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Gas-Solid Alkali Destruction of Volatile Chlorocarbons

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ABSTRACT

Many chlorocarbons are environmental dangers and health hazards. The simplest perchlorinated hydrocarbon, carbon tetrachloride, is near the top of the list of hazardous compounds. Carbon tetrachloride was used as a cleaning fluid, solvent, and fire-extinguishing agent. The nuclear and defense complexes also employed great quantities of carbon tetrachloride and other chlorocarbons as cleaning and degreasing agents. Many sites nationwide have underground chlorocarbon contamination plumes. Bulk chlorocarbon inventories at many locations await treatment and disposal. Often the problem is compounded by the chlorocarbon being radioactively contaminated. Waste inventory and groundwater contamination problems exist for many other chlorocarbons, especially methylene chloride, chloroform, and tri- and tetrachloroethylene.

In this work solid soda lime (a fused mixture of approximately 95% CaO and 5% NaOH in a coarse, granulated form) at 350°C to 400°C acts as the hydrolyzing, degradation, and off-gas scrubbing medium. Within soda lime CO_2 and HCl from hydrolysis and degradation convert immediately to calcium and sodium chlorides and carbonates, with water vapor as a volatile byproduct.

I. INTRODUCTION

Many poly- and perchlorinated hydrocarbons have been known for years as environmental dangers and human health hazards. The simplest perchlorinated hydrocarbon, carbon tetrachloride, is near the top of the list of hazardous compounds. Carbon tetrachloride was commonly used as a cleaning fluid, solvent, and small-scale fire-extinguishing agent. The nuclear and defense complexes employed great quantities of carbon tetrachloride as a cleaning and degreasing agent. The legacy is such that many sites have underground contamination plumes which threaten local water tables. Another problem throughout the nation is bulk waste-chlorocarbon inventories. Thousands of kilograms of waste chlorocarbons await disposal or treatment. Often the problem is compounded by the waste being contaminated with plutonium and other radioactive species. Similar waste inventory and groundwater contamination problems exist for several other chlorocarbons, especially methylene chloride and tri- and tetrachloroethylene.

In this work soda lime, a highly alkaline solid, is shown to destroy a variety of volatile chlorocarbons. The process is essentially one step, with the addition of water vapor and oxygen as coreactants. The relatively low reaction temperature range, 350°C–400°C, compared to that of traditional incineration processes, suggests some catalytic activity on behalf of the soda lime. Reaction efficiencies are about 10^5, with potential for significant improvement.

The power of soda lime to destroy chlorocarbons is evident from investigations by others. Smith[1] reported the destruction of certain chlorocarbons by a column packed with consecutive zones of Si, lime and/or soda lime, and copper oxide. The Si was heated at 350°C–500°C, and the lime was heated at 250°C–550°C. The apparatus was intended to treat waste gases from semiconductor manufacturing. The purpose of the Si was to react with oxidizing gases, and the lime or soda lime served to destroy the acid gases and halogenated fragments. The copper oxide served to scrub the gas of reductants such as hydrogen and carbon monoxide.

Koper et al.[2] showed that ultrafine particles of CaO reacted with CCl_4 to yield $CaCl_2$ and CO_2. Phosgene was an intermediate product but was avoided if excess CaO was used. Reactions of $CHCl_3$ yielded $CaCl_2$, CO, and H_2O, whereas C_2Cl_4 yielded $CaCl_2$, C, and $CaCO_3$. Kinetic parameters demanded that high-surface-area CaO be used. The observations using soda lime in this work are remarkably similar. Being a coarse, porous material, soda lime has a very high surface area. Phosgene is not a byproduct in my reaction system. In this reference, as well as in my work, the need for an oxidant is shown by the observation of C and CO.

An example of current methodology to destroy waste chlorocarbons is shown by Katami et al.,[3] who investigated the formation of chlorinated compounds by combustion of waste dry-cleaning materials. Phosgene and HCl in flue gas were removed by a wet scrubber using 10% NaOH solution. Reaction systems such as these rely upon combusting the chlorocarbon in an initial stage and treating the off gas in a subsequent step. Temperatures approaching 900°C are needed to ensure complete reaction. The single-stage soda lime system described herein reacts with such compounds at much lower temperatures. Acid gases are never seen.

A key reaction that occurs in the strongly basic environment of soda lime is dehydrohalogenation. Elimination of HF from fluorinated anesthetics to give the corresponding alkenes is described in recent literature (Refs. 4–7). Likewise, in my proposed system C_1 and C_2 compounds with adjacent H and Cl atoms undergo the same reaction to give radicals and unsaturated compounds. I postulate that at the surface of soda lime oxygen serves to react with radicals, and unsaturated compounds are formed to give the oxygenated intermediates necessary for a clean overall process.

II. EXPERIMENTAL

This process used a gas flow loop with a cylindrical reaction chamber. The reaction chamber had a 12" by 3/4" hot zone packed with soda lime. The exposed ends were water cooled. The flow loop had Fourier transform infrared (FTIR) spectroscopy and pressure diagnostics at the exit end of the furnace. Temperature was monitored within the furnace and at the core of the soda lime. The flow loop also had provisions for reagent delivery, along with helium and air supplies. The schematic is shown in Fig. 1.

For each experiment I evacuated the flow loop and entered chlorocarbon vapor into the system until it reached equilibrium. In cases where the vapor pressure was too low for the bellows pump to operate efficiently, I added helium to achieve efficient flow. Circulation was continued for five minutes to mix components. Data sets were as follows: Time, furnace temperature, reactor core temperature, and system pressure.

III. RESULTS AND OBSERVATIONS

Carbon Tetrachloride

Figure 2 shows three spectra of CCl_4 reacting with soda lime. Initially, I used approximately 66 torr of CCl_4 and 45 torr of carrier gas and let the temperature go straight to ~550°C. I used the peak at 805 cm^{-1} to monitor all CCl_4 reactions.

The temperature was taken to ~550°C to attempt a complete reaction. Because this batch of soda lime was used for three previous runs at or above 500°C, it contained no entrained water vapor. The lack of water vapor may have accounted for traces of CCl_4 remaining after 55 minutes. A pressure decrease was detected well before reaching 550°C, so the next experiment used fresh soda lime and more frequent IR sampling.

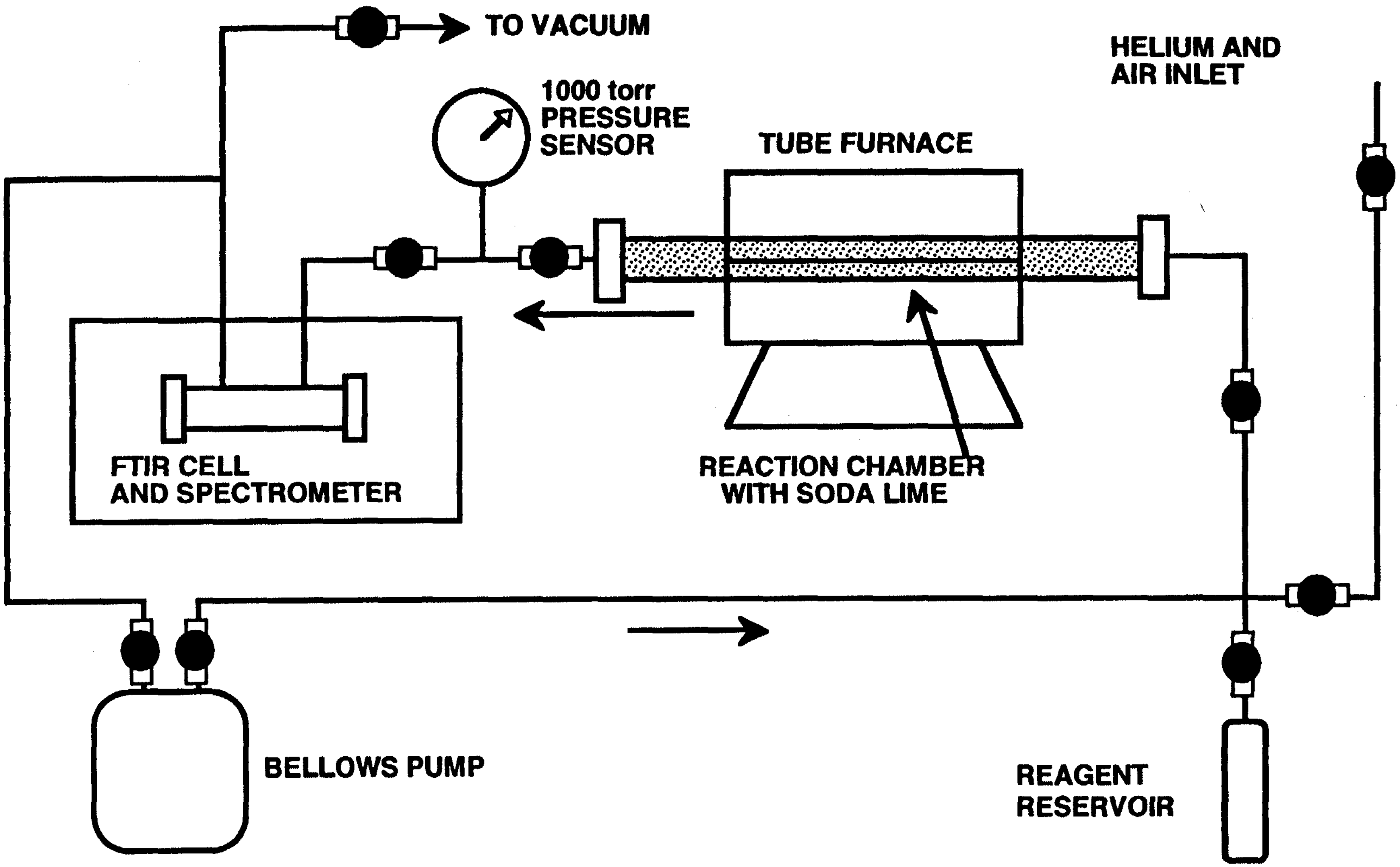

Figure 1. Chlorocarbon destruction flow loop.

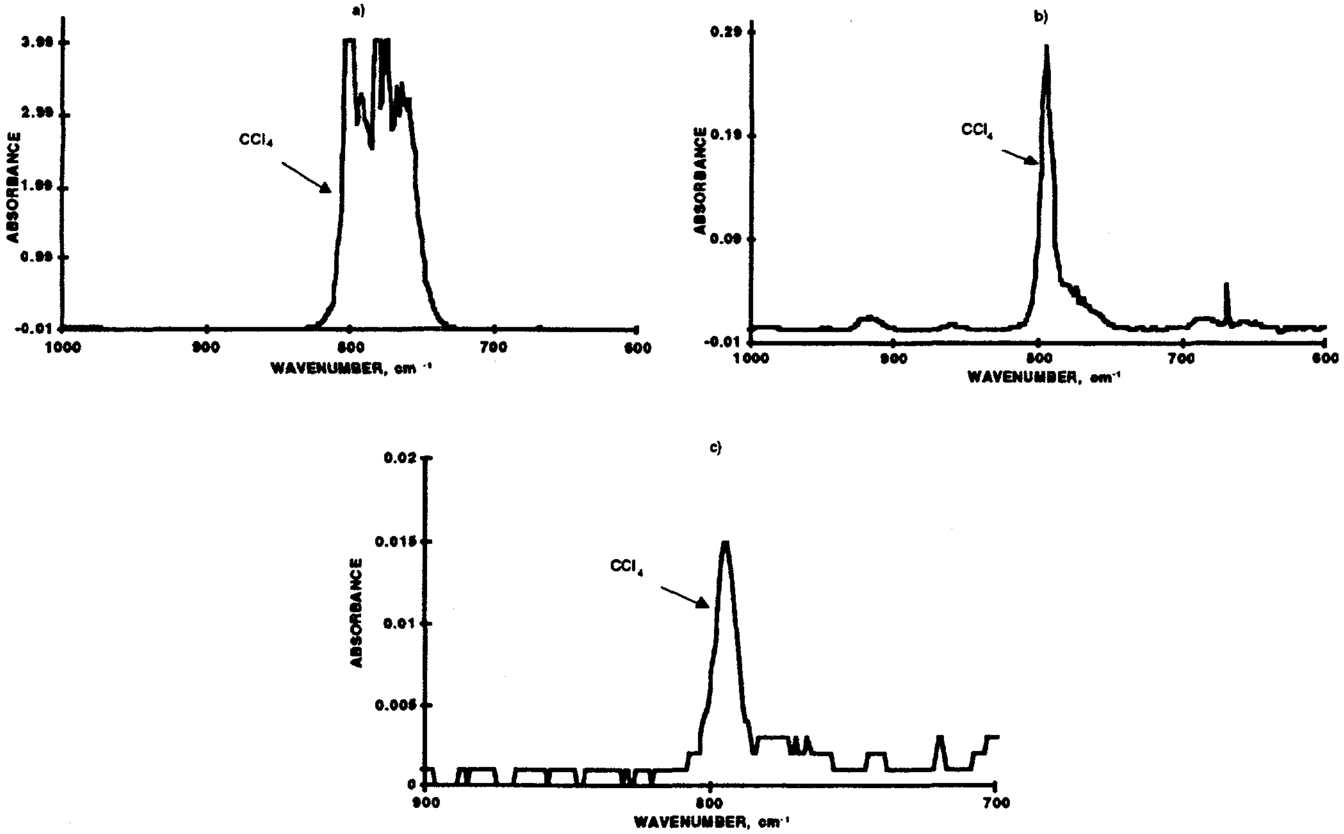

Figure 2. Pressure of 66 torr of CCl_4 with soda lime: (a) 85°C, 5 minutes; (b) 553°C, 25 minutes; and (c) 554°C, 55 minutes.

The next experiment used ~350 torr of helium to improve circulation of the flow loop; the temperature was brought again to 550°C. Figure 3 shows four spectra of CCl_4 reacting with fresh soda lime over approximately one hour.

It is evident from these spectra that soda lime can destroy CCl_4 completely. Because I used a flow loop and the entire loop was charged with vapor, the chlorocarbon at the exit end of the tube within the IR cell experienced constant dilution. Therefore, some residual chlorocarbon was detectable after one hour. Each batch of soda lime demonstrated its highest activity when it was fresh and had maximum associated moisture. This supports the need for water vapor in the reaction gases to enhance the destruction of the chlorocarbon species.

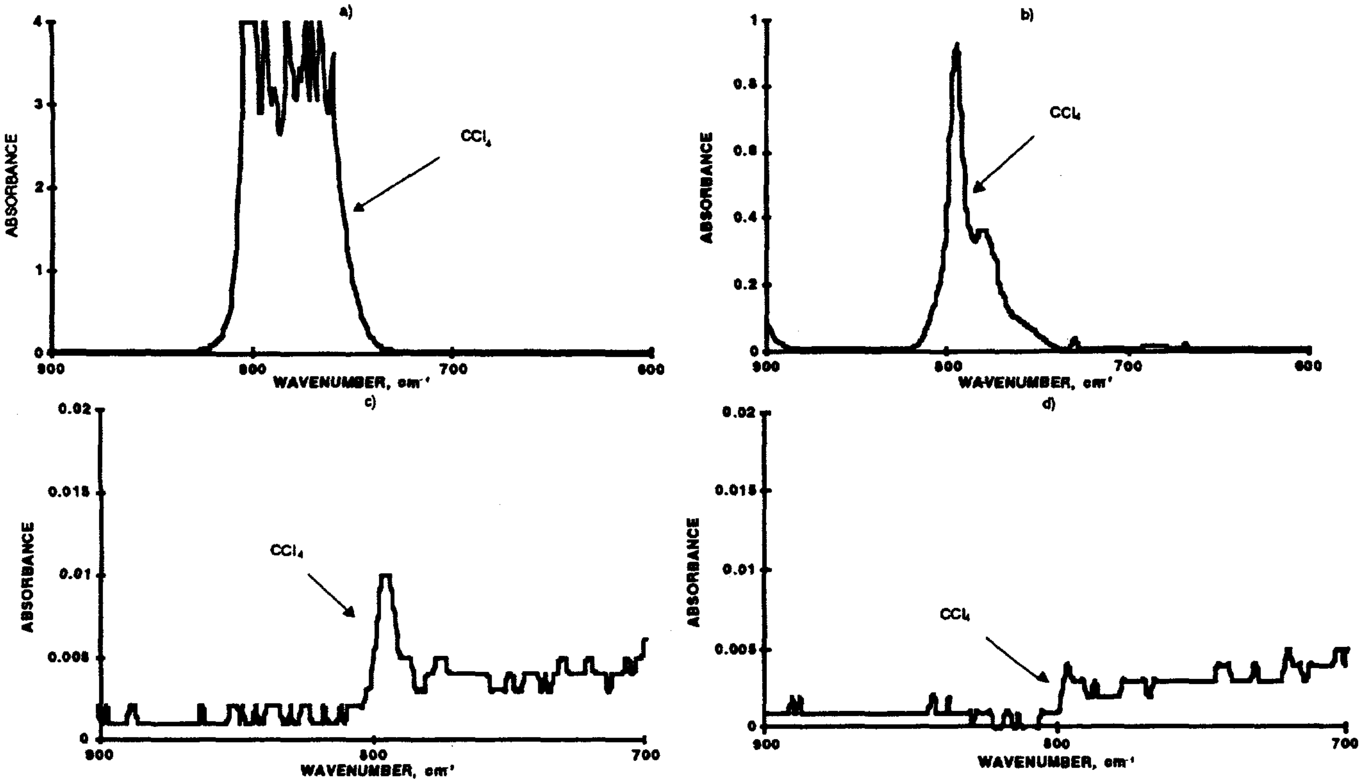

Figure 3. Pressure of 64.6 torr of CCl_4 with fresh soda lime, ~550°C: (a) 0 minutes, (b) 18 minutes, (c) 40 minutes, and (d) 55 minutes.

Figure 4 relates pressure versus temperature for this experiment. The pitch of the curve before 400°C suggests that the reaction initiates well before 400°C.

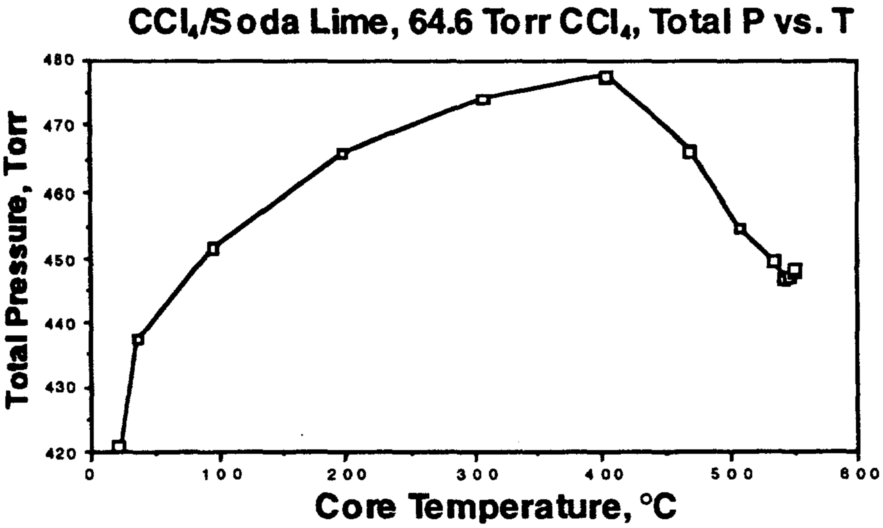

Figure 4. Pressure versus temperature curve for experiment using 64.6 torr of CCl_4.

To understand the reaction below 400°C, I performed a run using a lower furnace temperature gradient and fresh soda lime and set the furnace to 380°C. The next three FTIR spectra, shown in Fig. 5, follow the reaction progress.

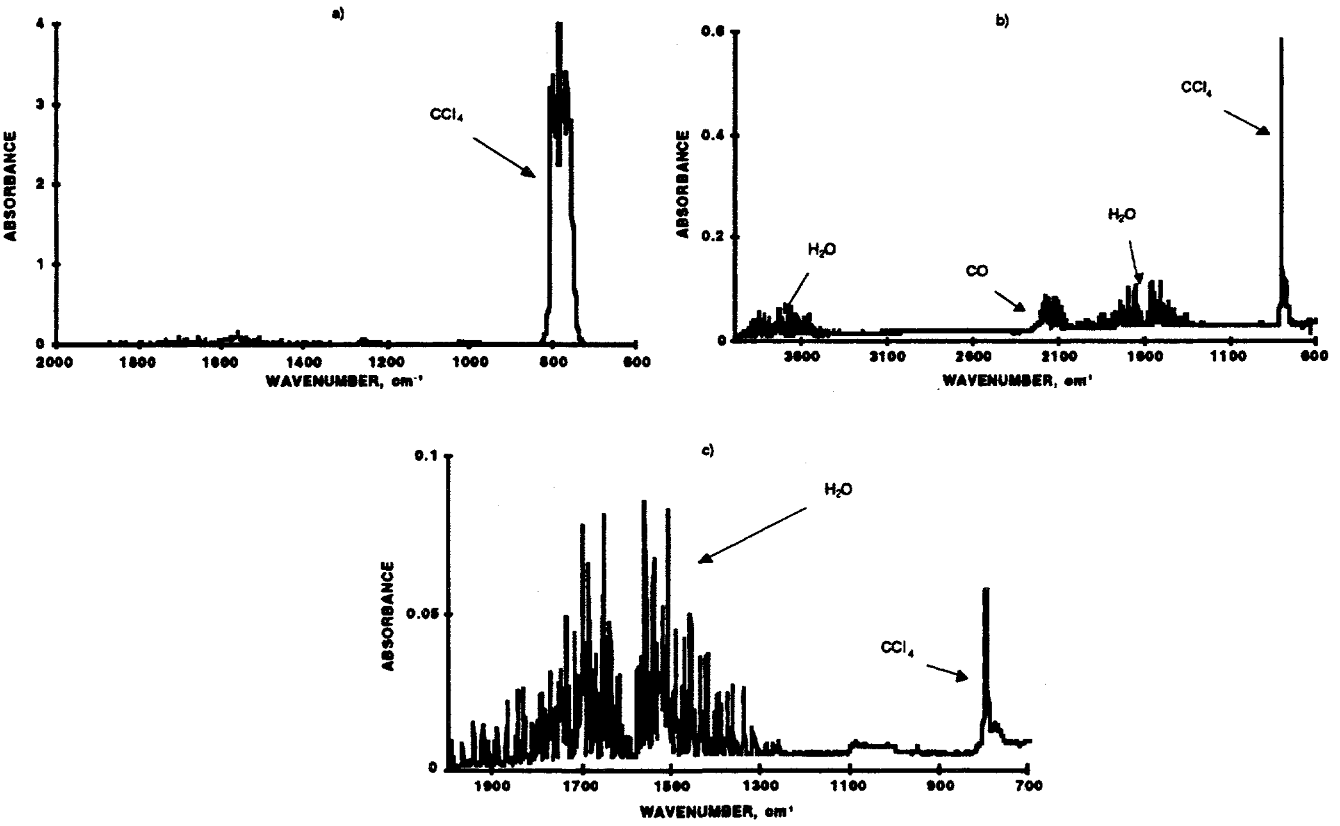

Figure 5. Pressure of 66 torr of CCl_4 with fresh soda lime, temperature to 380°C: (a) 173°C, 10 minutes; (b) 332°C, 20 minutes; and (c) 348°C, 25 minutes.

Water vapor is evident as multiple bands centered at ~1600 and 3600 cm^{-1}. The pressure versus temperature curve in this case, shown in Fig. 6, indicates a reaction below 300°C.

The slope of the curve at 350°C is steeply negative. This is where CCl_4 reacts at a significant rate. Also, adding additional CCl_4 to the gas stream caused rapid disappearance of the water vapor, and the relative reaction rate slowed, reinforcing the need for additional water vapor as a coreactant in future experiments.

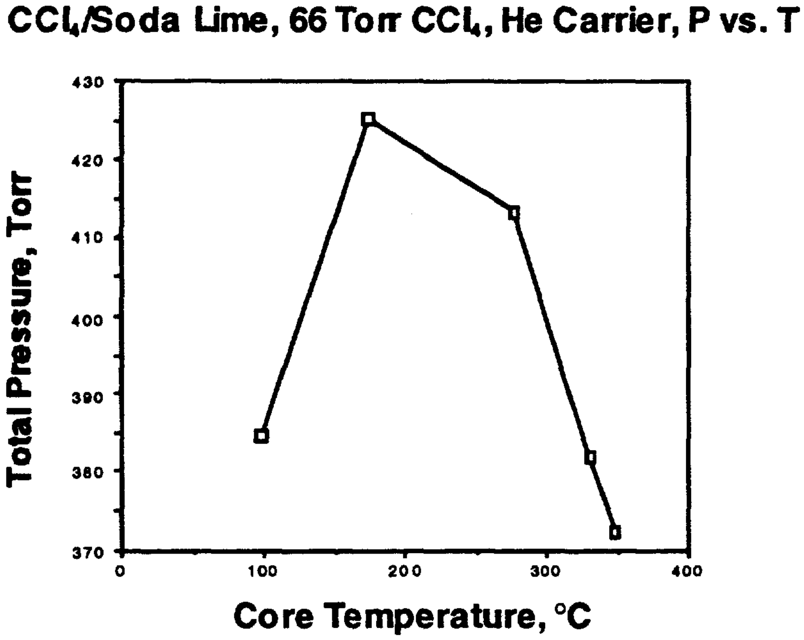

Figure 6. Pressure versus temperature curve for experiment using 66 torr of CCl_4.

Methylene Chloride

Methylene chloride, CH_2Cl_2, was of interest not only as a common solvent and groundwater contaminant; it also contains H and Cl in proximity. An increased reaction rate relative to CCl_4 was expected because of the driving force of dehydrohalogenation. In the first experiment soda lime reacted readily with CH_2Cl_2, breaking it down to a carbon species and HCl that reacted with the soda lime. By adding air to oxidize reducing gases, the reaction proceeded faster than those for CCl_4, as shown in the three spectra of Fig. 7.

Using the same batch of soda lime (which was essentially baked to ~300°C), I added neat CH_2Cl_2 and set the furnace to 420°C. This was an attempt to deduce the reducing gas byproducts for this system, as shown in the three spectra of Fig. 8.

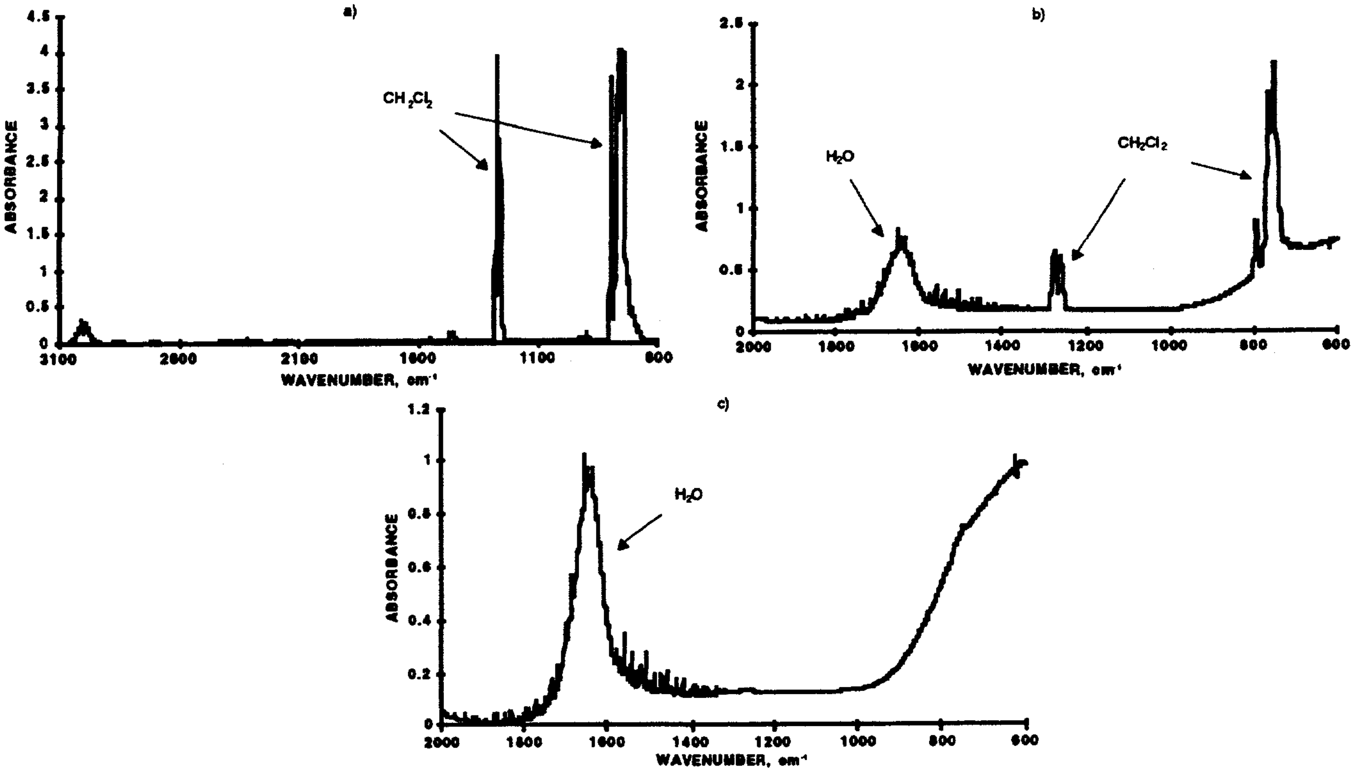

Figure 7. Pressure of 100 torr of methylene chloride with no added air, temperature to 245°C: (a) 100 torr, 25°C; (b) 197°C, 20 minutes; and (c) 245°C, 25 minutes.

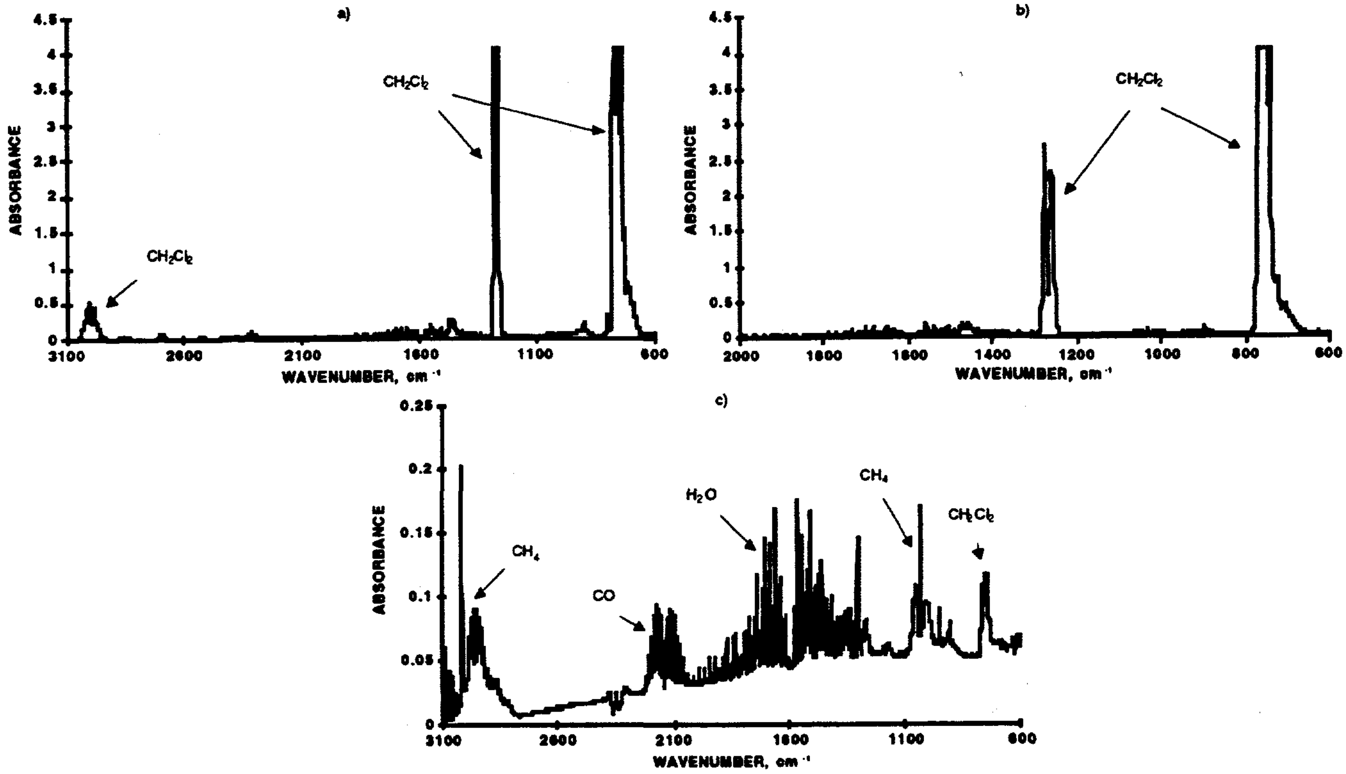

Figure 8. Pressure of 182 torr of methylene chloride, no added air, temperature to 370°C: (a) 182 torr, 128°C, 5 minutes; (b) 210 torr, 265°C, 20 minutes; and (c) 345 torr, 370°C, 25 minutes.

The formation of CO and CH_4 because of the lack of reagent oxygen is apparent; however, they are produced in relatively small amounts. During the entire experiment the total pressure rose from 182 to 392 torr. Subtracting the pressure rise caused only by temperature, the final pressure indicates the formation of a near equimolar amount of gases. The absorbance values of CH_4 and CO do not account for such an increase: I speculate that it is caused by hydrogen. The reaction of CH_2Cl_2 with soda lime can be written to account for the formation of hydrogen:

$$2\,NaHCa_3O_4 + 2\,CH_2Cl_2 \rightarrow 2\,NaCl + CO + CaCl_2 + CaCO_3 + 4\,CaO + 3\,H_2.$$

The presence of methane and water vapor in the final spectrum suggests that side reactions occur. The three spectra in Fig. 9 show the effect of added air towards an initial 70 torr aliquot of methylene chloride.

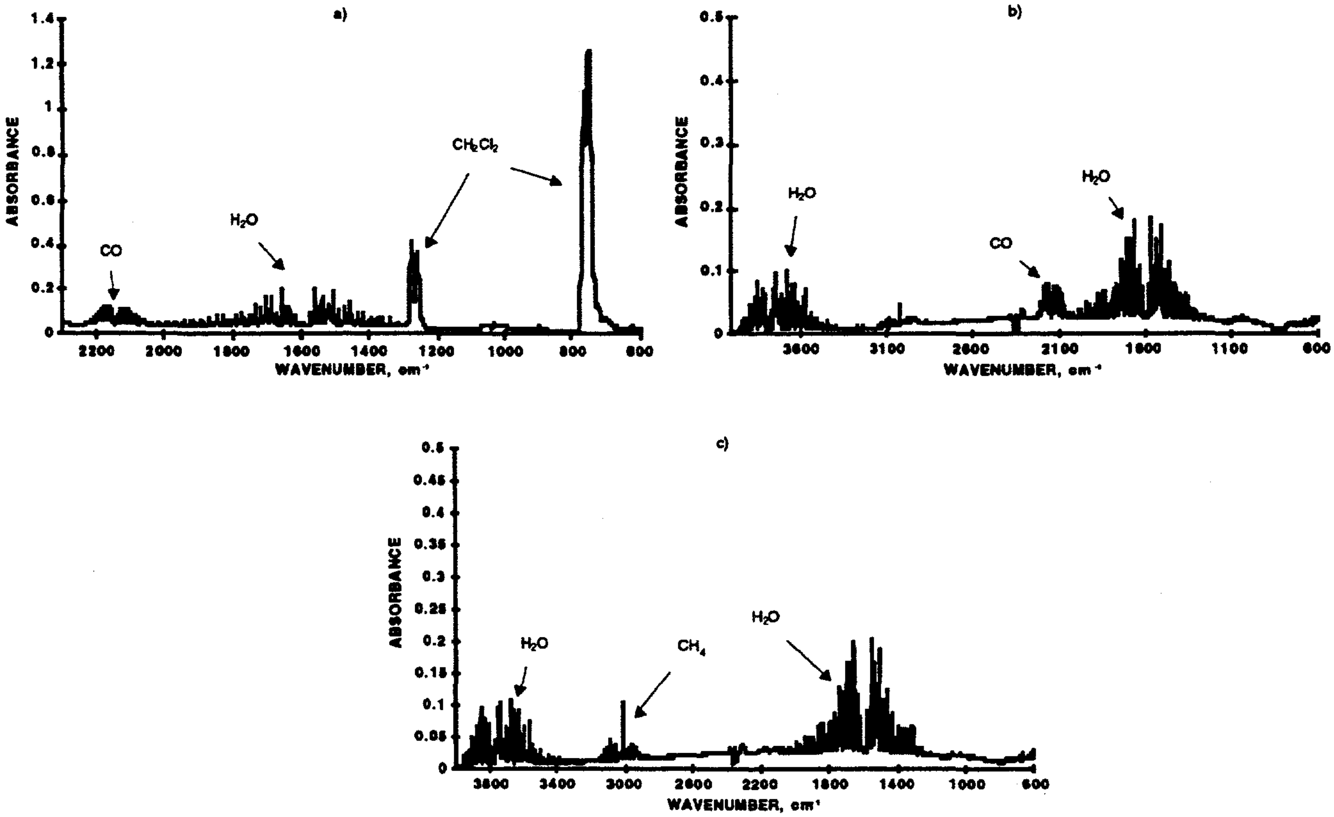

Figure 9. Pressure of 70 torr of methylene chloride with added air, temperature to 396°C: (a) 326°C, 20 minutes; (b) 380°C, 25 minutes; and (c) 396°C, 35 minutes.

The addition of oxygen prevents formation and accumulation of reducing and potentially flammable gases. In this case the overall pressure decreased from 447 to 415 torr in the temperature range of 41°C to 390°C. Note that CO is virtually eliminated.

Chloroform

With chloroform the reaction favors the formation of CO almost exclusively. The three IR spectra in Fig. 10 show a final CO absorbance well over 1. When I added air the formation of CO was suppressed to 20% of the previous value, as shown in the three spectra in Fig. 11. Obviously, a higher oxygen percentage would totally suppress CO formation. Carbon dioxide is almost never seen because of the formation of calcium carbonate.

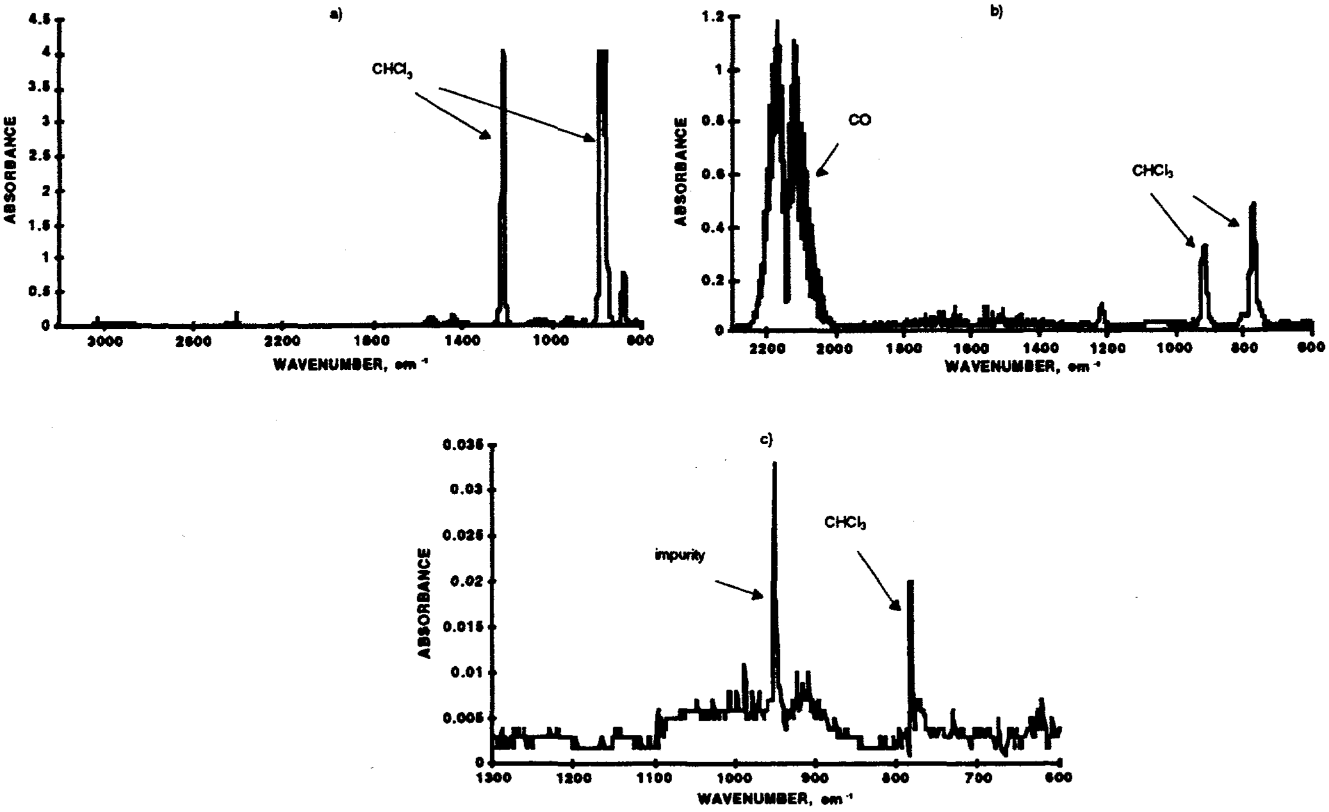

Figure 10. Pressure of 107 torr of chloroform with no added air, temperature to 354°C: (a) 0 minutes, (b) 30 minutes, and (c) 40 minutes.

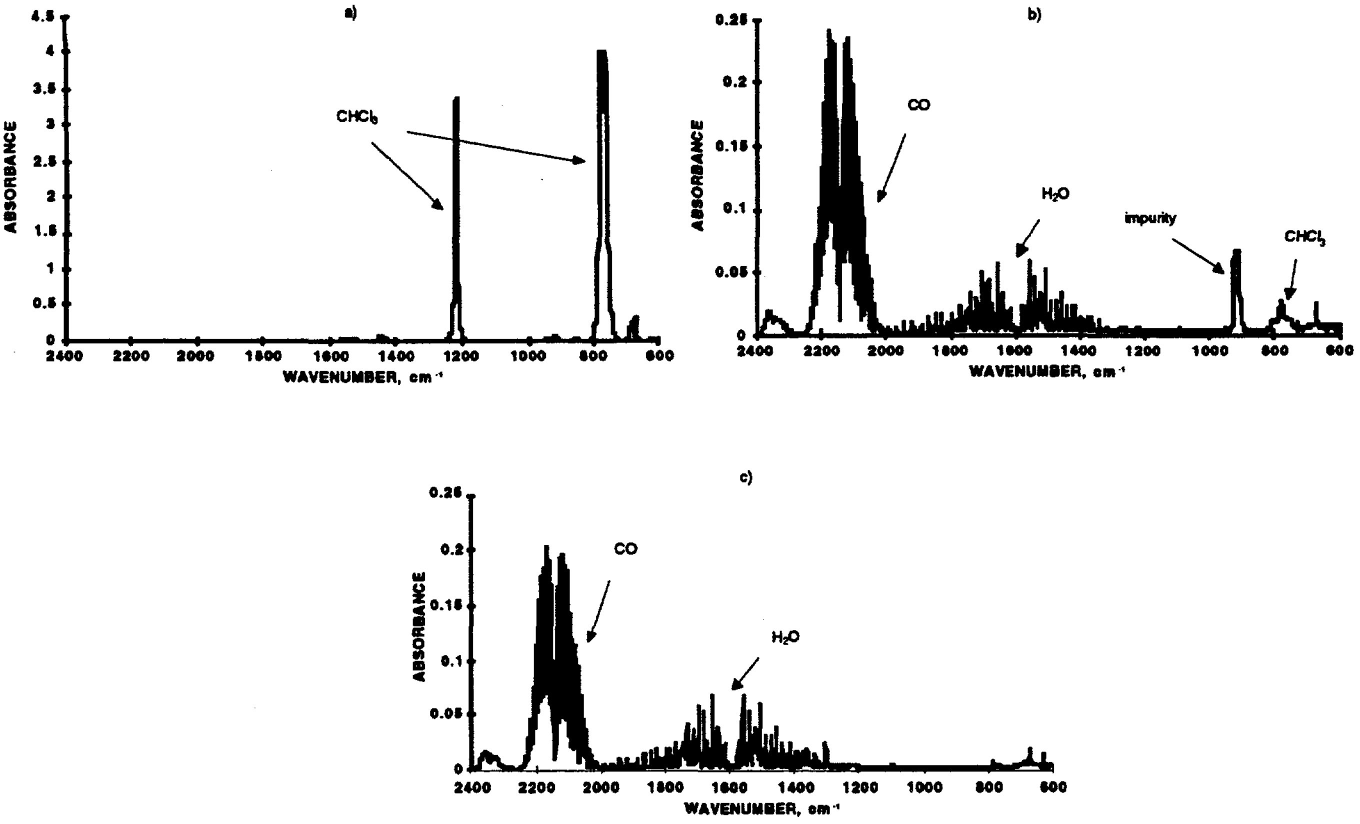

Figure 11. Pressure of 50 torr of chloroform with added air, temperature to 393°C: (a) 0 minutes, (b) 25 minutes, and (c) 35 minutes.

Trichloroethylene and Tetrachloroethylene

Results for trichloroethylene and tetrachloroethylene were similar to the above examples. Both reacted completely at 400°C and needed oxygen and water vapor to effect complete reaction without forming CO or carbon.

IV. DISCUSSION

Using a basic oxide mixture such as soda lime to destroy chlorocarbons relates to the ability of compounds like CCl_4 to chlorinate oxides. The action of CCl_4 on oxides is thermodynamically favored because of the formation of CO_2. The initial step of oxide chlorination by CCl_4 is represented by the dissociation of CCl_4 into chlorine atoms and dichlorocarbene. Dichlorocarbene scavenges oxygen and forms carbonyl chloride readily. However, carbonyl chloride is itself a good chlorinating agent and is rarely seen in continuous loop systems in more than trace quantities. For most gas-solid reactions of CCl_4, the optimum temperature is more than 600°C. Potentially, any perchlorocarbon can react with most metal oxides to give metal chlorides and carbon oxides.

Background Chemistry

Whereas CCl_4 requires relatively high temperatures for efficient reaction with most metal oxides, the first carbon-chlorine bond can react under significantly milder conditions. One way to achieve this is to react CCl_4 with a highly basic oxide or hydroxide. Using the hydroxide ion as an example, advanced organic chemistry texts describe hydrolysis of aliphatic chlorides by OH^-:

$$R\text{–}Cl + OH^- \rightarrow R\text{–}OH + Cl^-.$$

Upon attack of the hydroxide ion on the carbon atom adjacent to chlorine, a carbon-oxygen bond forms simultaneously as the chloride ion leaves. The facility of this reaction depends on the degree of polarity of the carbon-chlorine bond. The greater the polarity, the easier and faster the reaction will proceed. Conversely, this phenomenon determines the acidic character of the carbon center. The more electron-deficient (acidic) the carbon atom, the more reactive it is towards hydroxide. An example is the difference in reactivity of RCH_2Cl versus $RC(O)Cl$. The former requires a strong base such as NaOH to form the alcohol, while the latter needs only a weak base such as H_2O to form the corresponding carboxylic acid.

Carbon tetrachloride is also susceptible to hydrolysis, even by water at elevated temperature:

$$CCl_4 + H_2O \rightarrow \text{"}CCl_3OH\text{"} + HCl.$$

After each attack by water, the carbonaceous products are highly unstable and lose HCl instantaneously, ultimately leaving carbon dioxide and hydrogen chloride. The overall reaction is as follows:

$$CCl_4 + 2H_2O \rightarrow CO_2 + 4HCl.$$

In the gas phase at 25°C, the free energy of reaction is –61.6 kcal/mole of CCl_4. It follows that if we incorporate a chemical sink for HCl and CO_2 into this reaction, we have a basis for the complete and irreversible destruction of carbon tetrachloride. In this work solid soda lime (a strong base) replaces water in the hydrolysis reaction. Soda lime is a mixture of approximately 80%–95% calcium oxide and 5%–20% sodium hydroxide in a coarse, granulated form. Within this highly alkaline environment, CO_2 and HCl do not exist. They convert immediately to calcium and sodium chlorides and carbonates. Therefore, to use soda lime as a reaction medium and gas scrubber provides a route to digest carbon tetrachloride to produce a solid, nonhazardous byproduct.

Expanding the scope of the CCl_4 reaction to other volatile chlorocarbons, the premise for reactivity towards soda lime is like that for CCl_4, save for a property I will call "oxidative deficiency". Returning to the CCl_4 reaction with soda lime, the overall mass balance equation completely consumes CCl_4 with no off gas that is either oxidizing or reducing. If we substitute a compound such as CH_2Cl_2 for CCl_4, the mass balance equation contains either excess hydrogen or partially oxidized carbon (best represented as carbon monoxide). We solve this chemical dilemma by adding oxygen to the reactants to convert any H_2 and CO to H_2O and CO_2 in situ. If a chlorocarbon contains hydrogen or carbon-carbon bonds of any kind, it is "oxidatively deficient" and requires oxygen to react with soda lime to produce halides, carbonates, and water exclusively. This is done by adding ordinary air or oxygen with the chlorocarbon.

V. SUMMARY

This process to convert chlorocarbons has distinct advantages over competing technologies. Adsorption onto activated carbon may efficiently separate chlorocarbons from water, but there is still the task of desorption and treatment. Excess water vapor in the soda lime system does not affect its capacity to destroy chlorocarbons, therefore the unseparated vapors may be put through the system without degradation of the solid reagent.

Operating temperatures within the soda lime are at or below 400°C; thus this system is in the range of thermal catalytic oxidation processes, yet does not have drawbacks such as catalyst poisoning. Nor is a secondary scrubber system required for products such as HCl.

Photolytic and plasma-based technologies are efficient towards destruction of the original chlorocarbon species, but the reactions are nonspecific and often produce other toxic products. A secondary scrubber is necessary to handle the off gases.

Benefits of using soda lime to destroy various chlorocarbons are summarized below:

1. The end product is a mixture of benign, nonhazardous salts (Ca and Na chlorides and carbonates). By itself this benefit has a tremendous impact on waste minimization.

2. The reagent soda lime is inexpensive and available in bulk quantities. It retains its structural integrity despite large amounts of water vapor.

3. This method unitizes a reactor and an off-gas scrubber. Chlorocarbons and acid gas byproducts simultaneously react within the soda lime chamber. The reactor may be easily sized and configured to accommodate a wide range of throughput levels.

4. Reaction thresholds are below 400°C. Unlike standard incineration processes in which temperatures exceed 600°C, followed by gas scrubbing, this process uses relatively low temperatures. In trial experiments reactions of certain chlorocarbons were evident at temperatures as low as 250°C, increasing to a substantial rate by 350°C. An explanation is the possible catalytic activity of soda lime.

5. Potential reaction efficiencies are 10^6. Using a flow loop, relative chlorocarbon concentrations were measured in millitorr of pressure. Initial pressures were tens of torr. Fine-tuning parameters plus water vapor and oxygen addition can achieve "six nines" reaction efficiency.

6. The only additives are oxygen and water vapor. Oxygen converts reducing gases to carbon dioxide and water vapor within the reactor. Water vapor assists reactions.

7. This process can apply to chlorocarbons from other sources. Filtration and thermal desorption systems can separate chlorocarbon vapors from solids, particulates, and nonvolatile liquids. This benefits situations where chlorocarbons exist with solid waste, oils, radioactive particulates, and nonvolatile matrices.

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