorocarbon with the largest estimated emission, but has the shortest residence in the atmosphere. The reasoning behind the

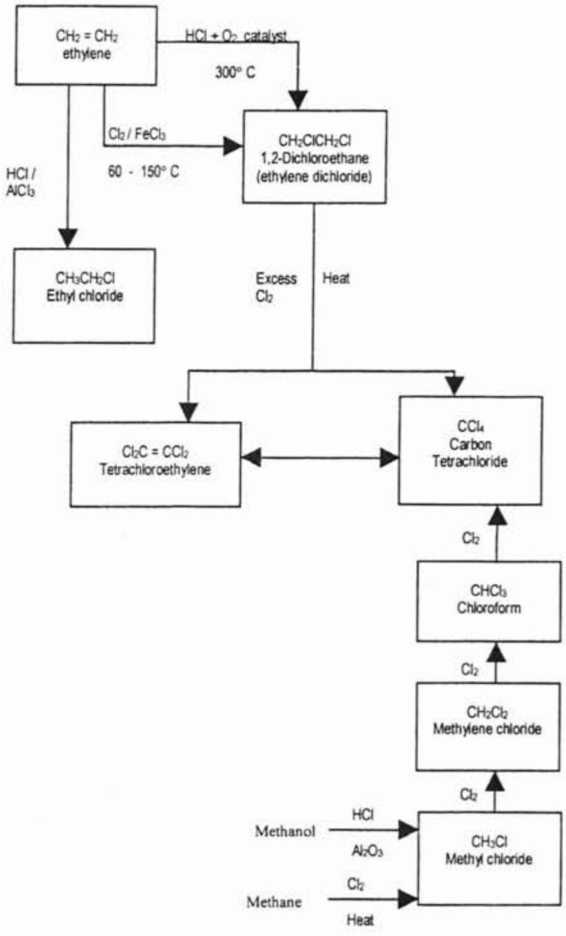

Figure 1. Manufacturing processes for C_1 and C_2 chlorohydrocarbons (adapted from reference 1)

short lifetime is the dominant reaction pathway that methyl chloride follows. The pathway involves a hydroxyl radical, from a photochemical reaction, reacting with the methyl chloride.[4] In contrast, carbon tetrachloride has a lifetime of forty-two years. This chemical does not react well with the hydroxyl radical and therefore takes longer to decompose. Due to carbon tetrachloride's prolonged existence, the compound is a concern to the environment.

Even though methyl chloride occurs naturally, it is additionally manufactured for use in industry. For example, it is used in the manufacturing of silicone. Other chlorocarbons are not naturally abundant and must be made from other starting compounds. Figure 1 shows the processes used for creating C_1 and C_2 chlorocarbons. Focusing on carbon tetrachloride, chloroform, methylene chloride, and methyl chloride processes in Figure 1, carbon tetrachloride can be produced through chlorination of chloroform produced from direct chlorination of methylene chloride, etc. From Figure 1, these chloromethanes can be interlinked with each other.[1] Some of the general properties of interest to chlorocarbons involve the variation in the chlorine content. As the chlorine content increases, the nonflammability, density, and viscosity increases. With decreasing chlorine content, the specific heat, dielectric constant, and water solubility increases.[1] Based on these general properties and carbon tetrachloride's long atmospheric retention time, concern should be taken when using this compound in any setting. Another problem, other than their stability and retention time in the environment, is the thermal decomposition of carbon tetrachloride can produce toxic products such as phosgene.[2] Due to the problematic nature of carbon tetrachloride in respect to the other chloromethanes, it is the focus of this discussion. An excellent history of carbon tetrachloride is located in reference 2. The uses and production of carbon tetrachloride dates back to the 1890's when it was first prepared.[2] Large-scale production of carbon tetrachloride in the United States started around 1907.[2] The chemical's primary use was for dry cleaning and fire extinguishers during the period up to World War II.[2] Carbon tetrachloride was then further used for grain fumigation and the rubber industry.[2] Then carbon tetrachloride started being gradually replaced with less toxic, trichloroethylene and perchloroethylene, chemicals.[2] Incidentally, the chemical found a use as a reactant in the production of CFC-11 and CFC-12.[9] The CFC's are used as refrigerator coolants.[9] Furthermore, the compound was used as a pesticide until 1986.[2] Due to carbon tetrachloride's toxicity and the possibility of toxic products, it is slowly being phased out.[2] Table 2, courtesy of the U.S. Federal Trade Commission, shows the amount of carbon tetrachloride produced since 1960 to 1988.[2] From 1960 to 1970, carbon tetrachloride production increased by 10.7% a year. The highest year of production is 1970. The total value of carbon tetrachloride is increasing every year partly to due the regulations placed on it. In 1997, Directory of Chemical Producers stated that 5000 tons of carbon tetrachloride was produced at two sites in the United States.[9] The production of carbon tetrachloride is decreasing every year due to regulations. For example, the EPA regulates the use of carbon tetrachloride under multiple regulations including the Clean Air Act and the Clean Water Act.[9] Another reason for a decrease in production is because carbon tetrachloride imports are increasing.[9] In 1987, carbon tetrachloride imports exceeded 111 million pounds (USDOC Imports, 1988).[9] For it to be in utilized for so long, multiple reactions using carbon tetrachloride have been researched. These reactions include in air, in water, and with metals. When one gram of carbon

Table 2. Total production, sales, and values of CCl_4 from 1960-1988

Year	Total production, 10E3 t	Total Sales, 10E3 t	Total Value, 10E6 $
1960	168.8	151.3	27.14
1965	269.3	231.1	37.49
1970	458.7	381.6	44.09
1975	411.2	219.6	65.9
1976	388.6	208.2	60.3
1977	367.67	175.22	49.08
1978	335.01	165.18	41.7
1979	324.76	159.47	40.02
1980	322.54	147.7	44.13
1981	330.22	175.28	48.78
1982	267.02	141.04	39.89
1983	260.38	156.43	44.46
1984	324.11	159.65	54.47
1985	293.46	163.79	58.22
1986	284.99	225.39	68.87
1987	305.52	326.28	102.07
1988	346.08	386.03	129.43

(adapted from reference 2)

tetrachloride is mixed with air and iron, .375 grams of phosgene are produced. Since phosgene is a toxic product, the reaction of carbon tetrachloride with air and iron with respect to the same reaction of chloroform, iron, and air, carbon tetrachloride produces 156 times more phosgene.[10] In excess water and heat up to 250° Celsius, carbon tetrachloride breaks down into carbon dioxide and hydrochloric acid. If water is not in excess, phosgene is again produced.[2]

Incineration of chlorocarbons

Due to the constant practice of carbon tetrachloride and its partners as solvents, etc. dating back fifty or sixty years and the environmental consequences of their use, an economical and safe way of disposing of them is necessary. Incinerators are the most commonly practiced ways of disposing of hazardous chemicals. The EPA estimates that the regulations concerning hazardous waste disposal of the liquid state will substantially increase the quantity of waste directed towards incinerators, boilers, and furnaces.[27] Several types of industrial furnaces are used to recover energy by destroying hazardous wastes.[27] The major incinerators include cement kilns, light-weight-aggregate kilns, halogen-acid furnaces, and metal-recovery furnaces.[27] During combustion, the temperature of the flame is sufficiently hot enough to allow various reactions between oxygen and nitrogen in the air and the gaseous wastes to are the products.[27] Predominately, carbon dioxide and water occur.[27] Depending on what is present in the waste, hydrogen halides, sulfur oxides, nitrogen oxides, metal oxides, dioxins, furans, and metal vapors can be formed.[27] To combat these products from escaping into the atmosphere, all waste-incinerator facilities include a form of air pollution control devices (APCD)[27]. The newest facilities have the latest devices and the older facilities do not. APCD's are designed to remove particulate matter and acid gases.[27]

Acid gases are flue-gas constituents that form acids when they combine with water of any state. Flue-gas pertains to the gases that are the products of the combustion reaction. The acid gases include the hydrogen halides, SO_2, SO_3, etc. The most commonly used APCD for the elimination of acid gases is a packed-bed absorber.[27]

The packed-bed absorber process involves trickling a "scrubbing" liquid through packing that the acid gases also pass through. The scrubbing liquid is usually water or an alkaline solution. The acids react to form neutral salts in wastewater. Care must be taken to avoid the chance of unreacted acids, trace organics, etc. removal from the waste water.

In Europe, dual-stage wet absorbers are contained in their facilities. The first stage contains an acidic scrubber to remove water soluble gases such as HCl and the second stage contains a alkaline scrubber to remove less water soluble acids such as SO_2.[27] The most important considerations for the absorbers is gas velocity, liquid-to-gas ratio, pH of the scrubbing liquid, and the materials that the device is constructed of.[27]

The other not so common method for destroying acid gases is the spray-dryer scrubbers. These scrubbers consist of a slurry of lime, sodium carbonate, or sodium carbonate as an alkaline source.[27] The water of the slurry evaporates leaving the alkali particles to react to form dry salts.[27] The particles are then caught by a fabric filter or electrostatic precipitator.[27] The criteria that must be considered for the spray-dryer scrubbers include gas temperature in the contact zone, reagent-to-acid gas stoichiometry, reagent type, etc.[27]

Several alternate methods for the destruction of the chemical and other chloromethanes have been researched that incorporate the incineration method. One method done for the destruction of chloromethanes is oxidative pyrolysis by Taylor *et al.*[11], where incineration conditions are mimicked. Taylor *et al.* ensured a chlorocarbon/oxygen ratio of 3 that is the same stoichiometry found in combustion reactions.[11] The only hydrogen for the reaction is available from water present in the air. For the oxidative pyrolysis of carbon tetrachloride, three major products were formed. These products were chlorine, tetrachloroethylene, and hexachloroethane. Two of these products, tetrachloroethylene and hexachloroethane, are more stable than the starting carbon tetrachloride. Taylor *et al.* concluded that potentially toxic and thermally stable products could be produced in significant yields during the oxidative pyrolysis of chloromethanes where small amounts of hydrogen are available.[11] In another pyrolysis study by Wu and Wong,[12] an investigation was done on the chloromethanes thermal stability and hydrodechlorination in excess hydrogen. Oxygen was absent during the experiment because during the oxidation process, oxygen and chlorine both compete for the available hydrogens.[12] The ratio of chlorocarbon to hydrogen was 1 to 24. Some of the major products created from the chlorocarbon and excess hydrogen reaction is chloroform, methylene chloride, methyl chloride, hydrochloric acid, methane, ethane, and ethane. Detailed reaction pathways are shown in Figure 1 of carbon tetrachloride and hydrogen.[12]

Metal Oxides

In addition to pyrolysis of chlorocarbons, heterogeneous catalytic oxidation of volatile organics, which include chlorinated compounds, is an extensively studied field.[14] There are two types of reagents used for oxidation reactions. These two basic types are metal oxides and noble metals. Furthermore, the reagents can be supported or unsupported, typically by another oxide such as γ-alumina oxide. In addition, they are more active and easier to poison than the metal oxides counterparts. During the reaction, oxygen is available in large excess so the reagent is always able to reabsorb the available oxygen. The metal oxide reagent is then able to have high surface oxygen content for further reactions to take place[14]. Noble metals, specifically platinum, palladium, silver, and gold, are frequently alloyed with cheaper closely related transition metals and are usually supported on a high surface area support such as gamma-aluminum oxide or silicon dioxide. Noble metals are the least stable to allow oxygen absorption, suggesting that reactions that do occur involving oxygen are from the molecular oxygen present in the gas stream. Both metal oxides and noble metals typically follow the Langmuir-Hinshelwood or Eley-Rideal type mechanism.[14] The Languir-Hinshelwood mechanism involves a reaction between the adsorbed oxygen and an adsorbed reactant. The Eley-Rideal mechanism involves a reaction between the adsorbed reactant and a gas-phase reactant molecule.[14]

Further investigation of metals leads to specific chemisorption interactions that the noble metals prefer to follow. For example, silver is a stronger absorber of oxygen inferring a redox reaction that mimics redox reactions of metal oxides.[15]

Metal oxides have two types of semiconductors that can occur. These are the n-type and p-type metal oxides.[14] Parameters for measuring the strength of a metal involve its adsorption to the reactants. A number of transition metals and metal oxides are involved in reactions as catalysts. A catalyst must not adsorb a reactant too weakly or too strongly. If the adsorption of the reactant is too strong, the catalyst will quickly deactivate itself as the active sites located on the catalyst become covered with the gas or liquid phase reactants. The definition for the strong adsorption is known as poisoning. Inversely, if the catalyst is unable to bind strongly enough to the reactants, the absorption of reactants is low and the few of the active sites are responsible for conversion to products. The catalyst is then termed to have a low catalytic activity. A catalyst with optimum activity will do neither. Figure 2 shows typical volcano plot of the catalytic rate versus atomic number using the transition metal series, courtesy of Ian Campbell.[30] All the metals chosen had the same conditions under which the reaction took place. The volcano plot indicates that the early transition metals chemisorption is strong and the metals decrease in chemisorption strength when moving to the right of the periodic table to the late transition metals.[30] N-type metal oxides are generally not used as reagents in the oxidation process. Instead, the metal oxides, termed insulators, can be used for catalytic supports. P-type metal oxides are the more active as catalysts. The positive holes that are created on the oxide allow surface reduction more readily to form oxygen adsorption sites. Overall, the interaction between oxygen and the metal oxides determines a catalyst's properties. The interaction can involve lattice or surface-adsorbed oxygen.[14] Haber suggests that the oxygen adsorbed onto the surface of the catalyst generally leads to complete oxidation whereas the lattice oxygen of the reagent only gives partially oxidized products.[17]

Hydrogen tungsten bronze

The metal, tungsten, when incorporated with oxygen, typically involves an oxidation state of six. When reacted with hydrogen, it is reduced to a hydrogen tungsten bronze commonly termed tungsten blue. The term 'bronze' is defined as "a ternary metal oxide with the formula $M'_x M''_y O_z$ where i) M'' is a transition metal, ii) $M''_y O_z$ is its highest binary oxide, iii) M' is some other metal, iv) x is a variable that falls within the range of 0 and 1".[18] Typically, these bronzes possess high electrical conductivity, which can be metallic or semi-conducting.[18] Mixed-valence compounds frequently display high electrical conductivities.[21] For example, each Na atom reduces a W(VI) to W(V). Alkali metal ions can transfer its valence electron(s) to the oxygen of the tungsten oxide's delocalized state. This possibility originates from the

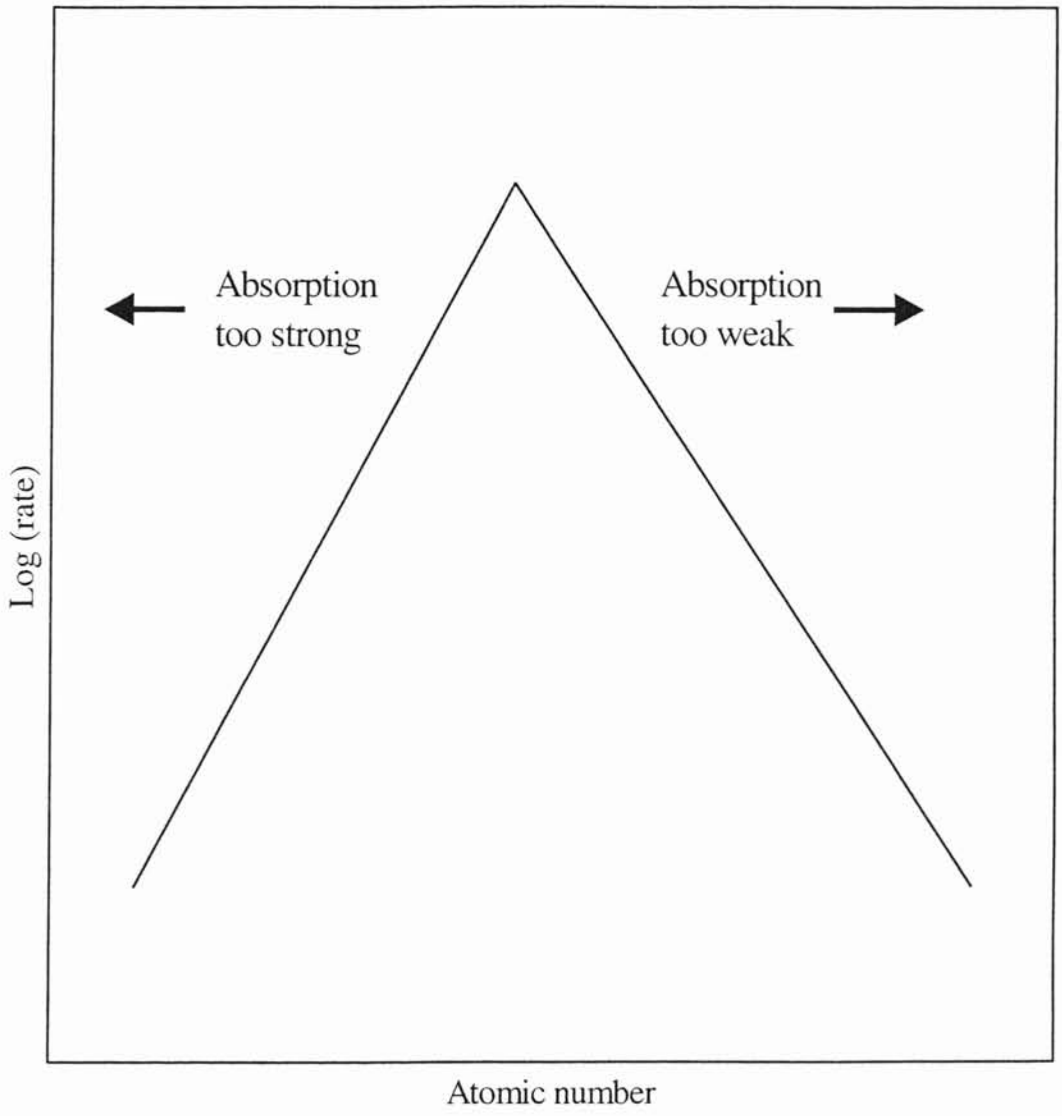

Figure 2. Idealized 'volcano' plot of the rate of a specified catalytic reaction under the same conditions along a transitions metal series. (adapted from reference 30, p. 162)

direct overlap of the transition metal t_{2g} orbitals or from the indirect overlap of the *d* orbitals through intervening oxygen π interactions.[19-20] Furthermore, hydrogen tungsten bronze is intensely colored blue. Typically, bronzes are chemically inert with the exception of the hydrogen bronze that are slowly attacked by air and rapidly oxidized by hot dichromate solution.[18] In addition, sequences of solid phases occur, through variation of x, with definite and sometimes wide ranges of homogeneity.[18] In most scenarios, the hydrogen ratio is 0.35 to 0.50. Besides the generalized physical characteristics of tungsten bronzes, they also maintain different lattice structures dependent on the three features. First of all, as the value of x in the M_xWO_3 decreases, so does the symmetry of the crystal line phase. Secondly, the structure of a particular compound is controlled to an extensive degree by the ionic radius of M. Finally, all structures are based on the linking together of WO_3 octahedra by the sharing of its corners.[18] The three-dimensional structure pictured as Figure 3 is the foundation block for the bronzes. It is of 6:2 coordination with each W surrounded by 6 O, and 2 W linearly coordinates each O. The unit cell has a large central cavity.[21] The Figure 4 is a depiction of bronze- forming atoms inside the holes of WO_3 octahedra in a ReO_3-type solid[3]. When the atom inserts itself into the metal-oxygen framework, the lattice parameters are changed very little and the framework is mainly preserved.[28] At high values of the bronze-forming atom, amorphous products are occasionally found indicating the framework of the metal-oxygen structure has collapsed. Thermochemical data supports a view indicating that the H in H_xWO_3 or any metal of vanadium, uranium, or molybdenum exists as –OH groups with the hydrogen strongly bonding to the lattice oxygen. Although thermodynamic data indicates the bonding of hydrogen and oxygen, it is difficult to find the actual location of

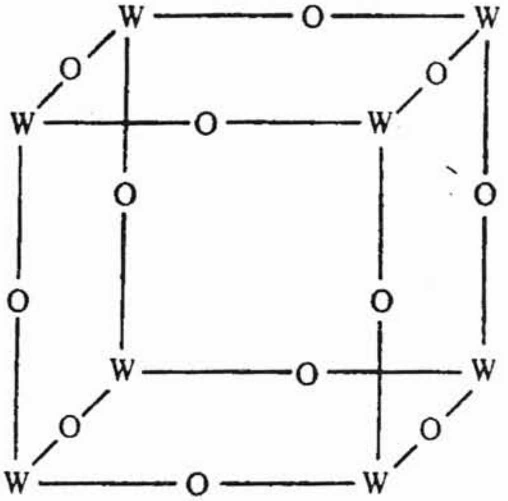

Figure 3. WO_3 unit cell
(adapted from reference 21)

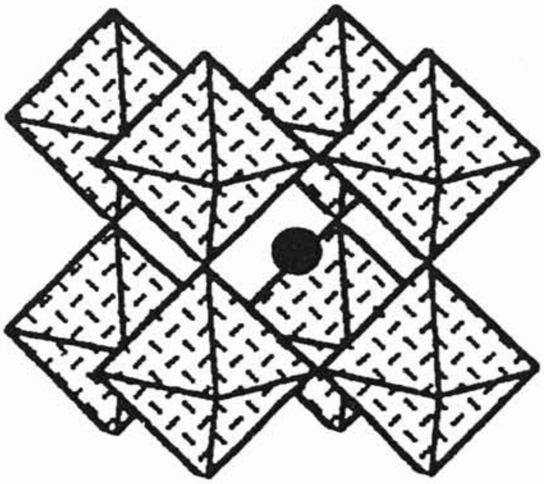

Figure 4. H_xWO_3 crystal structure
(adapted from reference 24)

the hydrogen experimentally. The first reason for characterization difficulty is the preparative methods in the production of the hydrogen bronze are predisposed to poorly crystalline and, commonly, inhomogeneous products. In addition, XRD methods are inappropriate for locating the hydrogen atom due to the heaviness of the tungsten atom with respect to hydrogen. Finally, the compound frequently has non-stoichiometric and random order to which the atoms of hydrogen are located. Based on the $H_{0.5}WO_3$ structure of Dickens and Chippendale,[28] the presence of –OH groups is confirmed by an intense peak in the inelastic neutron scattering spectrum falling in the range of 950-1300 cm^{-1} which is consistent with an in-plane bending mode. Figure 5 shows the relationship between the crystal structure and composition for the alkali-metal tungsten bronzes. The cubic structure that is preferred for the stoichiometry $Na_{0.3}WO_3$ to $NaWO_3$ is representative of a distorted perovskite structure. Tetragonal I or tetragonal II phases are preferred below $Na_{0.3}WO_3$ until the monoclinical $Na_{0.17}WO_3$ is reached. The tetragonal I phase consists of WO_6 octahedra exclusively shared at the corners.[29] In the octahedral phase, they are arranged to form rings consisting of three, four or five octahedra. The metal ions are then inserted into the larger of the interstitial areas. The tetragonal II structure is again composed of WO_6 octahedra arranged similarly to the perovskite structure of the cubic bronze but is deformed from the cubic structure. The structure, delegated by Hagg and Magneli, also includes the tungsten atoms forming puckered layers extending at right angles to the tetragonal axis.[29] Due to the similar arrangement by which the tetragonal structures are designed, a possible explanation for the similarities can be stated by Hagg and Magneli.[29] They state that "the bronzes of degenerated perovskite type(tetragonal I and II) to be an intermediate state in the transition with decreasing alkali content from the cubic sodium bronzes of perovskite to tungsten trioxide."[29] It has been shown by X-ray and neutron diffraction methods that hydrogen tungsten bronze is structurally related to the sodium tungsten bronzes.[22-23]

Several methods are available for the synthesis of tungsten bronzes, including thermal reduction, electrolytic reduction, chemical reduction, and solid-state reaction. The first method is the vapor-phase reaction or thermal reduction. It is ideal for metals that are substantially volatile at high temperatures and can be controlled somewhat easily at room temperature.[18] Solid/solid, molten/molten, molten/solid, and gaseous/solid state reactions are some of the various styles of preparing bronzes.[3] The next method available is electrolytic reduction. The procedure involves molten mixtures of tungstate and tungstic oxide that are decomposed with the aid of platinum or tungsten electrodes. This method is the most successful for the growth of large crystals, but the control of the melt temperature is crucial.[18] In addition to the electrolytic reduction, chemical reduction is another method of interest. This is a favorable method for producing the hydrogen tungsten bronze. WO_3 is reduced in an acidic media via a dissolving metal reduction.[3] Finally, there is the solid-state reaction method that is very versatile. Finely ground reagents are heated *in vacuo* to produce the bronze.[18] In this study, chlorocarbon degradation by a hydrogen tungsten bronze is the primary target. At Oklahoma State University, Dr. Allen Apblett's group has done recent studies on the reactions of hydrogen tungsten bronzes as potential carbon tetrachloride remediators.[31] The chlorocarbons of interest are chlorocarbons are located in the chemical burial site west of campus and other chemicals that are difficult to remove from the environment. Side possibilities are considered to determine the specificities of the reagent.

EXPERIMENTAL

Procedure for the making of the reagent

Tungsten (IV) oxide is the starting material from which the reagent, hydrogen tungsten bronze is made. The method used is A. B. Ellis *et al*'s book, Teaching General Chemistry: the Materials Science Companion.[24] An equation, shown by Equation 1, involving the reduction-oxidation between WO_3 and Zn.[25]

$$2WO_3 + (x)Zn \rightarrow 2WO_3^{x-} + (x)Zn^{2+} (1)$$

Equation 2 shows a basic addition of an acid with tungsten oxide to produce the hydrogen tungsten bronze and water.[25]

$$WO_3^{x-} + xH_3O^+ \rightarrow H_xWO_3 + xH_2O (2)$$

The method given by A.B. Ellis was adapted for use by Dr. Apblett's group prior to the work done in this project.[31] Dr. Apblett's group synthesis involved adding thirty grams of tungsten oxide to a 500 milliliter filtering flask. Enough deionized water is then added for the tungsten oxide to suspend. Then 56.7 grams of zinc metal is placed in the filtering flask and swirled around in order to disperse the zinc into the tungsten oxide slurry. A magnetic stirring rod is placed in the filtering flask in insure stirring of the solution during the reaction. The filtering flask is positioned in an ice bath to keep the reaction of the solution from getting too hot. The ice bath is then placed on a stirring plate. An excess amount, 250 milliliters, of concentrated hydrochloric acid is placed in 250 milliliter separatory funnel. The separatory funnel is placed on the top of the filter flask with the aid of a rubber stopper in between the two pieces of glass and there is also a clasp at the top of a stand to hold the top of the separatory funnel. The stopcock of the separatory funnel is slowly adjusted to a point where a drop of the concentrated hydrochloric acid is dripped into the solution at a rate of one drop every two or three seconds. The solution is being stirred during the entire process. The process produces a large amount of hydrogen gas, so the reaction vessel is underneath the fumehood for the duration of the reaction. Once the reaction has gone to completion, hydrogen tungsten bronze solid and zinc chloride solution are the products.[31] The solution is allowed to settle and then the supernatant solution is decanted. Then 250 milliliters of 5 M hydrochloric acid is added to the solid. The solution is then stirred again for one hour to allow the hydrochloric acid plenty of time to react. The solution is then allowed to settle and the supernatant liquid is once again removed. Another 250 milliliters of 5 M hydrochloric acid is again poured into the solid and allowed to stir. Once it has stirred for an hour, the isolation of the tungsten hydrogen bronze can occur. The suspended solution is poured into a Buchner funnel with a vacuum pump attached to pull the solution down into a 500 milliliter filtering flask. The entire solid is removed by means of deionized water. Once the solid is in the bottom of the buchner funnel, 250 milliliters of 5 M hydrochloric acid is pulled through the funnel to completely confirm the removal of all zinc compounds. The solid hydrogen tungsten bronze, located in the Buchner funnel, is placed into a vacuum oven. The oven is evacuated at room temperature and the solid is allowed to dry. The drying process is allotted twenty-four hours to ensure complete evaporation of the liquids. The next day, the solid is removed from the oven and placed into vials that are sealed around the cap with parafilm®. Care must be taken to keep this compound away from as much air as possible. The compound will be oxidized if left out in the open. The schematic of the reaction is shown in Figure 5.

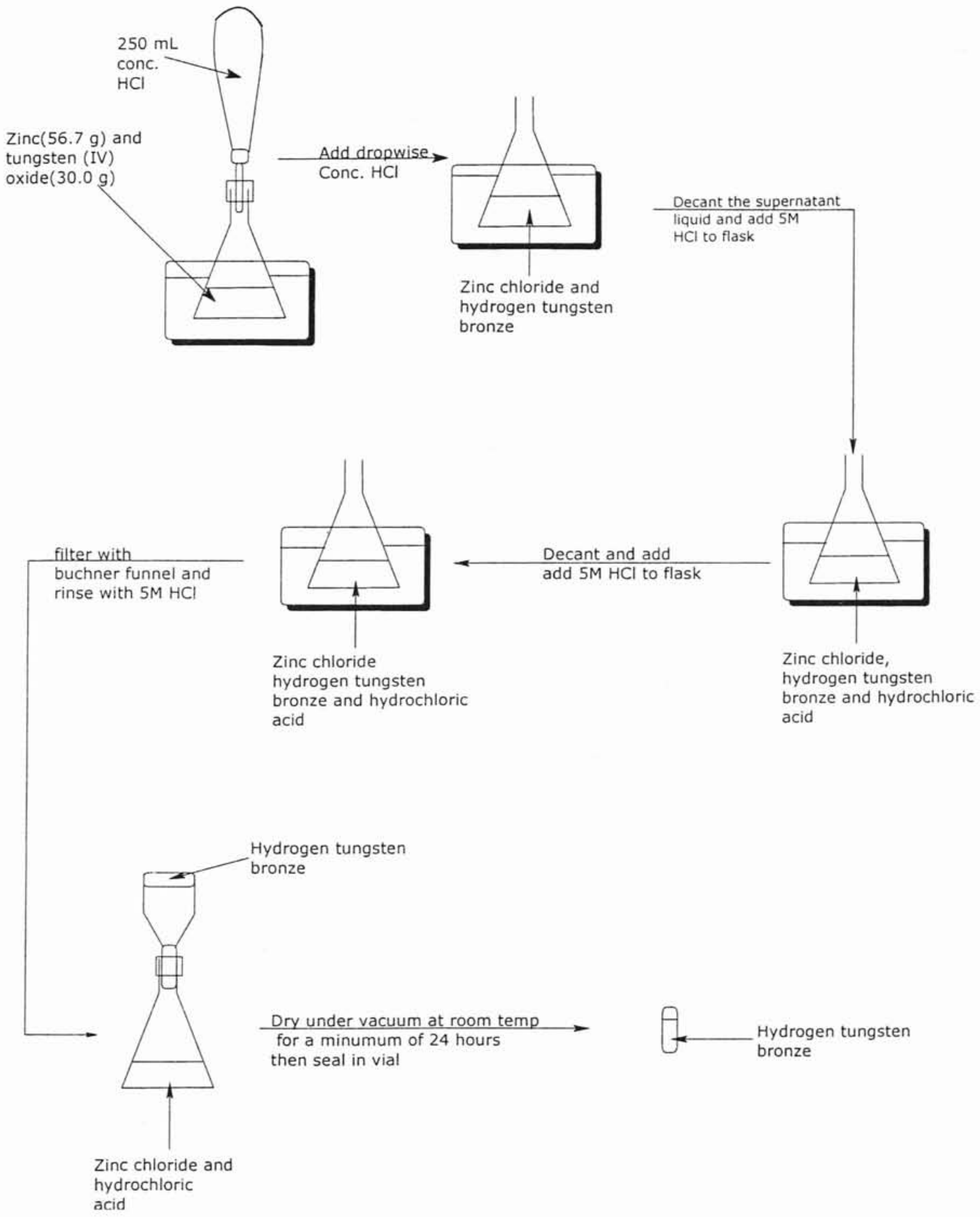

Figure 5. Schematic for reaction of zinc and tungsten (IV) oxide

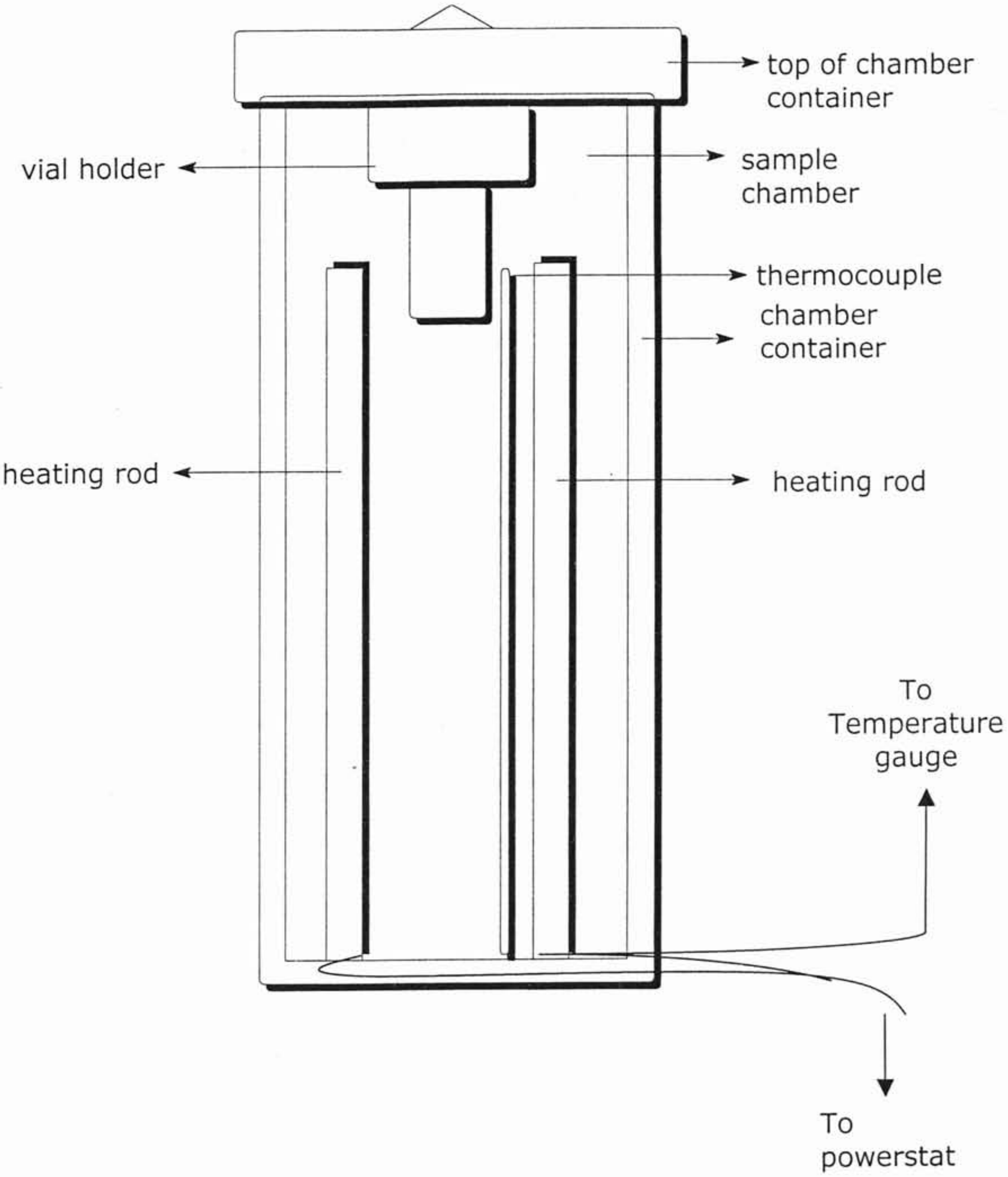

Figure 6. Schematic of heating chamber

EXPERIMENTAL EQUIPMENT

Heating Chamber

The heating chamber consists of two heating rods placed to obtain maximum heat. The heating rods are then connected to a powerstat to keep the current constant. In the center of the chamber contains a position called the sample chamber where the sample vial is placed. A thermocouple is located at the same height as the middle of the sample chamber and as close as feasibly possible to the wall of the vial without actually being in sample chamber with the vial. The thermocouple is then connected to a digital temperature meter. The container that also holds the thermocouple and the heating rods in place surrounds the heating chamber. The heating chamber is then sealed by the top, which encompasses both the heating chamber and the container. Figure 6 shows the schematic of the heating chamber.

Apparatus

The instrument used for observing the conversion of reactants to products is a gas chromatograph/mass spectrometer. The column of the gas chromatograph is 30.0 meters in length with a diameter of 0.25 millimeters. Helium is the selection for gas carrier. The flow is maintained at 1.0 millimeter per a minute. No solvent delay for the detector was used due to the products of the reaction eluting sooner than the typical solvent delay of three minutes. The mass range for the detector is 45 amu to 200 amu. This increases the sensitivity of the detector and decreases the possibility interference by air leaks.

The injection port temperature is kept at 250° Celsius and the detector is maintained at 280° Celsius. The oven's initial temperature is 35° Celsius and programmed to increase 3 degrees per a minute until it reaches 115° Celsius.

Typically, ten microliters of headspace above a vial containing the reaction mixture is injected into the inlet. On occasion fifteen to twenty microliters have been injected in order to insure a proper identification of the products and the reactant. The peak areas of the products and the reactant are taken to determine qualitatively if the reaction is proceeding.

Chemicals Studied

Carbon tetrachloride was initially the main chemical of interest in this study. In addition, calcium carbonate is employed in a reaction with carbon tetrachloride. Also, zinc metal and zinc chloride are used in a reaction with carbon tetrachloride. Focus then varied on additional chlorinated compounds. These compounds include: chloroform, methylene chloride, 1,2,3-trichloropropane, chlorobenzene, and tetrachloroethylene. Most of these compounds are found in the chemical burial site. Finally, 1,2-dibromoethane was studied due to its placement in the chemical burial site.

Halocarbon addition

Between 0.25 and 0.27 grams of hydrogen tungsten bronze are placed into a specially made vial. A mininert screw valve is placed on top of the vial to seal the chamber. The screw cap has a Teflon valve body and a needle-seal septum. A volume of sixteen microliters of the chloromethane is added through the top of the vial with a 100-microliter syringe. The chloromethane generally was carbon tetrachloride. The vial was then placed in a chamber for heating. The temperature of the chamber was kept at 128°

Celsius. The sample stayed in the chamber until the reaction was completed between the carbon tetrachloride, or other chloromethane, and the hydrogen tungsten bronze.

Evaluation of the reaction

All reactions were observed using a gas chromatograph mass spectrometer. Spectra of carbon tetrachloride, chloroform, methylene chloride, and 1,2,3-trichloropropane are shown in Figures 7-10 respectively. On average, after twenty-four hours of heating the vial containing the reaction, a ten-microliter sample is injected into the instrument. The only exceptions were if the reagent was reacting with the halocarbon quickly. The products were observed and recorded with respect to the percent of the peak area that the products secured.

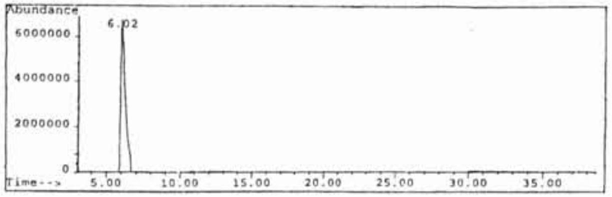

Figure 7 Carbon tetrachloride, initially

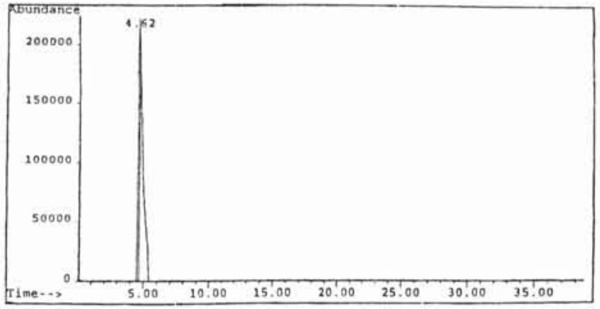

Figure 8 Chloroform, initially

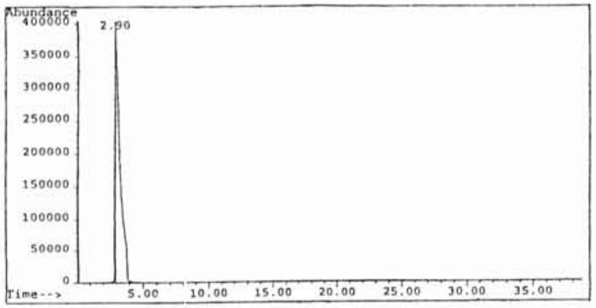

Figure 9 Methylene chloride, initially

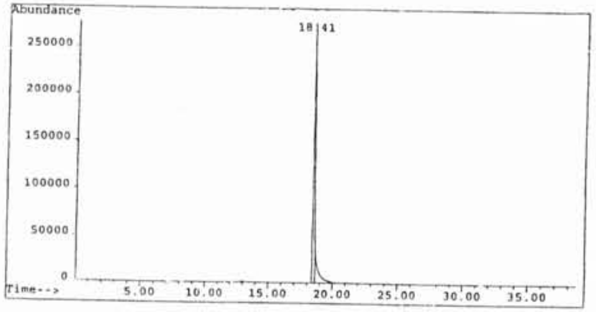

Figure 10 1,2,3-trichloropropane, initially

RESULT AND DISCUSSION

Dechlorination of CCl_4

In the removal of chlorines from carbon tetrachloride, several compounds arise. At Oklahoma State University, Dr. Apblett's group was able to react carbon tetrachloride with hydrogen tungsten bronze.[31] One new product yet to be reported in literature is the production of phosgene. The release of lattice oxygen from the reagent or oxygen contained in the air when the vial was closed directed the phosgene production. The chemisorption abilities of the reagent allowed for the taking of the reactants and the release of the products. Phosgene was only produced after the products, methylene chloride and chloroform, were formed as shown in Figure 11-13. Figure 11 shows, at 48 hours, chloroform, methylene chloride, TCE and phosgene. Phosgene is the major product at the time of the injection. After 78 hours, another injection was done showing the major product to still be phosgene. Shown in Figure 12, the methylene chloride peak and the TCE peak have increased. Notice should be taken though, on the abundance levels between Figure 11 and 12. The abundance have decreased from the highest peak being 10^6 to 10^5, indicating the absorbance of the products back onto the reagent surface. Also, the chloroform is absent from the spectrum. After 96 hours, shown in Figure 13, the phosgene and the methylene chloride are almost equal in height with the phosgene being lower than the methylene chloride. The TCE is still showing, but it has reduced in size, but not as fast as the other two peaks did. In conclusion, the reaction of carbon tetrachloride and hydrogen tungsten bronze's products can be variable due to the conditions the reaction was taking place in.

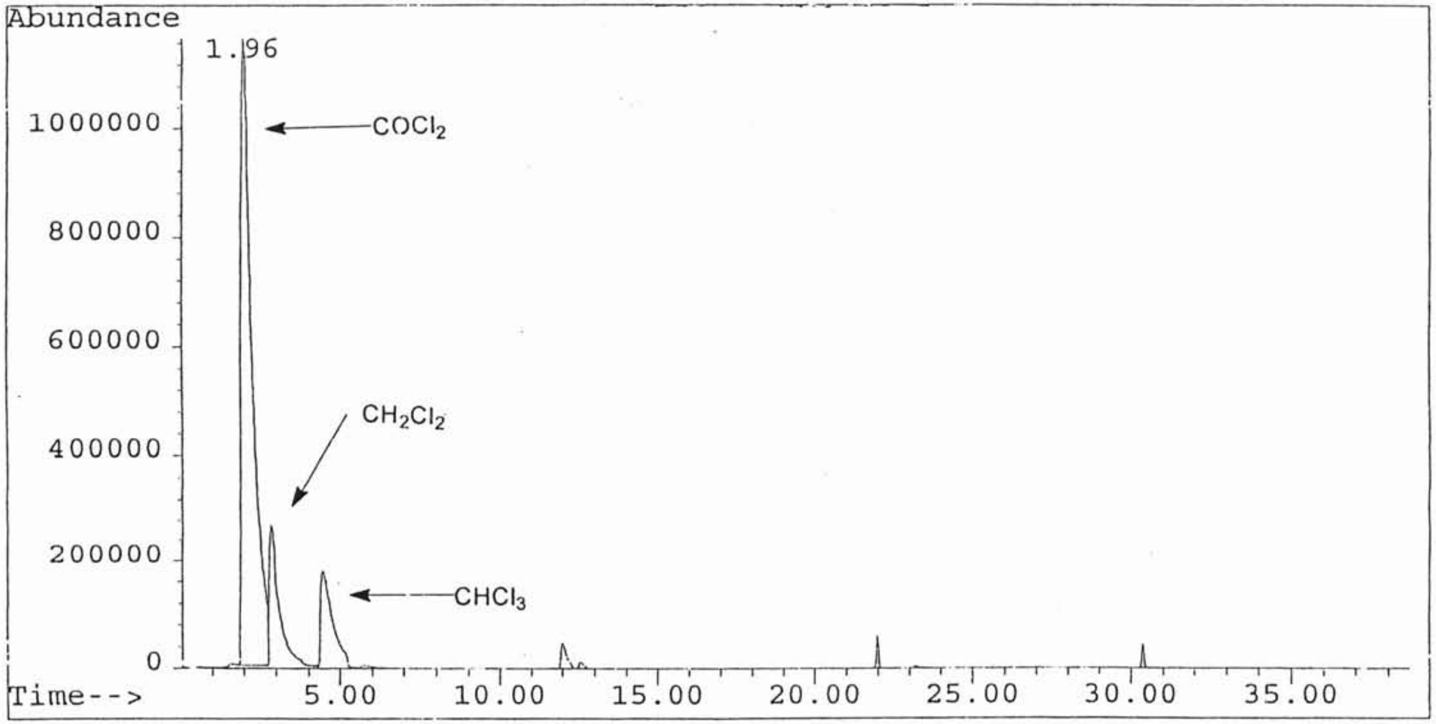

Figure 11. Dechlorination of CCl_4, 48 hours

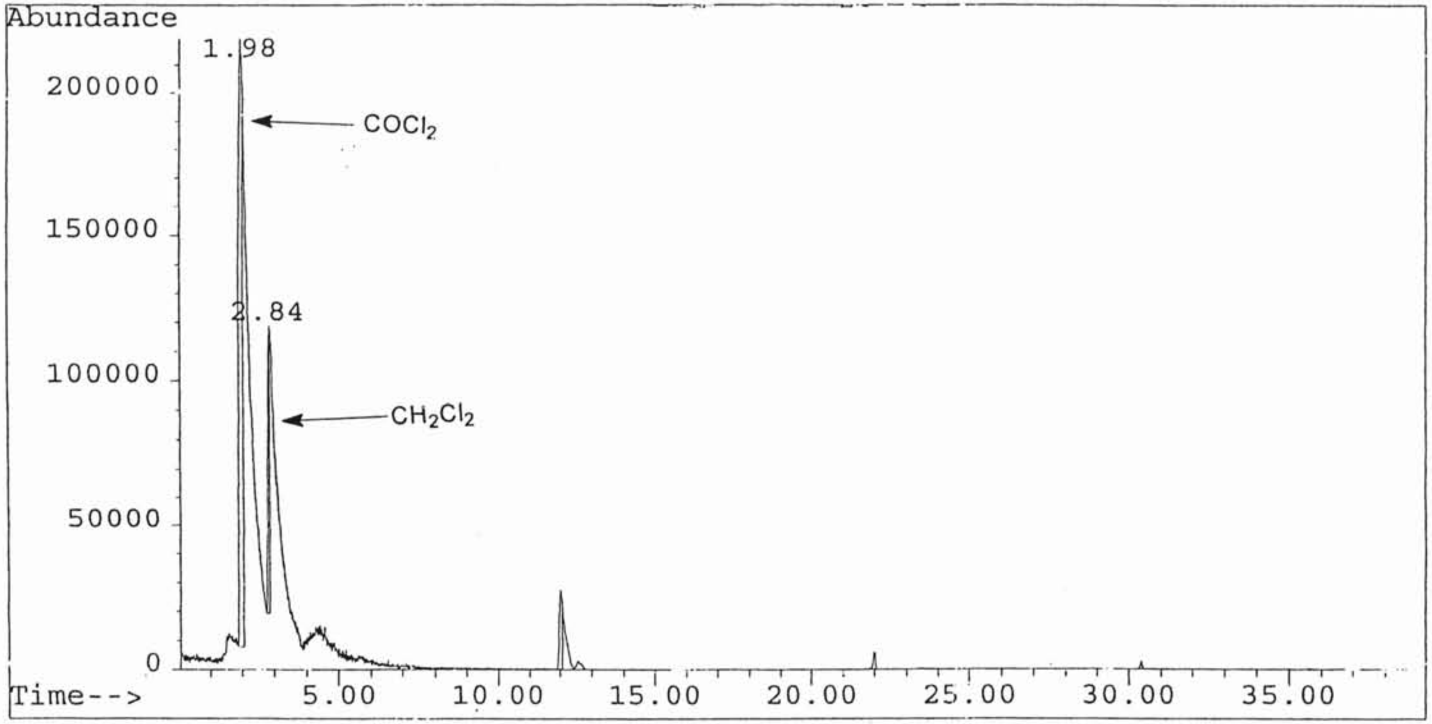

Figure 12. Dechlorination of CCl_4, 78 hours

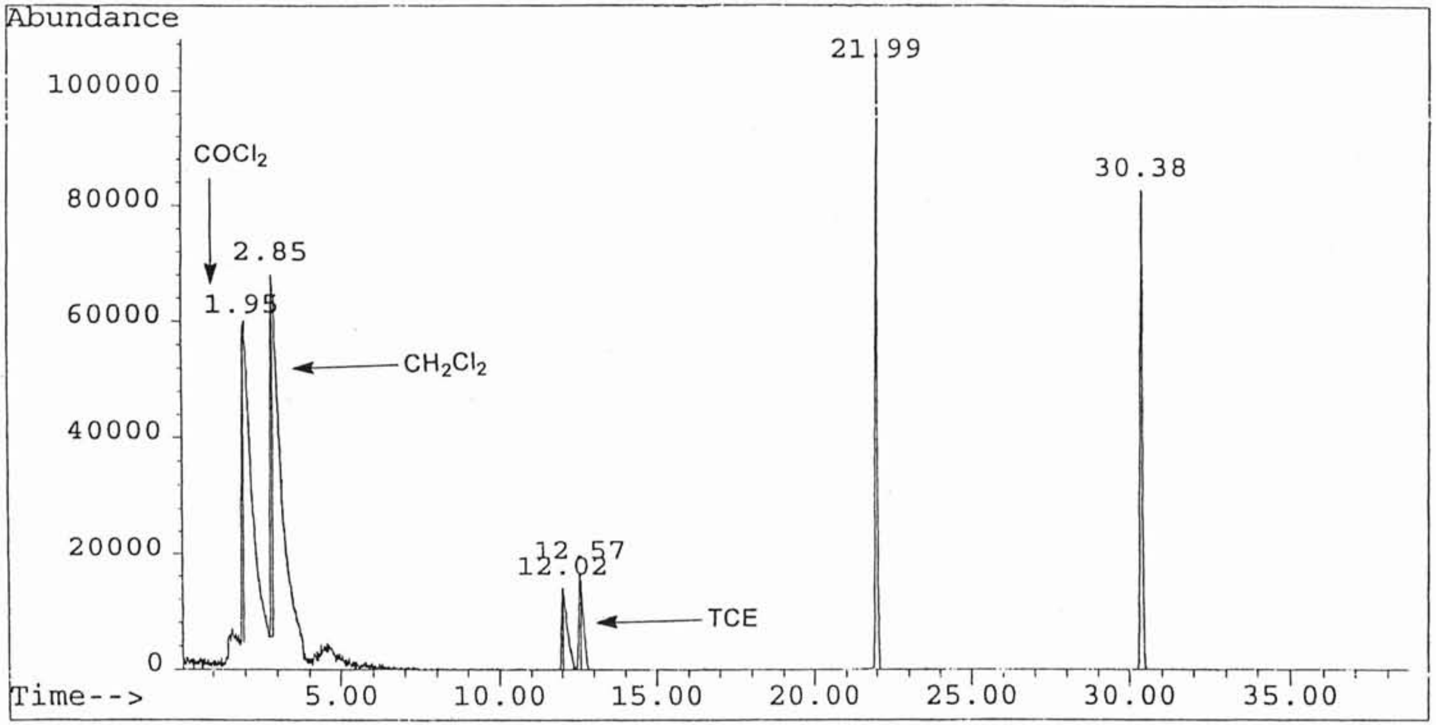

Figure 13. Dechlorination of CCl_4, 96 hours

Effect of Zinc and Zinc Chloride on Reagent

Pointing to the fact that tetrachloroethylene was also another new product in the previous spectra involving the reaction of carbon tetrachloride and hydrogen tungsten bronze, concern was taken as to why and what had caused the TCE to be produced. The first thought was that zinc chloride was left over from when the reagent was being filtered. It might have coated the surface of the reagent giving it the ability to knock out the reagent's capabilities. A reaction was performed where 0.06 grams zinc chloride was placed in a vial with 0.25 grams hydrogen tungsten bronze and then 16 microliters of carbon tetrachloride were then inserted through the vials septum. The results of this reaction, shown in Figure 14 and 15, conclude that zinc chloride was ineffective for the accidental production of large amounts of tetrachloroethylene. Figure 14 shows products of methylene chloride, chloroform, and small amounts of phosgene and tetrachloroethylene. Figure 15 illustrates methylene chloride and chloroform still with small amounts of tetrachloroethylene. The next strategy was to assume that not all of the zinc was consumed during the reaction to produce the reagent. In the context of the previous statement, the reagent was not one hundred percent hydrogen bronze. In order to tell this hypothesis, 0.06 grams of zinc was added to 0.25 grams of the reagent. The carbon tetrachloride was then added. After the vial was heated, a sample was taken to inject the headspace into the GCMS. Figure 16 exhibits methylene chloride and chloroform with small amounts of methyl chloride, trichloroethylene, and tetrachloroethylene. Figure 17 presents chloroform and methylene chloride and a larger peak of tetrachloroethylene. In comparing the spectra taken of the carbon tetrachloride with zinc and zinc chloride, the conclusion can be made that zinc reacts readily with the

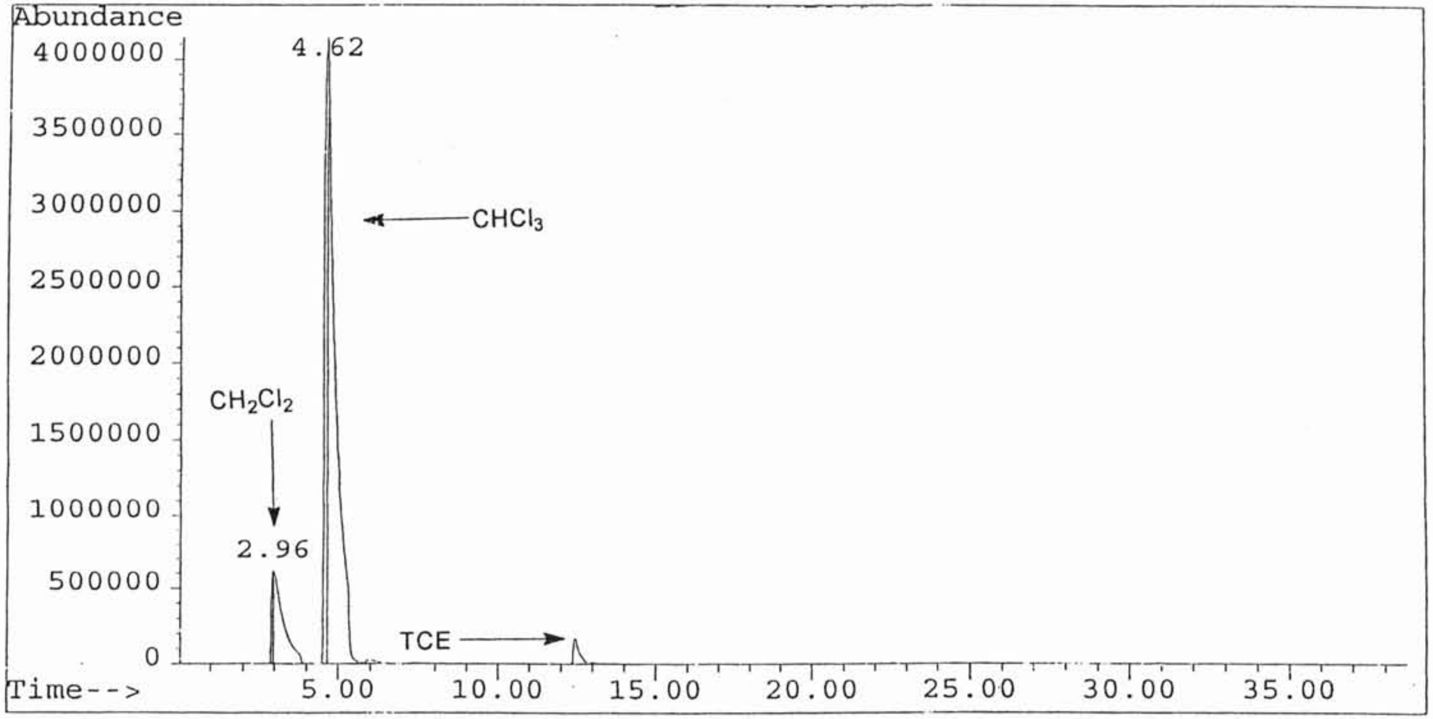

Figure 16. Reaction of zinc with CCl_4, 7 hours

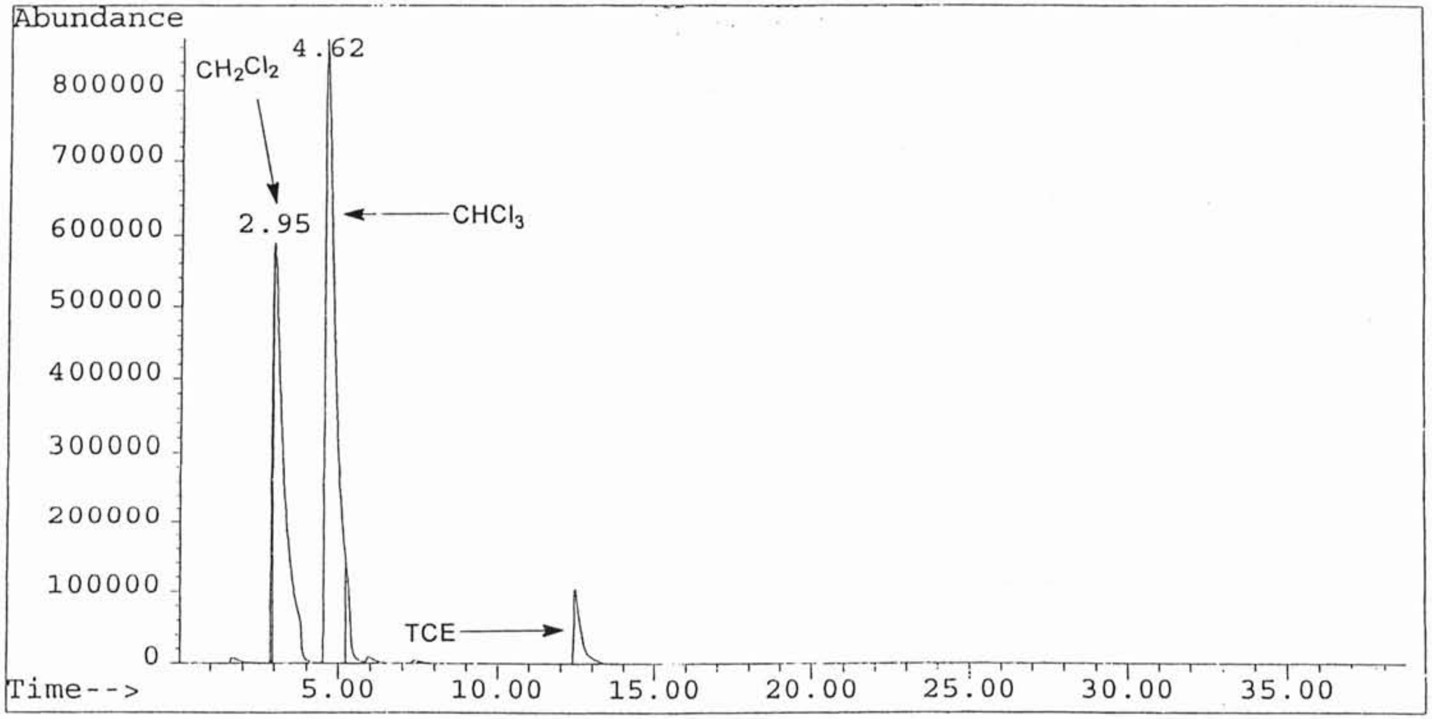

Figure 17. Reaction of zinc with CCl_4, 21 hours

carbon tetrachloride and causes coupling to occur. Zinc chloride inhibits the reaction slightly but does not effectively create a significant coupling reaction for the carbon tetrachloride.

Effect of Calcium Carbonate on the dechlorination of CCl_4

Due to the large amount of hydrochloric acid produced during the process of dechlorination of carbon tetrachloride, a compound was required to rid the reaction of the hydrochloric acid product. The compound chosen was calcium carbonate. Small capsules were made that could fit into the vial that the experiment was taking place in. The reactants contained 20 microliters of carbon tetrachloride and 0.25 grams of hydrogen tungsten bronze. In addition, a small amount of calcium chloride was ground up into a fine powder and placed into the open-ended capsule. The capsule was contained inside the vial. The experiment was then placed in the heating chamber where it was kept at the same temperature as the rest of the constant temperature reactions were kept. The ending of the experiment determined that hydrochloric acid was necessary for the dechlorination of carbon tetrachloride to occur. Since the calcium carbonate reacted with the hydrochloric acid instead of continuing the dechlorination of carbon tetrachloride, it proved that the calcium carbonate inhibited the reaction between the reagent and chlorocarbon from occurring. The spectrum of 24 hours, shown in Figure 18, indicates no reaction is occurring between the reagent and the carbon tetrachloride. As Figure 19 changes to 57 hours, the spectrum shows signs of a reaction taking place between the two compounds. The peak area of the chloroform being 25% and the other

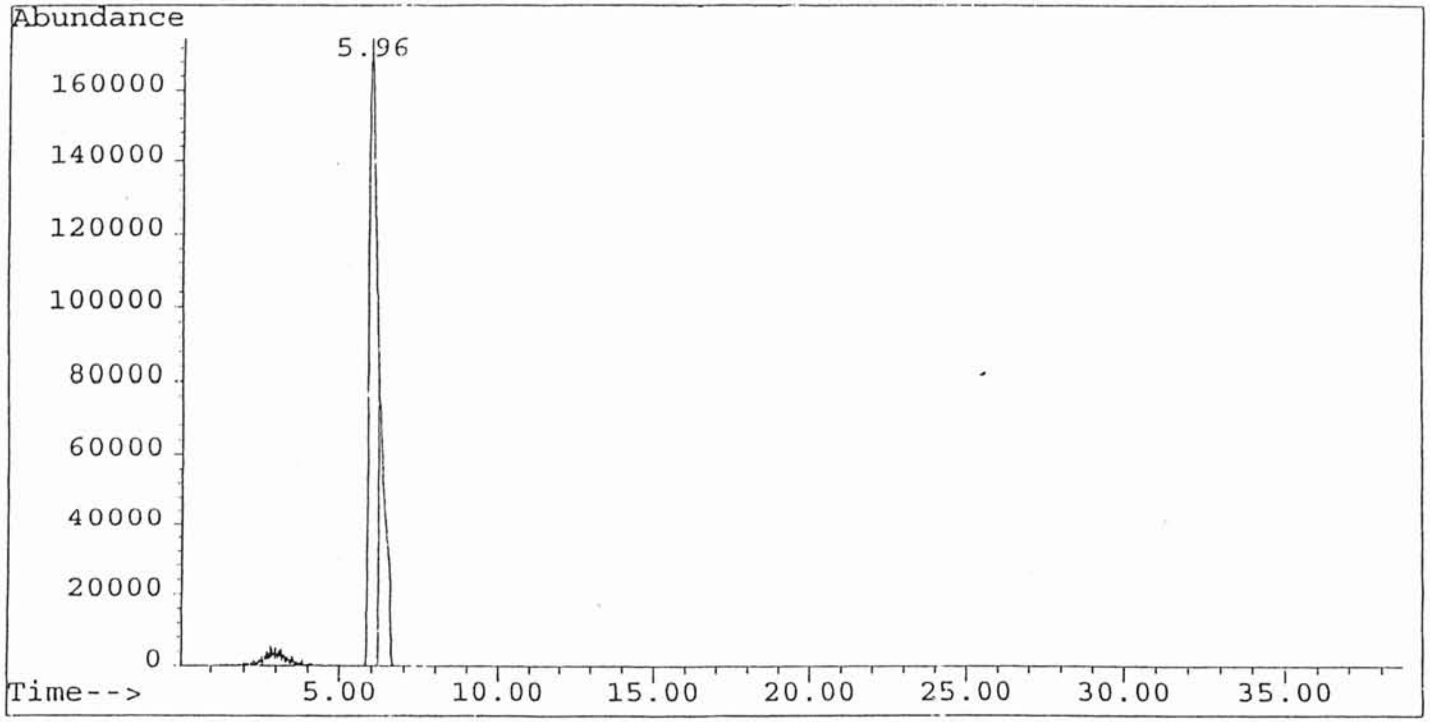

Figure 18. Reaction of calcium carbonate with CCl_4, 28 hours

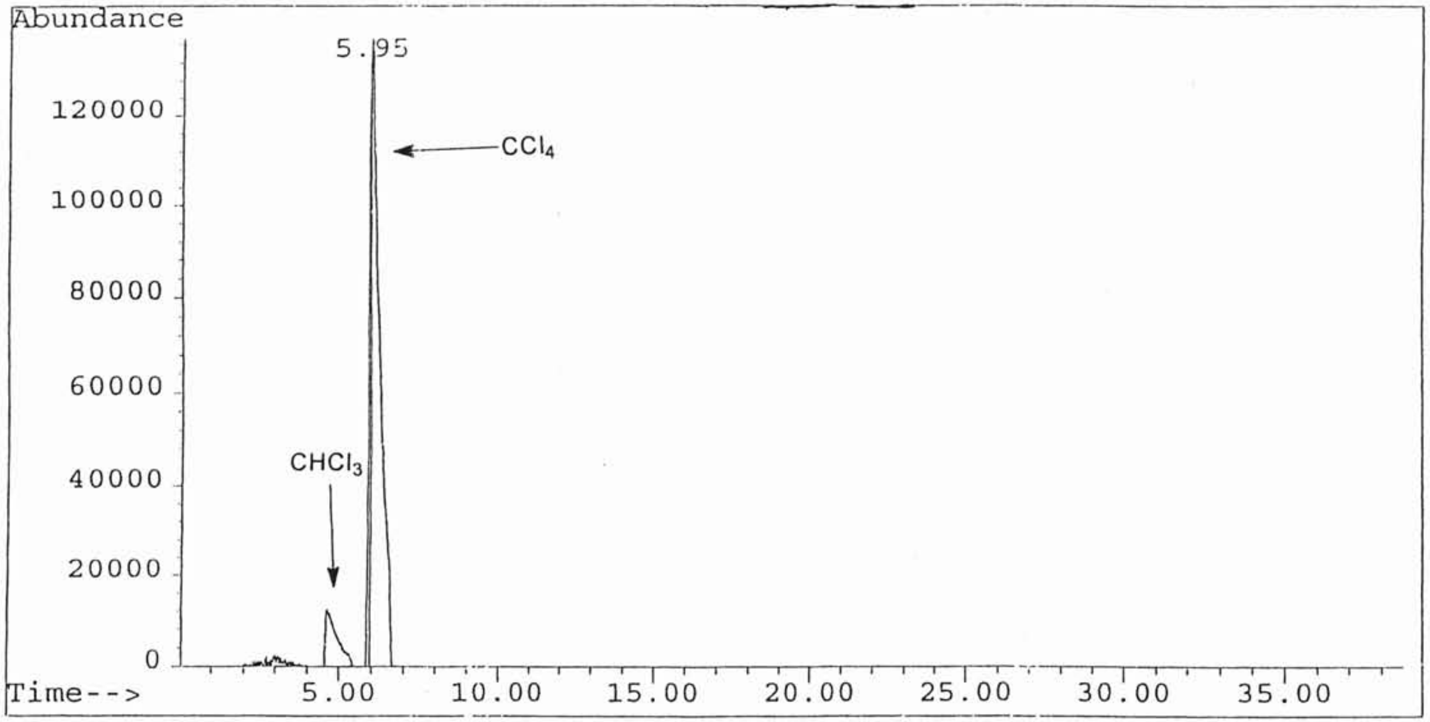

Figure 19. Reaction of calcium carbonate with CCl_4, 57 hours

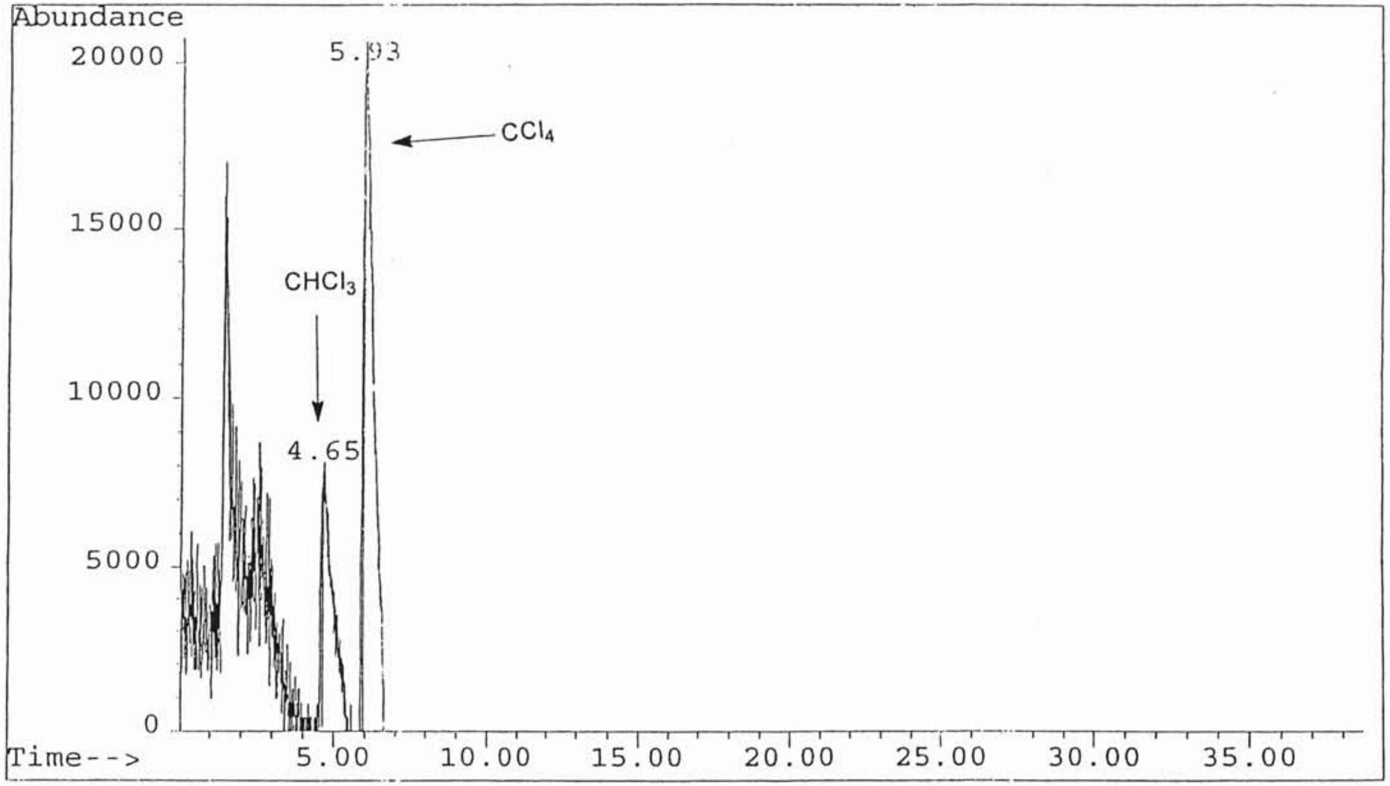

Figure 20. Reaction of calcium carbonate with CCl_4, 74 hours

percentage is carbon tetrachloride. The spectra shown in Figure 20 portrays, even after 72 hours, that the reaction between CCl_4 and hydrogen tungsten bronze was able to occur and at that, the reaction was in small amounts. Only 35% of the peak area was made of chloroform, the other 65% being carbon tetrachloride.

Dechlorination of Chloroform

Since carbon tetrachloride dechlorinated to chloroform, it was only logical to see if chloroform dechlorinated into methylene chloride. The experiment kept the same temperature and GCMS parameters as before. Sixteen microliters of chloroform was injected into 0.25 grams hydrogen tungsten bronze. Figures 21 shows the results after three days in the vial. Chloroform is still the only compound shown in large amounts. Continually, methylene chloride was only produced in very small quantities(less than 5% peak area). On occasion, it was not produced at all. In conclusion, chloroform does not completely dechlorinate into methylene chloride and no other gas-phase products are seen.

Dechlorination of methylene chloride

Even though, in the previous experiment, chloroform did not dechlorinated into methylene chloride by a large amount, experiments were done with the reagent and 16 microliters of methylene chloride to determine whether or not methylene chloride would even decompose either. As seen in Figure 22, three days after the sample was placed in the heating chamber, no gas phase products were observed and the methylene chloride was lower in intensity to its initial methylene chloride peak in Figure 8.

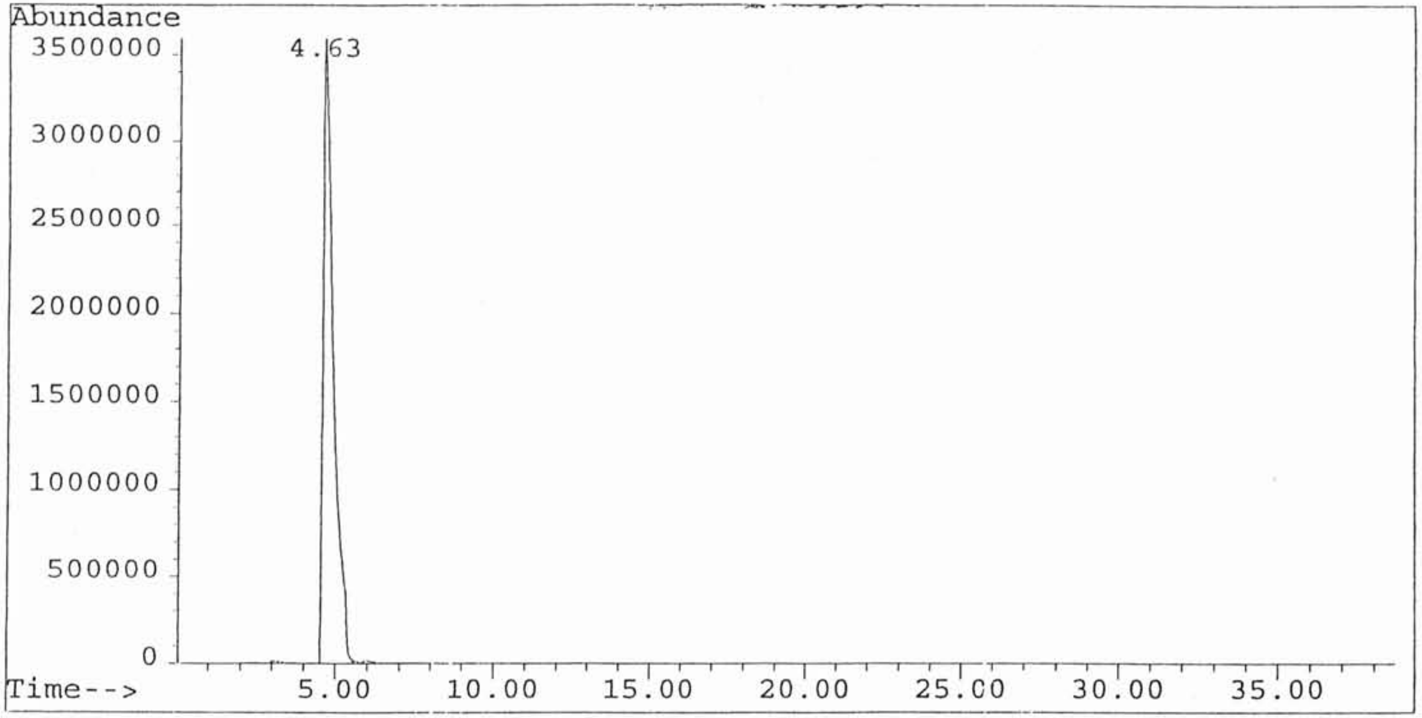

Figure 21. Chloroform, 72 hours

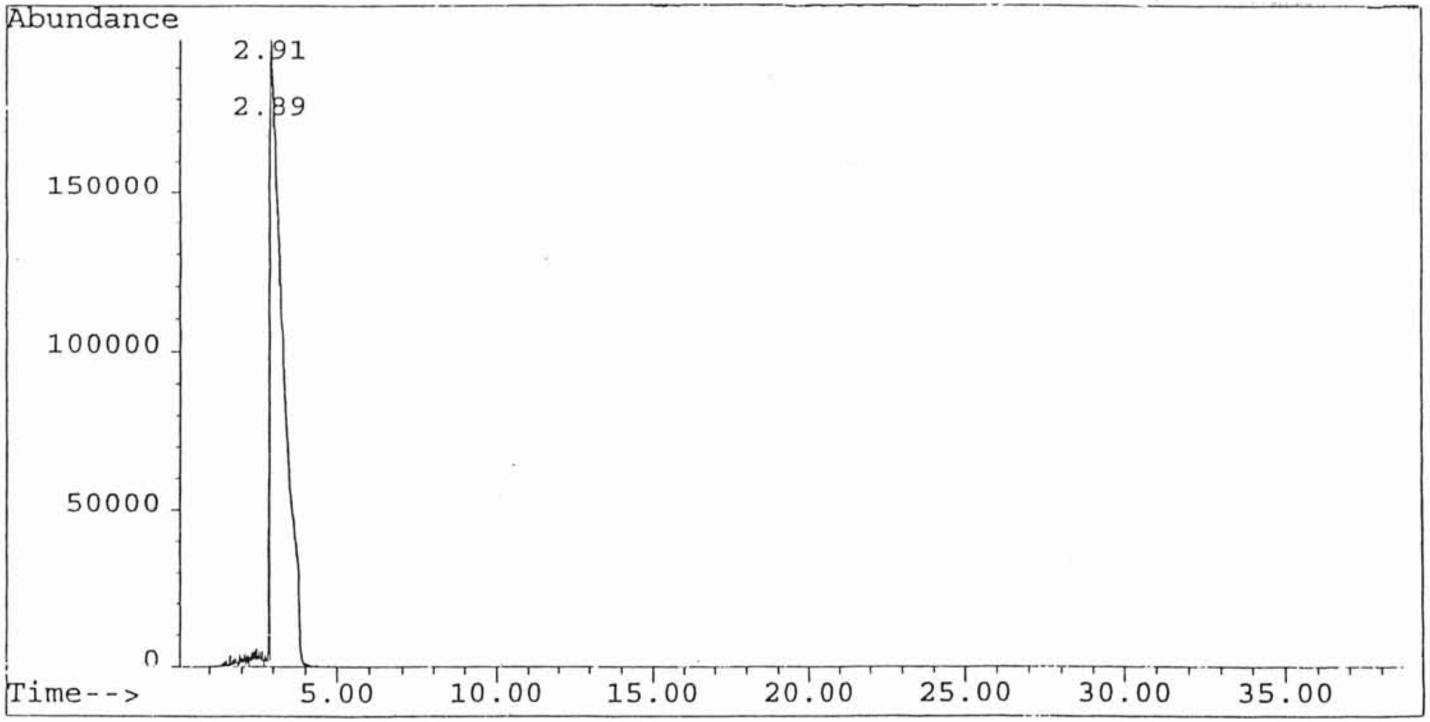

Figure 22. Methylene chloride, 63 hours

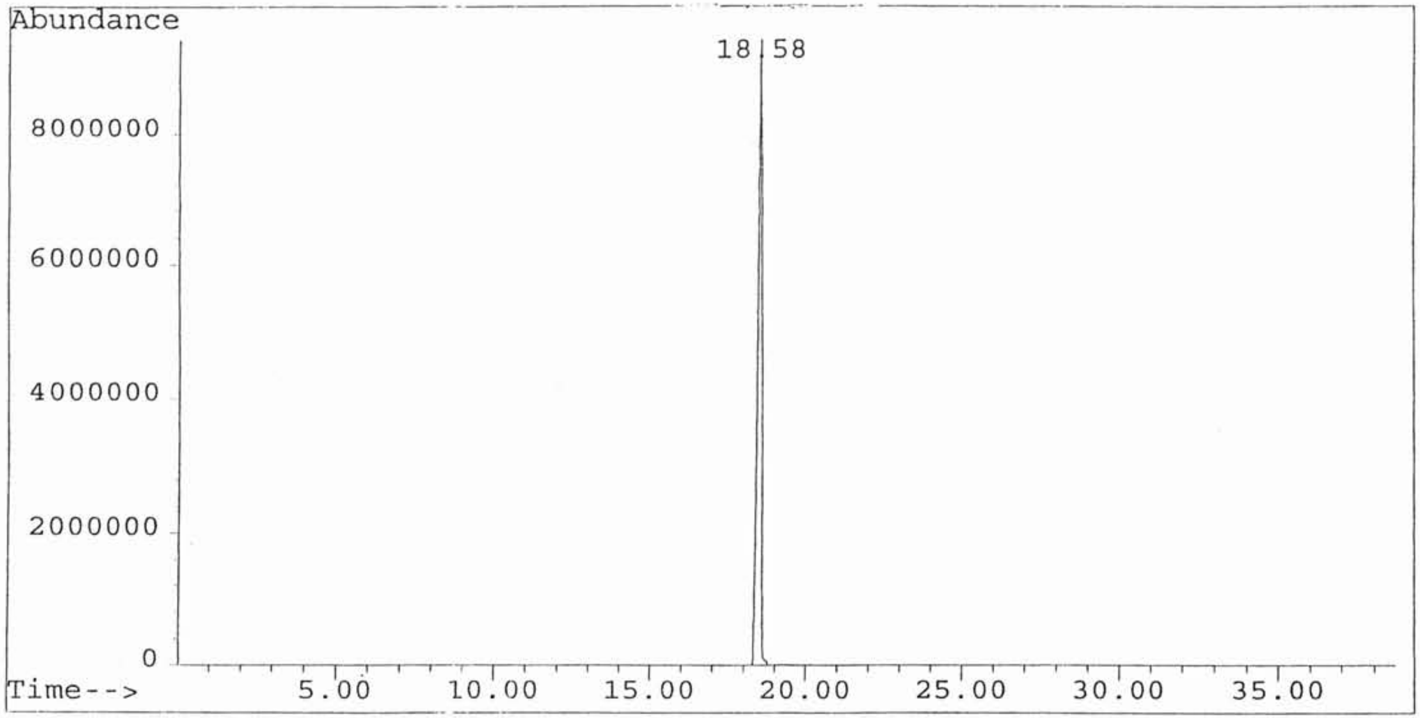

Figure 23. 1,2,3-trichloropropane, 7 days at 138° Celsius

Dechlorination of 1,2,3-Trichloropropane

The observation has been made that a compound with a single carbon surrounded by four chlorines will dechlorinate. However, this does not lead to a prediction of whether inner, outer or both types of chlorines in the 1,2,3-trichloropropane will be attacked when reacted with the reagent. An experiment was then performed to determine if the reagent is selective to inner or outer chlorines. Assuming the same parameters are met once more, 16 microliters of 1,2,3-trichloropropane was injected into a container including 0.25 grams of hydrogen tungsten bronze. The experiment produced no gas-phase products after three days at 128° Celsius. The only evidence that a reaction might be occurring is located directly after the 1,2,3-trichloropropane. The mass spectrum of the peak indicates a chlorinated cyclohexene. Since the reaction was inconclusive after 72 hours, the temperature was increased ten degrees to 138° Celsius. After three days, there still was no change to the status of no gas-phased products. The chlorinated cyclohexene peak is still there, but it has not increased by a significant degree. Figure 23 shows the sample after another seven days in the chamber. In conclusion, no gas-phased products were seen in the reaction of 1,2,3-trichloropropane and hydrogen tungsten bronze.

Dechlorination of Tetrachloroethylene

Tetrachloroethylene, also abbreviated as TCE, is a chlorinated compound of interest, not only because of its production in the carbon tetrachloride experiment, but also as a carcinogenic compound that is located in various chemical burial sites, including Oklahoma State University's list of buried chemicals.[32] Due to TCE's stability, difficulty arises when trying to dechlorinate or decompose the TCE into another compound. In order to determine whether or not hydrogen tungsten bronze can convert this compound into easier compounds for disposal, an experiment was prepared in order to determine TCE's durability. Sixteen microliters of tetrachloroethylene were place in a vial with 0.25 grams of hydrogen tungsten bronze. The vial was then heated for three days with spectra taken every 24 hours. Figure 24 presents the compound after 72 hours in the oven. The carbon tetrachloride and chloroform are present in small amounts, but the concentration of the two products remains constant. On further dissection of the spectrum, even smaller amounts of methylene chloride are present. The methylene chloride production, in addition to the carbon tetrachloride and chloroform, is insignificant in size. Since the TCE is rather unresponsive to the hydrogen tungsten bronze, the sample was left alone in the chamber for one week. Tetrachloroethylene is a lot harder to destroy than previous thought. The TCE is satisfied to mainly stay in its form and not break down into other products.

Dechlorination of Chlorobenzene

Chlorobenzene was chosen as the next compound for the experimental dechlorination with respect to the hydrogen tungsten bronze reagent. Chlorobenzene is another chemical located in various burial sites. Major environmental releases of chlorobenzene occurred due to its use as a solvent for pesticides. Chlorobenzene could possibly be located in the chemical burial site at OSU due to the large deposits of pesticides into the ground. Sixteen microliters of chlorobenzene were placed into a vial containing 0.25 grams of hydrogen tungsten bronze. The sample was then heated for three days while

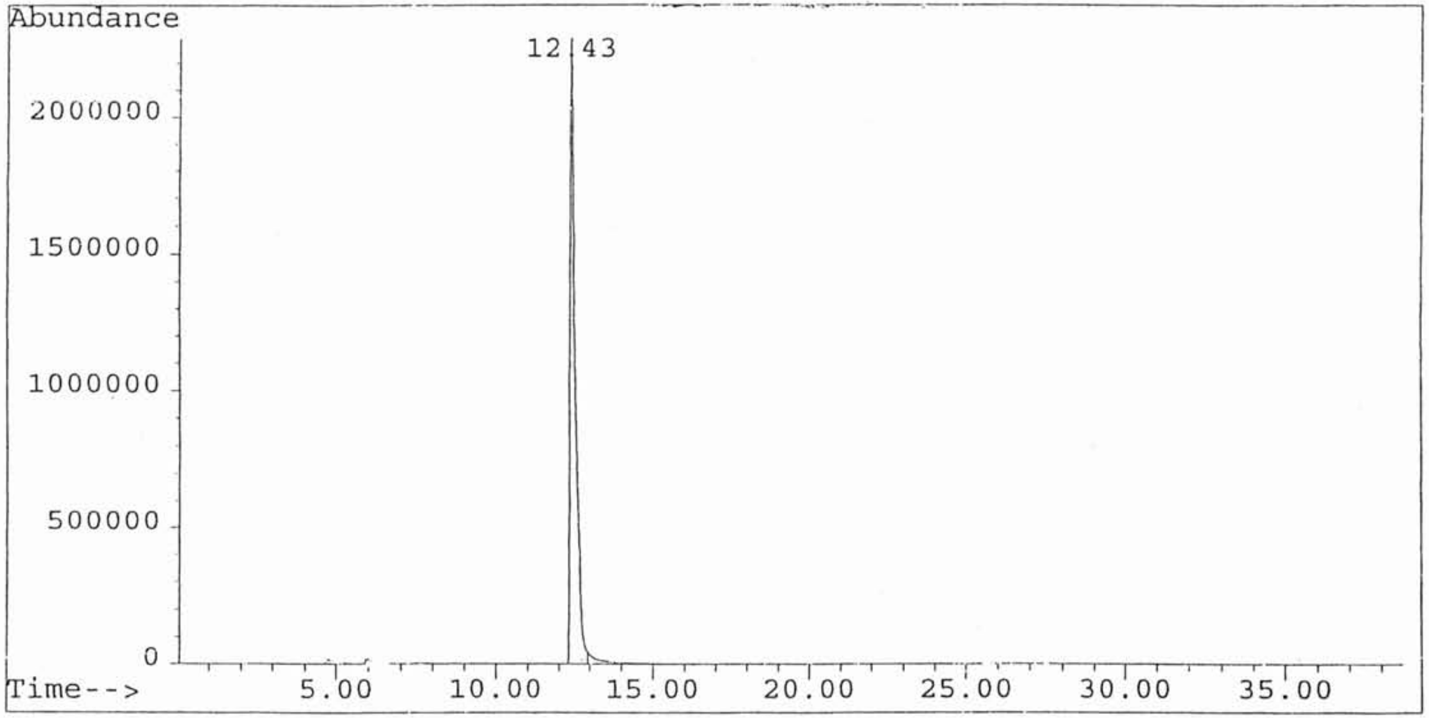

Figure 24. Tetrachloroethylene, 72 hours

every 24 hours gaseous samples were taken to be injected into the GCMS for monitoring purposes. After 72 hours, shown in Figure 25, hydrogen tungsten bronze is ineffective at dechlorinating chlorobenzene.

Debromination of 1,2-dibromoethane

Although not a chlorinated compound, 1,2-dibromoethane is another compound that is found in the chemical burial site southeast of campus. Furthermore, bromines are can be more selective than chlorines when bonding to carbons. Ten microliters were added to 0.26 grams of hydrogen tungsten bronze. The reaction was kept at the same conditions as the carbon tetrachloride experiments. Figure 26 shows no gas-phase products formed from the reaction. The two peaks that are shown in the spectrum other than the 12.34 minute peak, were present in a blank injection of 1,2 dibromoethane.

Future Research

Since it has been determined that carbon tetrachloride is the only chlorocarbon in this study that significantly dechlorinated, further study will be done to confirm phosgene, chloroform and methylene chloride as major products. Focus on the reagent specifics could be done.

Also a study could be done to see if the reagent only responds to completely chlorinated compounds or if the presence of hydrogen chloride is detrimental to its ability to reduce the chlorinated compound down to a hydrocarbon. Furthermore, studies could be done where HCl gas is injected into the vial with the chlorocarbon to see if it initiates reactions to occur faster or in larger quantities.

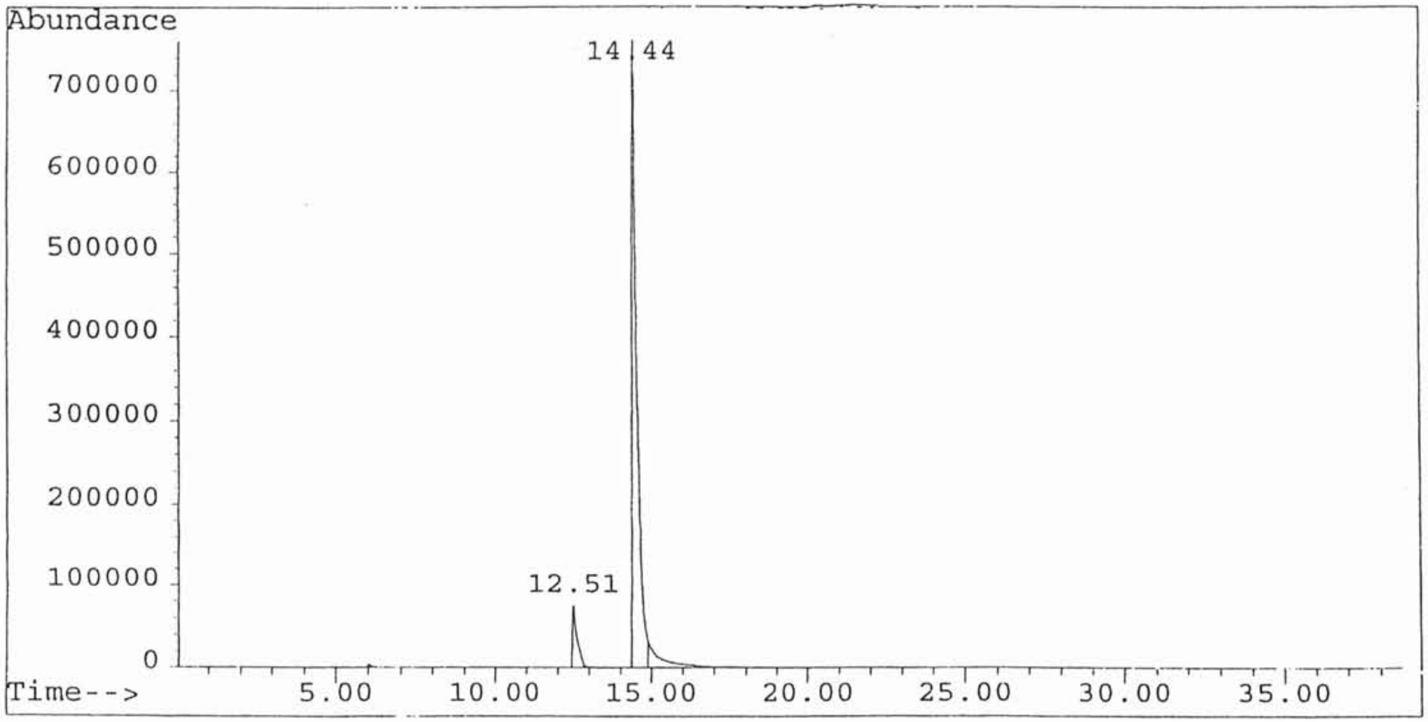

Figure 25. Chlorobenzene, 73 hours

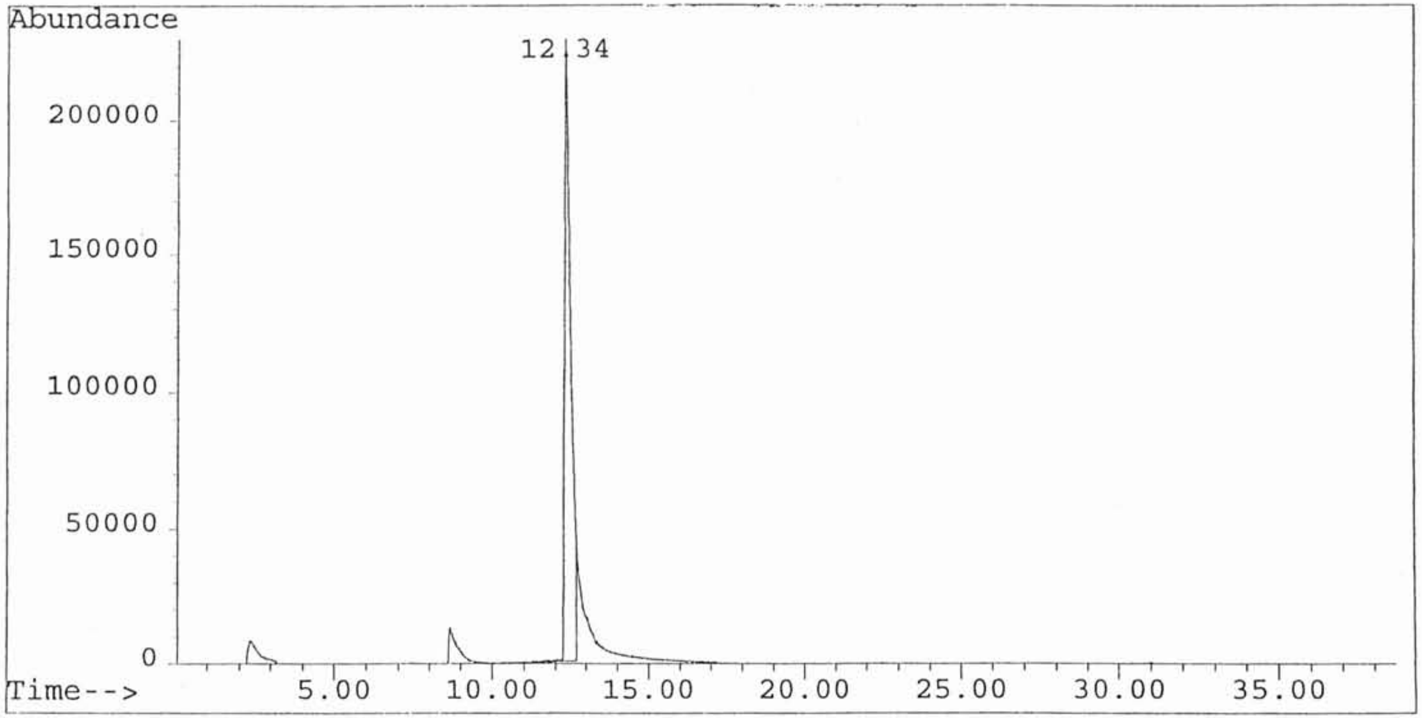

Figure 26. 1,2-dibromoethane, 72 hours

Summary

Hydrogen tungsten bronze has been shown to reduce carbon tetrachloride into chloroform, methylene chloride, and phosgene. After the experiment of carbon tetrachloride, chloroform and methylene chloride experiments were performed in order to determine whether or not the carbon tetrachloride was a stepwise reaction from chloroform to methylene chloride or an equilibrium reaction. Since chloroform was insignificantly converted into methylene chloride and methylene chloride was unreactive towards hydrogen tungsten bronze, determination of an equilibrium developing between chloroform and methylene chloride is evident. Furthermore, the experiment involving 1,2,3-trichloropropane was unable to conclude which chlorine in 1,2,3-trichloropropane would be removed first. A possible indication towards the complete encasing of the carbon(s) is indicated by the reaction of chloroform and methylene chloride. These chlorocarbons had hydrogen and then two hydrogen located on their axis respectively. In addition, hydrochloric acid production is necessary to maintain the reaction of carbon tetrachloride and the reagent to sustain a dechlorination process. This concept was given by the reaction of these two reactants with calcium carbonate. Finally, it was shown that careful preparation must be taken in order to confirm total makeup of the reagent as hydrogen tungsten bronze. As shown, zinc effectively allows the production of tetrachloroethylene to be produced. The tetrachloroethylene is shown to be very stable in its refusal to convert to less hazardous products. Minute amounts converted itself while a majority of TCE stayed fixed. Chlorobenzene and 1,2-dibromoethane proved to be unreactive towards hydrogen tungsten bronze. In conclusion, the reagent, hydrogen tungsten bronze, needs further characterization into its abilities to dechlorinate chemicals. The reagent indicates that it is not a very strong reagent for consuming chlorines or possibly the reagent contains its hydrogen too strongly. Depending on the level of hydrogen in the reagent, whether it be $H_{0.5}$ or $H_{0.33}$, might help to determine which concentration is more successful at dechlorinating all chlorinated compounds.

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VITA 2

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