Pyrolytic destruction of polychlorinated biphenyls in a reductive atmosphere

Daniel H. Evans[a], Massoud Pirbazari[b,*], Sidney W. Benson[a],
Theodore T. Tsotsis[c] and Joseph S. Devinny[b]

[a]*Loker Hydrocarbon Research Institute, Department of Chemistry*, [b]*Environmental Engineering Program, Department of Civil Engineering, and* [c]*Department of Chemical Engineering, University of Southern California, Los Angeles, CA 90089 (USA)*

Abstract

This paper discusses the development of an innovative technology for the pyrolytic destruction of halogenated hydrocarbons in a reductive environment. The technology developed demonstrated the potential for resource recovery, as reaction products could be commercially used. The process was specifically directed at the dehalogenation of polychlorinated biphenyls (PCBs), a class of chlorinated compounds most difficult to thermally decompose due to the high strength of their carbon–chlorine bonds. PCBs have extensive industrial applications, and are regarded as pollutants of serious environmental concern due to their persistence and insidious health effects. Pyrolysis experiments were conducted under controlled laboratory conditions in batch reactor systems with Aroclor 1254 (a mixture of PCB congeners) to evaluate the process feasibility, and to determine the destruction and removal efficiencies (DREs). The pyrolysis was conducted under a variety of operating conditions to investigate the effect on DREs due to changes in process variables such as reactor residence time, reaction temperature, and reactant (methane) concentration. Under optimal conditions — a residence time of 7 minutes, reaction temperature of 1000°C, and stoichiometric excess methane — a DRE of over 99.999% was achieved. The reaction products were dehalogenated hydrocarbons, hydrogen chloride, and soot. The dehalogenated compounds formed were identified as aliphatic and aromatic hydrocarbons by gas chromatography/mass spectrometry (GC/MS). The study also included a scientific analysis of free-radical reactions and associated mechanisms involved in the decomposition of the halogenated hydrocarbons. Achievement of the highest DREs suggests that the process needs further investigation as a method for dehalogenation of chlorinated hydrocarbons with the potential of product recovery for commercial use.

Introduction

Halogenated hydrocarbons have created monumental hazardous waste problems on account of their high levels of toxicity, carcinogenicity, mutagen-

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*Author to whom correspondence should be addressed.

icity, bioaccumulative tendency, resistance to biodegradation, and persistence in the environment. Classic examples include polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs), trichloroethylene, perchloroethylene, DDT, Freons, and a broad spectrum of other halogenated compounds of industrial significance. Safe disposal and management of wastes containing these hazardous chemicals has become an important environmental issue, as they can potentially cause several environmental problems such as ground and surface water contamination, soil pollution, air pollution, and accumulation in food chain, to name a few.

Among various halogenated hydrocarbons, PCBs are considered as major environmental pollutants. Although their manufacture was discontinued in the U.S. by congressional legislation in 1976 [1], they had been widely employed up to that time in several industrial applications ranging from dielectric materials for capacitors and transformers to chemicals used in plasticizers, waterproof aids, printing inks, carbonless paper, nonflammable wooden coatings, dust-control agents, special adhesives and pesticides. Despite the imposed ban, PCBs are still used in over 2.8 million capacitors and 150,000 transformers [2]. About 100,000 leaks of PCBs are annually reported, which lead to contamination of subsurface and surface water resources, as well as pollution of terrestrial and atmospheric environments. Therefore, development of appropriate technologies for the ultimate destruction of such halogenated hydrocarbons has indeed become a matter of concern.

Very few technological options are available for the ultimate destruction or transformation of halogenated or chlorinated compounds, among which incineration is important. A major problem associated with incineration processes for chlorinated compounds is that they are difficult to control, and therefore generate undesirable products of incomplete combustion (PICs) such as PCDDs and PCDFs [3,4]. Additionally, even well-controlled incineration processes produce sulfur dioxide when sulfur compounds are present in the waste, and nitrogen oxides due to oxidation of atmospheric nitrogen. In the present scenario, the newly developed technology can effectively destroy chlorinated hydrocarbons by pyrolyzing them under a reductive environment of methane (or hydrogen) and an alkane solvent, without forming oxygenated species such as dioxins, furans, or oxides of sulfur and nitrogen. This technology can be potentially employed as a dehalogenation process, and the dehalogenated hydrocarbons produced can subsequently be collected and separated for commercial use.

The present research was intended to study the feasibility of the process for the pyrolytic dechlorination of PCBs under a reductive environment, so that they could be transformed into non-halogenated hydrocarbons, hydrogen chloride, and soot. The rationale behind the choice of PCBs as model chlorinated hydrocarbons was based on several reasons. Firstly, the carbon–chlorine bonds in PCBs are stronger and more difficult to cleave than those in aliphatic com-

pounds, and are assumed to be comparable in strength to the carbon–chlorine bond in chlorobenzene. Secondly, PCBs have been responsible for some of the most severe environmental problems in recent years. Lastly, PCBs manifest a high level of flame suppressing characteristics due to their high degree of chlorination, and they cannot be easily destroyed by incineration without forming dibenzodioxins and dibenzofurans. The objectives of the study are the following: (i) investigation of the process feasibility for the destruction of PCBs in batch reactor systems as a prelude to the design of more realistic continuous flow reactor systems, and determination of the destruction and removal efficiencies (DREs); (ii) studying the dependence of DRE as a function of process variables such as reactor residence time, reaction temperature, and reactant (methane) concentration, so that process optimization could be achieved; and (iii) scientific study of the free-radical reactions and associated mechanisms involved in the process.

Theoretical background

Technologies for destruction of chlorinated hydrocarbons
    Alternative technologies for destruction of chlorinated hydrocarbons that have been extensively discussed in literature include incineration and catalytic dehydrochlorination. Incineration processes have often been found effective with DREs of over 99.99% for many chlorinated hydrocarbons. Nevertheless, a few problems have been reported by some researchers regarding the incineration of halogenated hydrocarbons in general, and chlorinated hydrocarbons in particular. It is indeed well known that polychlorinated and polybrominated hydrocarbons manifest fire or flame suppressant characteristics, potentially inhibiting the oxidation of carbon monoxide to carbon dioxide, which justify their application as fire retardants [5,6]. This property is especially pronounced in the case of PCBs owing to their high chlorine content. Additionally, incineration processes are to be carefully controlled to reduce the generation of several undesirable products of incomplete combustion (PICs). As incineration processes are carried out under oxidizing conditions, the potential for the formation of oxygenated species such as PCDDs and PCDFs is high [3,4]. The PICs might also include other types of chlorinated hydrocarbons such as organic acids, depending on the chlorine content of the incinerated wastes. A group of researchers [3,4] reported that approximately 0.004% of PCBs in the feed was converted to PCDDs, while about 0.001% of them was transformed into PCDFs. The transformation reactions, the multiple reaction pathways, and the mechanisms associated with the formations of these products are very complex, involving a number of factors such as generation of oxygenated products and changes in the chlorine numbers. Other strong evidences for the generation of PCDDs and PCDFs include identification of those compounds in soot residues produced by accidental transformer fires [7–12]. Apart from the

formation of PCDDs and PCDFs, incineration processes generate oxides of sulfur if the wastes contained sulfur, and nitrogen oxides due to oxidation of atmospheric nitrogen.

In recent years, thermal processes have emerged such as catalytic hydro-dechlorination for the destruction of chlorinated compounds in a reductive environment of hydrogen, without the formation of oxygenated species such as dioxins, furans, or sulfur and nitrogen oxides. Among these, two catalytic hydrogenation technologies are important, one designed by KTI, Inc., known as the Chloroff Process [13], and the other attributed to Manion [14] referred to as catalytic hydrogenolysis. The Chloroff Process essentially represented the hydrodechlorination of PCBs over a catalyst at high pressures of 50–60 bar, and a temperature of 250 to 300°C. The hydrogenolysis of Manion also employed a similar catalyst, although the reactions were carried out at a lower pressure of one atmosphere, but at a higher temperature of 900°C. Both the processes were effective and achieved DREs of 99.9% for PCBs. Nevertheless, this level of treatment was less than the DRE of 99.9999% recommended by the U.S. Environmental Protection Agency (EPA). The two processes also had a few disadvantages when employed as dechlorination technologies. The Chloroff Process employed high-pressure reactors which were associated with potential accident risks due to explosion. Both the processes required catalysts that were easily susceptible to poisoning and deactivation. In addition to these two processes, another technology involving the application of microwave-induced plasma was developed by Barat and Bozzelli [15]. However, this process yielded DREs of about 98% when tested for chlorobenzene, which could not meet the treatment objectives for halogenated hydrocarbons.

In comparison with the other technologies described above, the pyrolysis of halogenated hydrocarbons such as PCBs in a reductive environment of an alkane solvent such as n-hexane, methane (or hydrogen) discussed in this article, appeared a very promising dehalogenation process. This technology could be effectively used for the transformation of halogenated hydrocarbons to non-halogenated hydrocarbons, hydrogen chloride, and soot. The non-halogenated hydrocarbons and soot can be very easily oxidized by incineration to yield carbon dioxide and water vapor. A detailed description of this new technology is provided in the next section.

Description of the reductive pyrolysis process

The pyrolysis of halogenated hydrocarbons under a reductive environment represents a new decomposition and dehalogenation technology. The pyrolytic reactions are carried out in reactors made of refractory materials, maintained at a temperature of 825–1125°C by an external heat source or by the combustion of methane and oxygen. In the latter situation, the necessary reducing conditions are provided by employing methane in excess of the stoichiometric amount corresponding to the reaction

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$
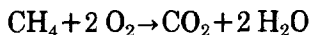
The reducing atmosphere is created by mixing methane or hydrogen with the halogenated compound to be pyrolyzed in an alkane solvent. Methane is preferred to hydrogen for creating the reducing atmosphere for several reasons: methane is generally available as a low-cost fuel in the form of natural gas; and, during pyrolysis, methane effectively transforms methyl chloride to aliphatic and aromatic hydrocarbons, and hydrogen chloride [16].

The process is similar to the pyrolytic cracking of petroleum hydrocarbons, commonly employed for the production of such hydrocarbons as ethylene, propene, butenes, and aromatics [17]. The fundamental difference between these process reactions and petroleum cracking is the initial presence of a chlorinated hydrocarbon, and the formation of hydrogen chloride. The reactions of free radicals (transient reactant species with an unpaired electron) corresponding to the pyrolysis process are quite similar to those associated with catalytic cracking of petroleum hydrocarbons, and are characterized by the same initiating, propagating and terminating steps; however, a few additional reactions of the chlorine radical are also involved in the dehalogenation process. Detailed explanations on these aspects are provided in the next section on reaction mechanisms. The initiation reactions are those that represent the cleavage of the weakest bonds, which are usually the C–C bonds, resulting in the formation of free radicals from organic molecules. The propagation reactions are those associated with hydrogen and methane free radicals, wherein more free radicals are evolved. The termination reactions include the combinations of free radicals to yield non-radical products. The termination reactions are very crucial in controlling the conversion, product formation, and product selectivity of the overall process. The products of petroleum cracking usually range from hydrogen, methane, acetylene, ethylene, ethane, to larger cycloalkanes, aromatics, and coke (solid carbon). Similar products are generated during the pyrolysis of chlorinated hydrocarbons, except that hydrogen chloride is also formed. As no oxygen is present in the reactor, no oxygenated products such as dioxins and furans are formed, and because the dehalogenation is very effective no halogenated hydrocarbons are produced. The hydrogen chloride formed can be stripped out of the gas phase in water or an alkaline solution (such as lime). The hydrocarbons and soot produced can be potentially used as fuel for combustion.

Proposed reaction mechanisms for the reductive pyrolysis of PCBs

The pyrolytic decomposition and dehalogenation of PCBs in a reductive environment can be explained by the reaction mechanisms described here. A significant aspect concerning these reactions at elevated temperatures is the formation of free radicals. The occurrence of such free radical reactions is important from a mechanistic standpoint as they generally manifest faster ki-

netics than non-radical organic reactions. The similarities and differences between the pyrolysis of PCBs and catalytic cracking of petroleum have been explained in the previous section. The decomposition of PCBs at elevated temperatures involves a series of steps including the formation and scavenging of free radicals. The free-radical reactions involve three important steps which are described below, namely: (i) initiation; (ii) propagation; and (iii) termination.

The initiating reaction is the cleavage of the C–Cl bond in the PCB moiety, when unimolecular decomposition of PCB occurs, yielding the chlorine radical and the aromatic dechlorinated biphenyl radical, as illustrated below:

$$(Ph)_2Cl_n \rightarrow {}^{\bullet}(Ph)_2Cl_{n-1} + {}^{\bullet}Cl \tag{1}$$

Here, Ph and $(Ph)_2$ denote the phenyl and biphenyl groups, respectively, while $(Ph)_2Cl_n$ and ${}^{\bullet}(Ph)_2Cl_{n-1}$ represent the PCB molecule and the PCB free radical, respectively. The above reaction occurs because the C–Cl bond is weaker than the C–H bond from bond dissociation energy considerations. For instance, the dissociation energies for the Cl–CH$_3$ and H–CH$_3$ bonds are 83.6 and 105.1 kcal/mol, respectively [16], while the energies corresponding to the Ph–Cl and Ph–H bonds are 95 and 110 kcal/mol, respectively [18]. It is assumed that in terms of bond strength and dissociation energies, the C–Cl bond in the PCB moiety is quite comparable to the Ph–Cl bond.

The next step involves the reaction of the chlorine radical, leading to the abstraction of the methane molecule and the formation of HCl and a methyl radical. The reaction shown below occurs when the PCBs are pyrolyzed in a reductive atmosphere of methane.

$${}^{\bullet}Cl + CH_4 \rightarrow HCl + {}^{\bullet}CH_3 \tag{2}$$

The relative stabilities of various species are dictated by bond energy considerations. The bond dissociation energy for HCl is 103.2 kcal/mol [19], while the energies corresponding to C–Cl and Cl–Cl bonds are 95 and 58 kcal/mol, respectively [18,19]. Hence, it can be said that the H–Cl bond is more stable than other bonds. Nevertheless, in the presence of an alkane solvent (such as n-hexane), the cleavage of the C–Cl bond in the PCB molecule, $(Ph)_2Cl_n$, as shown in reaction (1), is not the fastest free radical forming reaction. The formation of the aromatic and methyl radicals in reactions (1) and (2), respectively will be involved in subsequent reactions that guarantee the complete conversion of PCBs to dehalogenated hydrocarbons and hydrochloric acid.

The next important reaction is the decomposition of the alkane solvent (n-hexane in this case) represented by the formula R_1–H, where the cleavage of the C–C bonds occurs at a significantly fast rate forming the alkyl free radicals ${}^{\bullet}R_2$ and ${}^{\bullet}R_3$, as shown below:

$$R_1\text{–}H \rightarrow {}^{\bullet}R_2 + {}^{\bullet}R_3 \tag{3}$$

It must be noted that the above equation only represents the form of decomposition of the alkane molecule, and that different combinations of alkyl radicals are possible. For example, the decomposition of the n-hexane molecule may result in the formation of different combinations of alkyl radicals, as exemplified by the following reactions:

$$C_6H_{14} \rightarrow {}^{\cdot}C_2H_5 + {}^{\cdot}C_4H_9 \qquad (4)$$

$$C_6H_{14} \rightarrow 2\ {}^{\cdot}C_3H_7 \qquad (5)$$

$$C_6H_{14} \rightarrow {}^{\cdot}CH_3 + {}^{\cdot}C_5H_{11} \qquad (6)$$

The above reactions represent the initiation steps due to the pyrolysis of the alkane solvent employed (n-hexane). In the presence of such alkane solvents which have relatively weaker carbon–carbon bonds than the carbon–halogen bonds of PCBs, the free radicals can be generated more efficiently. The energy of dissociation corresponding to the C–C bond in the alkane is about 86–88 kcal/mol, while that associated with the carbon–halogen bonds in the PCBs is about 95 kcal/mol. The presence of n-hexane is very important from the standpoint of free radical formation on account of two factors: (i) the high concentration of n-hexane in the n-hexane–PCB solution; and (ii) the weaker carbon–carbon bonds in n-hexane, as compared to the carbon–carbon and/or carbon–halogen bonds in PCBs. The Arrhenius frequency factors for the cleavage of the carbon–carbon bonds in alkanes is much greater than those for the carbon–chlorine bonds in the PCBs, and therefore the reaction rates are higher by about two orders of magnitude. It is important to note that when an alkane solvent such as n-hexane is present to initiate the free radical reactions, the use of a reducing agent such as methane may not be necessary. The alkyl free radicals of the form ${}^{\cdot}R_2$ and ${}^{\cdot}R_3$ can undergo unimolecular decomposition to yield a variety of alkenes along with methyl or hydrogen radicals. These reactions are of the form:

$${}^{\cdot}R_2 \text{ or } {}^{\cdot}R_3 \rightarrow \text{Alkenes} + {}^{\cdot}CH_3 \text{ or } {}^{\cdot}H \qquad (7)$$
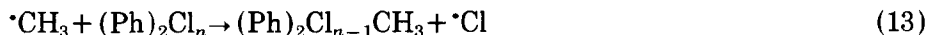
Specifically in the case of n-hexane, the alkyl free radicals formed decompose into successively smaller alkyl radicals, alkenes, and eventually leading to the formation of hydrogen and methyl radicals, as shown under:

$${}^{\cdot}C_5H_{11} \rightarrow C_2H_4 + {}^{\cdot}C_3H_7 \qquad (8)$$

$${}^{\cdot}C_4H_9 \rightarrow C_2H_4 + {}^{\cdot}C_2H_5 \qquad (9)$$

$${}^{\cdot}C_3H_7 \rightarrow C_2H_4 + {}^{\cdot}CH_3 \qquad (10)$$

$${}^{\cdot}C_2H_5 \rightarrow C_2H_4 + {}^{\cdot}H \qquad (11)$$

It can be observed that ethylene is the alkene produced during the successive decomposition of larger alkyl radicals into smaller ones. These reactions rep-

resent the consumption of the alkane solvent, and the subsequent formation of free radicals. The hydrogen and methyl radicals progressively replace the chlorines in the PCB moiety, as illustrated below:

$$^{\bullet}H + (Ph)_2Cl_n \rightarrow (Ph)_2Cl_{n-1}H + {}^{\bullet}Cl \tag{12}$$

$$^{\bullet}CH_3 + (Ph)_2Cl_n \rightarrow (Ph)_2Cl_{n-1}CH_3 + {}^{\bullet}Cl \tag{13}$$

Eventually, all the chlorines will be removed from the PCB molecule. In the case of the hydrogen radical reactions, benzene (denoted by Ph–H) and the phenyl radical may be formed as shown below.

$$n\,^{\bullet}H + (Ph)_2Cl_n \rightarrow Ph{-}Ph + n\,^{\bullet}Cl \tag{14}$$

$$^{\bullet}H + Ph{-}Ph \rightarrow Ph{-}H + {}^{\bullet}Ph \tag{15}$$

The addition of methyl groups due to the reactions of PCBs with the methyl radical will enlarge the size of the biphenyl moiety after dehalogenation. Nevertheless, these large molecules will eventually decompose into several smaller hydrocarbon molecules. The chlorine free radical undergoes reactions with hydrogen and methane molecules from the alkanes formed during the pyrolysis steps (each being represented as R–H), leading to the formation of the hydrogen and methyl free radicals along with hydrogen chloride.

$$^{\bullet}Cl + H_2 \rightarrow Hcl + {}^{\bullet}H \tag{16}$$

$$^{\bullet}Cl + R{-}H \rightarrow HCl + {}^{\bullet}R \tag{17}$$
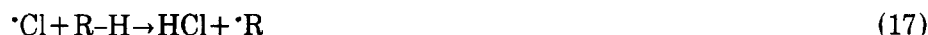
The combination of two methyl radicals to form an ethane molecule leads to destruction of free radicals, and therefore represents a termination step, as shown below:

$$2\,^{\bullet}CH_3 \rightarrow C_2H_6 \tag{18}$$

Subsequently, through a series of reactions initiated by the chloride radical, the ethane formed is converted into ethylene and acetylene [20], through a series of steps as described under:

$$C_2H_6 + {}^{\bullet}Cl \rightarrow HCl + {}^{\bullet}C_2H_5 \tag{19}$$

$$^{\bullet}C_2H_5 (+M) \rightarrow C_2H_4 + {}^{\bullet}H (+M) \tag{20}$$

$$C_2H_4 + {}^{\bullet}Cl \rightarrow HCl + {}^{\bullet}C_2H_3 \tag{21}$$

$$^{\bullet}C_2H_3 (+M) \rightarrow C_2H_2 + {}^{\bullet}H (+M) \tag{22}$$

The formation of acetylene is important from several considerations; it leads to molecular weight growth by polymerization, and causes soot formation [15,20,21]. A detailed discussion on the reactions involved in molecular weight growth is provided by Weissman and Benson [20]. An important aspect of the pyrolysis of PCBs under reductive conditions is the spectrum of stable dehal-

TABLE 1

Tentative compounds identified in the liquid products from the batch reactor

Formula	Name of the compound(s)
C_6H_{12}	Hexene
C_9H_{18}	1-Propylbenzene
$C_{10}H_8$	Naphthalene; azulene
$C_{11}H_{10}$	Methylnaphthalene; 1-ethylidene-1H-indene; 1,4-Dihydro-1,4-methanonaphthalene
$C_{12}H_8$	Acenaphthalene; biphenylene
$C_{12}H_{10}$	Biphenyl; acenaphthene; 2-ethenylnaphthalene
$C_{12}H_{44}O_4$	Diethylphthalate
$C_{13}H_{10}$	1-H-phenalene; 9H-fluorene
$C_{13}H_{28}$	3,8-Dimethyl undecane
$C_{14}H_{10}$	Phenanthrene; diphenylethyne
$C_{15}H_{12}$	Methyl anthracene
$C_{16}H_{10}$	Pyrene; fluoranthene
$C_{15}H_{22}O_4$	Butyl-2-methylpropyl ester-1,2-dibenzenedicarboxylic acid
$C_{18}H_{12}$	Chrysene
$C_{24}H_{38}O_4$	Bis (2-ethylhexyl) phthalate
$C_{28}H_{58}$	Octacosane

ogenated hydrocarbons formed. Stein and Fahr [21] have provided a comprehensive discussion on the stabilities at high temperatures of various hydrocarbons formed. In the present study, the products formed during the pyrolysis of PCBs were identified by analyzing the liquid phase in the reactor (after cooling) using the gas chromatography/mass spectrometry (GC/MS) technique. The reactions products identified are listed in Table 1.

The mechanisms described above for the decomposition and progressive dehalogenation of PCBs account for some of the important reactions occurring in the reductive pyrolysis. It must be noted that multitudes of other reactions may also be involved in the process, eventually forming HCl and a wide variety of dehalogenated hydrocarbons. Nevertheless, the reaction pathways and the mechanisms explained above present a general approach that can possibly account for the products generated. The dehalogenated hydrocarbons formed can be effectively burnt as fuel to provide sufficient energy for maintaining the reactor systems at the required temperatures.

Materials and methods

This research involved the pyrolysis of PCBs under a reductive environment created by an alkane solvent and/or methane in bench-scale batch reactor systems. Elaborate sampling and analytical procedures were employed for the qualitative and quantitative analyses of reaction products. The process DREs were determined by quantifying the unreacted PCBs, and these results were

verified by measuring the amount of hydrogen chloride generated. The halo-genated hydrocarbons formed in the reactions were identified by the GC/MS technique.

Chemicals

The PCBs selected for this study was Aroclor 1254, a mixture of several congeners, consisting of 54% of chlorine (by weight), at a high purity level of 99.8% (Chem Service; West Chester, PA). The solvent used for the PCB mixture was Optima grade n-hexane (Fisher Scientific, Fairlawn, NJ). The purified methane employed in these pyrolysis experiments was supplied by Amweld (Long Beach, CA). The determination of hydrogen chloride involved titration with silver nitrate solution using a potassium chromate indicator. The titrant solution of required concentration was prepared from reagent grade silver nitrate (Spectrum Chemical Mfg. Corp.; Gardena, CA), while the indicator solution was prepared from reagent grade potassium chromate (Mallinckrodt; Paris, KY).

Reactor design

The pyrolysis experiments for PCBs were performed under controlled laboratory conditions in a completely sealed batch reactor system, the schematic of which is shown in Fig. 1. The reactor was constructed of quartz, a material resistant to high temperatures and pressures, with the following dimensions: length of 13 cm, i.d. of 48 mm, wall thickness of 1 mm, and an approximate capacity of 240 ml. One end of the reactor consisted of a 6-mm i.d. tube of length 15 cm, which could be hermetically sealed using a methane/oxygen torch. The reactor was heated by a furnace comprised of a pair of electric clamshell heaters with quartz-wool packing for insulation. Temperature monitoring and control of the furnace was essential to maintain the necessary reaction conditions. The temperature in the center of both the top and bottom sections of the furnace were monitored by means of thermocouple probes and an Omega DP80 Series digital temperature indicator (Omega Engineering; Stamford, CT). The furnace was temperature controlled by an Omega Model CN2002K controller.

The reactor was first evacuated using a glass manifold line, and then methane was introduced either from a gas bulb or a gas cylinder (Fig. 1). The vacuum was produced by a high-vacuum rotary pump, equipped with a liquid nitrogen trap to protect the line from contamination due to backstreaming of oil. High vacuum in the line was ensured by monitoring the line with a thermocouple pressure gauge interfaced with an Edwards Model 507 thermocouple controller (Edwards High Vacuum; Crawley, West Sussex, U.K.). The pressure in the system was measured by a mercury or oil manometer. The reactor was sealed airtight by operating the valve A, and through the injection port approximately 0.3 ml of a 10 mg/l solution of PCB (Aroclor 1254) in n-hexane
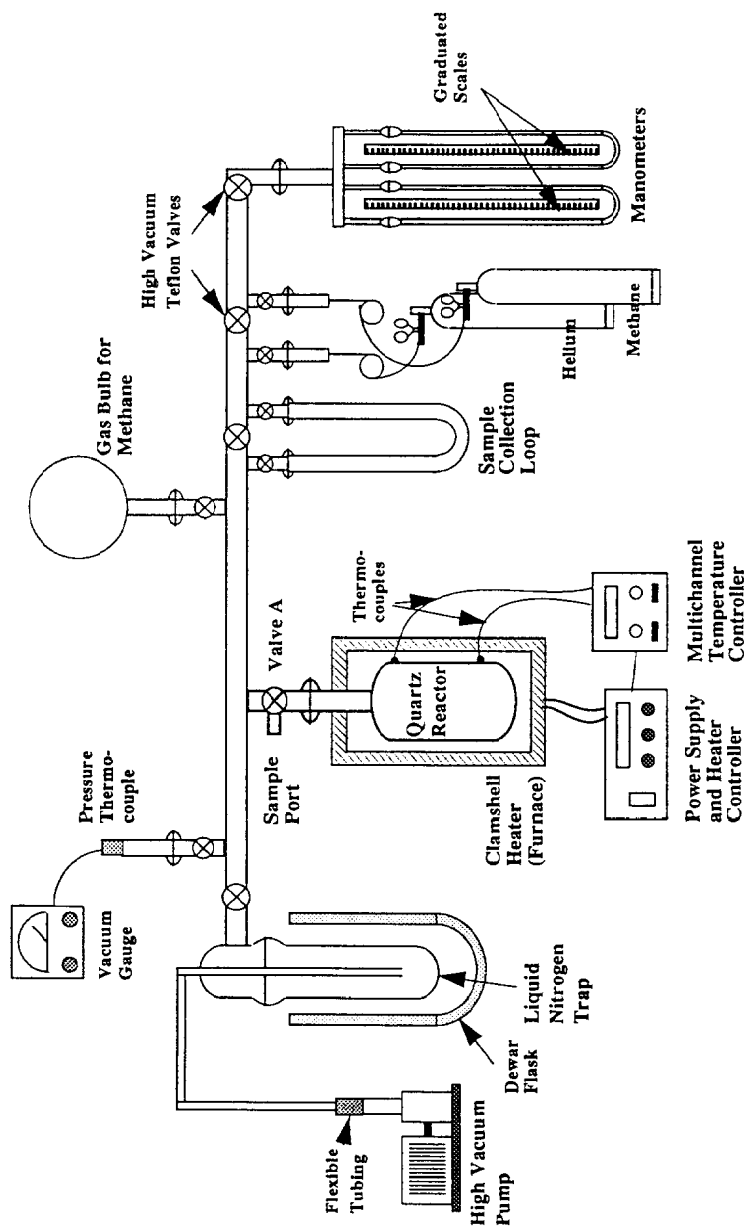
Fig. 1. Schematic of the batch reactor for the reductive pyrolysis.

was introduced by means of syringe. Subsequently, two 0.1-ml injections of n-hexane were made to ensure that all the PCBs were completely washed into the reactor. The reactor was then introduced into a Dewar's flask containing liquid nitrogen, while its neck was heated so that any PCBs remaining in the neck would enter into and be frozen in the body of the reactor (the temperature of liquid nitrogen was 77 K, at which the vapor pressure of PCBs was as low as 10 torr or 133 Pa). Due to the low temperature of liquid nitrogen, the reaction mixture consisting of PCBs, n-hexane, and methane was frozen within the reactor. Some of the experiments were performed without using methane, wherein the reductive environment was created primarily by the decomposition of the alkane solvent (n-hexane). Valve A was opened for removing any unfrozen methane, and after being quickly sealed airtight with the methane/oxygen torch, the reactor was introduced into the furnace for a duration corresponding to a predetermined residence time, so that pyrolysis could proceed. This duration consisted of the time taken to heat the reactor contents to the required reaction temperature, and the time for which the reaction was allowed to proceed at that temperature. After the reactor was heated for the required duration, it was removed from the furnace, allowed to cool, and then attached to a glass manifold by means of flexible tubing for sampling the reaction products. The neck of the reactor was then scored with a file, bent inside the tubing, and broken. The glass manifold was again used for the collection of reaction products. The gaseous products were passed through the sample collection loop containing trimethylamine for selective absorption of the hydrogen chloride formed during the reaction. The liquid products were extracted by thoroughly washing the reactor with n-hexane.

Analysis of PCBs

The quantitative analysis of PCBs in the liquid-product extract was performed using a Hewlett Packard 5790 A Series gas chromatograph (Hewlett Packard; Avondale, PA) equipped with an electron capture detector. The chromatographic column was packed with SP-2250/1.95% SP-2401 on 100/200 Supelcoport (Supelco, Inc.; Bellefonte, PA), and the carrier gas employed was 5% methane in argon. The injector, column, and detector temperatures were maintained at 250, 200, and 300°C, respectively. The detector output was recorded using a Hewlett Packard 3390A integrator. External standards were used for calibration of the gas chromatograph. The samples were analyzed without any clean-up procedure, and no interfering chromatographic peaks were observed.

Analyses of liquid and gaseous hydrocarbon products

The liquid and gaseous hydrocarbon products of the pyrolysis reactions were identified using the GC/MS technique. A Varian Model 3400 gas chromatograph (Varian Instruments; Sunnyvale, CA) was employed, which was equipped

with a DB5 30-m capillary column and interfaced with a Finnigan MAT IN-COS 50 mass spectrometer (Finnigan Mat; San Jose, CA). The injector and detector temperatures were maintained at 250 and 50°C, respectively. The column temperature programming used was different for liquid and gaseous samples. In the case of the former, the column temperature was maintained at 60°C for the first three minutes, and was subsequently increased to 250°C at a steady rate of 15°C/min. For gaseous samples, the temperature was initially maintained at 40°C and increased to 60°C at a uniform rate of 5°C/min. The mass spectrometer was equipped with an electron impact ionizer and a quadrupole mass filter. In order to protect the filament two precautionary measures were observed. The sample concentration was limited to approximately 50 ng for each component; and, the filament was kept out of operation while the solvent eluted from the column. The volumes of liquid as well as gaseous samples for the GC/MS analyses were 1 μl. The output from the mass spectrometer was stored, processed, and analyzed on a Data General computer (Data General Corp.; Southboro, MA). The compounds were identified by comparison of their mass spectra with those of over 44,000 compounds maintained in a library database.

Analysis of hydrogen chloride

The quantification of the hydrogen chloride (HCl) produced was attempted by two different collection methods: (1) passing the product gas through a tube coated with triethylamine to form triethylammonium chloride; and (2) freezing the product gas in a vial at liquid nitrogen temperature. In each method, the collected HCl was solvated in an aqueous solution, whose chloride content was determined by the Mohr Titration Method described by Skoog and West [22]. A small amount of potassium chromate was added as an indicator, and the solution was titrated with a 0.00949 N silver nitrate solution to the end point indicated by the formation of red silver chromate.

A second method used for quantitation of the product HCl involved gas chromatography. The frozen product was allowed to thaw, and a 10-ml sample of HCl was collected using a gas-tight syringe and injected into a Varian Model 3700 gas chromatograph equipped with a thermal conductivity detector, and interfaced with a Linear Model 282/MM integrator/recorder (Linear Instruments Corp.; Irvine, CA). The stainless steel chromatographic column (5 ft × 1/8 in I.D.) contained a Carbosieve G packing (Supelco, Inc.; Bellefonte, PA). Helium was used as the carrier gas at a flow rate of 30 ml/min. The injector was operated at room temperature (25°C), while the detector was maintained at 200°C. The column temperature was programmed so that it remained at 30°C for the first six minutes, and subsequently increased to 150°C at a steady rate of 50°C/min.

Results and discussion

Destruction and removal efficiency of Aroclor 1254

The pyrolysis reactions performed were directed at investigating the effects of three important factors on the DREs of the PCB mixture, Aroclor 1254 (A-1254): (i) reaction temperature; (ii) reactor residence time; and (iii) methane concentration. The pyrolysis experiments were carried out with the A-1254 dissolved in n-hexane at a concentration of 62,000 mg/l. Different sets of experiments were conducted under various reaction conditions to study the impacts of the variables mentioned above on the DREs of A-1254. One set of experiments was conducted to examine the effect of reaction temperature (furnace temperature), maintaining a constant residence time of 7 min. A second set of reactions was carried out at different residence times, but under the same reaction temperature of 1000°C. A third set of investigations involved different methane concentrations, maintaining residence times and reactions temperatures of 7 min and 1000°C, respectively.

Effect of reaction temperature

The impact of reaction temperature on the DREs of PCBs is significant from an energy consumption standpoint. It is important that the reaction temperature is maintained as low as possible to achieve an optimal DRE, so that a considerable fraction of energy costs can be reduced. In order to investigate the dependence of DREs on reaction temperature, the reactor residence time was held constant at 7 min, and a stoichiometric excess of methane was employed, while the reactor temperature was progressively varied from 700 to 1000°C. The results of these investigations depicted in Fig. 2 clearly indicate that the DREs are an increasing function of reactor temperature. A closer analysis of the results shows that the DRE is as low as 94.7% at 700°C, but exceeds 99.99% at temperatures of 900°C and above. It was found that below 700°C, the DREs decreased drastically. The high DREs (exceeding 99.99%) attainable above 900°C offer strong testimony to the fact that alkane hydrocarbons such as methane and n-hexane are indeed effective reducing agents for the ultimate destruction of PCBs.

Effect of residence time

Another critical factor that can potentially determine the economic and commercial viability of a process is the reactor residence time. In order to investigate the effect of this parameter on the DREs, it would indeed be appropriate to employ continuous flow reactors instead of batch systems for specific reasons. Batch reactors inherently suffer from uncertainties in process efficiencies arising from transient heating and mixing phenomena, as it is difficult to maintain a uniform temperature throughout the reactor. Hot and cold spots develop randomly at various locations, so that the reaction conversion is not
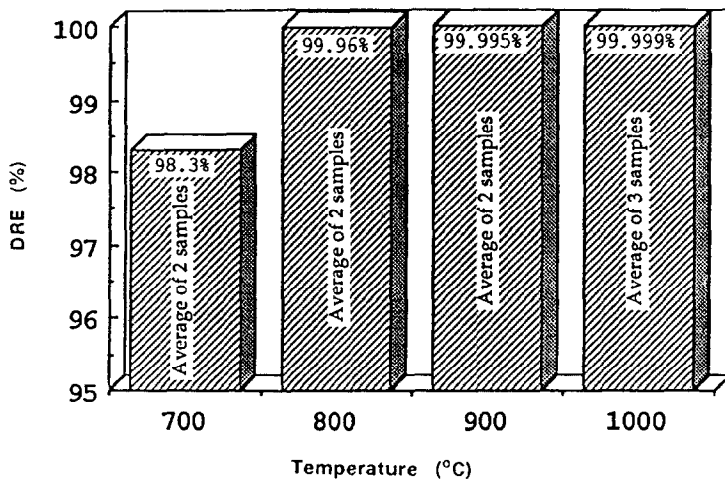
Fig. 2. Effect of reaction temperature on DRE of Aroclor 1254 with excess of methane (batch reactor).

uniform throughout the reactor volume. This disadvantage is less prevalent in continuous flow systems, where the extent of reactant mixing and degree of heating are more uniform throughout the reactor volume. A second advantage of using continuous flow reactors is that they permit a more comprehensive investigation of different parameters such as reactor residence times, reactor heating, and reactant concentrations. Continuous flow experiments are in progress to critically examine the effects of residence times on the DREs for PCBs. Nevertheless, batch experiments prove valuable as an inexpensive method for estimating the potential feasibility and ultimate DRE of the process.

The results of residence time investigations conducted with batch reactors are reported in Fig. 3. In these experiments the reactor temperature was maintained at 1000°C, while the residence times were carefully varied from 1 to 7 min. The significance of residence time as an important parameter affecting the process DRE is evident from the results depicted in Fig. 3. It can be easily seen that the DREs increase steadily as a function of residence time. The DRE corresponding to a residence time of 1 min is 27.68%, and such a low value can be attributed to a number of factors: slow heating and transient effects, insufficient mixing, and inadequate reaction time. A close analysis of data shown in Fig. 3 reveals that the DRE increases sharply to 98.4% as the residence time is increased to 3 min. A further improvement in DRE to over 99.999% is observed for a residence time of 7 min, although the incremental enhancement in DRE is gradually lowered at higher residence times. It is important to note that batch reactor experiments provide good estimates for the minimum DREs obtainable from continuous flow systems, as the latter may not experience unfavorable reaction conditions such as transient heating and poor mixing.
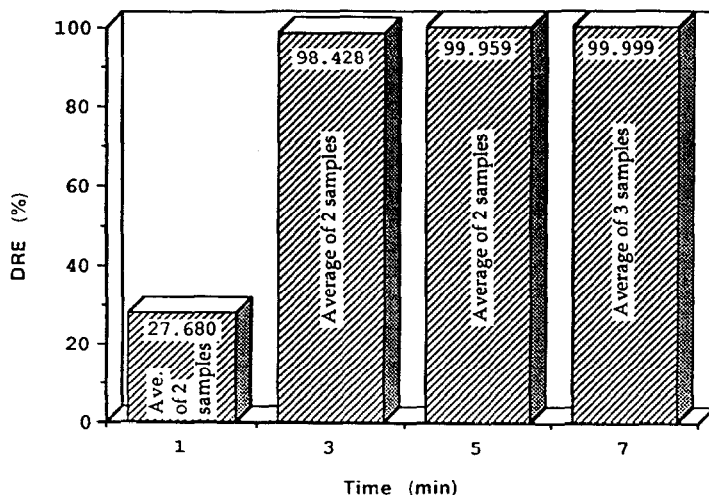
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Fig. 3. Effect of residence time on DRE of Aroclor 1254 at a reaction temperature of 1000°C and a stoichiometric excess of methane (batch reactor).

Effect of methane concentration

The experiments directed at the investigation of reactor temperature and residence time effects on the DREs of PCBs utilized methane concentrations far exceeding the stoichiometric requirement. In order to study the effect of methane concentration on the DREs of A-1254, the pyrolytic decomposition was conducted over a broad spectrum of methane concentrations ranging from no methane to a slight stoichiometric excess, followed by a substantial excess of the reducing agent. In all the experiments, the reactor residence times and reaction temperatures were maintained constant at 7 min and 1000°C, respectively. The results shown in Fig. 4 indicate that regardless of the methane concentrations, the DREs exceeded 99.99%. This demonstrates the fact that the reducing atmosphere for the pyrolysis of PCBs can be created by using an alkane solvent such as n-hexane, and methane is not necessary. An interesting observation is that even though no methane was employed in the feed, it was identified in the product gas. It is therefore obvious that methane is generated as a product when n-hexane is pyrolyzed along with the PCB mixture.

Mass balance on chlorine

An attempt was made to perform a mass balance based on the chlorine content of the PCBs reacted to form hydrogen chloride. However, this could not be satisfactorily carried out because the hydrogen chloride formed during the pyrolysis was below the detection limits of the analytical techniques used. This approach could, nevertheless, be employed in continuous flow systems, where the hydrogen chloride formed would be in quantifiable amounts.
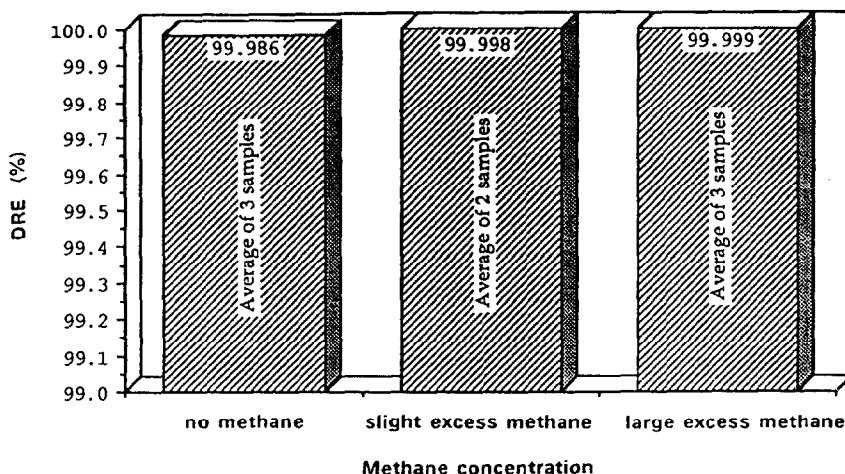
100.0
99.9
99.8
99.7
99.6
99.5
99.4
99.3
99.2
99.1
99.0

DRE (%)

99.986 Average of 3 samples

99.998 Average of 2 samples

99.999 Average of 3 samples

no methane   slight excess methane   large excess methane

Methane concentration

Fig. 4. Effect of methane concentration on DRE of Aroclor 1254 at 1000°C (batch reactor).

Reaction products

The liquid and gaseous products of the reductive pyrolysis of PCBs were analyzed by the GC/MS technique, as described earlier. The reaction products in the gas phase besides HCl were identified as methane and benzene. The products in the liquid phase contained trace levels of the organic compounds listed in Table 1 that were not quantifiable. No unreacted PCBs could be observed in the product stream, either in the liquid or gaseous phase, as their concentrations were well below the detection limits of the GC/MS technique. The list presented in Table 1 contains a few oxygenated organic compounds which resulted from the contact of the reactants with plastics. When care was taken that no solvent was stored in a plastic container, and no plastic component came into contact with the glassware or the experimental samples, no oxygenated species were detected. It is therefore clear that the nonoxygenated compounds listed in Table 1 are products that are inherently characteristic of the reductive pyrolysis of PCBs. The soot deposits in the reactor were extracted and analyzed, and found to contain traces of species listed in Table 1.

Summary and conclusions

The pyrolytic destruction of halogenated hydrocarbons in a reductive environment was investigated using Aroclor 1254, a PCB mixture. Feasibility studies were conducted in batch reactor systems, and the variations in process DREs were studied as a function of process variables such as reactor residence time, reaction temperature, and reactant composition (methane concentration). The

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free-radical chemistry and the reaction mechanisms associated with the pyrolytic decomposition of PCBs into dechlorinated hydrocarbons, hydrogen chloride and soot were investigated. The conclusions derived from the studies were the following:

- The reductive pyrolysis demonstrated DREs in excess of 99.999% for PCBs in batch reactor systems under optimal conditions: a residence time of 7 minutes, and a reaction temperature of $1000\,^{\circ}C$.

- The results of batch reactor indicated the feasibility of the reductive pyrolysis process for the destruction of PCBs, warranting the investigation of continuous flow reactor systems, which is currently under way.

- The free-radical chemistry of the pyrolysis process, and the associated mechanisms were examined in this study. These included the free-radical reactions involved in the dechlorination of PCBs, formation of simpler dehalogenated hydrocarbons, decomposition of an alkane solvent such as n-hexane, and the formation of soot.

- The process yielded reaction products including several dechlorinated aliphatic and aromatic hydrocarbons, soot, and the thermodynamically stable hydrogen chloride. Reaction in an oxygen-free environment prevented the formation of undesirable products such as dibenzodioxins or dibenzofurans.

- The findings indicated that the pyrolytic destruction of PCBs could be accomplished in the presence of an alkane solvent such as n-hexane. The use of methane was not necessary for creating a reductive environment condusive for subsequent free-radical reactions.

- The reductive pyrolysis represents a dehalogenation technology superior to catalytic hydrodechlorination techniques such as the Chloroff Process of KTI, Inc., and the hydrogenolysis of Manion. Unlike the Chloroff Process, the reductive pyrolysis is operative in low-pressure reactors, and employs no catalyst. Therefore, the new process is neither susceptible to reactor explosion, nor vulnerable to catalyst poisoning or deactivation.

Acknowledgments

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