



Dechlorination of polychlorinated biphenyls using magnesium and acidified alcohols

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ABSTRACT

Polychlorinated biphenyls (PCBs) were widely used in industry until their regulation in the 1970s. However, due to their inherent stability, they are still a widespread environmental contaminant. A novel method of degradation of PCBs (via hydrodehalogenation) has been observed using magnesium powder, a carboxylic acid, and alcohol solvents and is described in this paper. The rates of degradation were determined while varying the type of acid (formic, acetic, propionic, butyric, valeric, benzoic, ascorbic, and phosphoric), the amount of magnesium from 0.05 to 0.25 g, the amount of acetic acid from 0.5 to 50 μL and the concentration of PCB-151 from 0.1 to 50 $\mu\text{g}/\text{mL}$, as well as the alcohol solvent (methanol, ethanol, propanol, butanol, octanol, and decanol). The results of these studies indicate that the most rapid PCB dechlorination is achieved using a matrix consisting of at least 0.02 g Mg/mL ethanol, and 10 μL acetic acid/mL ethanol in which case 50 ng/ μL of PCB-151 is dechlorinated in approximately 40 min.

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1. Introduction

The name polychlorinated biphenyl refers to a collection of molecules that have a biphenyl backbone on which 1–10 hydrogens have been replaced by a chlorine atom; in all this encompasses 209 distinct congeners. Physical properties of PCBs include: low water solubility ($(4.0\text{--}7.6) \times 10^{-4} \text{ g}/\text{m}^3$), low vapor pressure ($(1.1\text{--}1.4) \times 10^{-6} \text{ Pa}$), low flammability, low electrical conductivity, and high degrees of both chemical and thermal stability [1]. Due to these properties, PCBs, in the form of mixtures of congeners sold under various trade names, were used in a myriad of industrial application's most notably as dielectric fluids in capacitors and transformers. Unregulated manufacture and disposal of PCBs prior to the passage of the Toxic Substances Control Act (TSCA) [2] has led to highly concentrated localized contamination sites around former production and disposal facilities and virtually worldwide background contamination. The numerous studies of PCB concentrations in plants, animals, air, soil, and water, when considered in total, paint a picture of a truly global pollutant. Many studies, dating back to 1936 [3], have investigated the effects of PCB

exposure on humans, however the multi-congener nature of most occupational and environmental exposures, as well as the presence of other pollutants, has led to conflicting conclusions as to actual PCB toxicity. Presently, the Environmental Protection Agency (EPA) classifies PCBs as probable human carcinogens based on predictive studies of other species [4]. As such, the need exists for practical PCB remediation technologies.

There are several disposal and remediation techniques currently in use including landfilling, incineration, plasma arc systems, and microbial and chemical dechlorination processes. However, each of these processes has certain drawbacks. The inherent stability of PCBs makes nondestructive treatment methods such as landfilling less desirable due to the possibility of PCB volatilization [5] and leaching. Additionally, transportation and long term monitoring costs as well as local public opposition must be considered. The most common destructive technique employed today is incineration. Under optimal conditions highly efficient destruction of PCBs on a wide variety of contaminated materials can be achieved, however incomplete combustion can lead to the formation of highly toxic polychlorinated dibenzofurans and polychlorinated dibenzodioxins [6]. In addition, with the rise of fuel costs, incineration becomes less economically viable. Plasma arc technology is similar to incineration with the advantage of having nearly instantaneous atomic ionization, but as with any energy intensive process fuel costs are an important factor in determining its practicality. Studies have shown that *in situ* microbial degradation of PCBs under

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anaerobic (reducing) [7] and aerobic (oxidizing) [8,9] conditions can occur. However strict control over environmental conditions must be maintained and even then reaction rates are low and complete dechlorination of higher chlorinated congeners is difficult to achieve.

Although the category of chemical destruction of PCBs encompasses a wide variety of techniques, one area that has shown great potential is the use of zero valent metals for reductive dechlorination. Chuang et al. [10] demonstrated the ability of zero valent iron to dechlorinate PCBs at temperatures from 300 to 600 °C. In light of certain disadvantages seen in early research in this area, such as incomplete dehalogenation and the need for high reaction temperatures, a great deal of subsequent research focused on identifying a reduction based technology that produced no toxic byproducts and that could be employed under ambient reaction conditions. A process that met these criteria could possibly be used for *in situ* applications. To this end, Boronina et al. [11] used zero valent Mg, Sn, and Zn in place of iron with mixed results and Grittini et al. [12] created a bimetal by depositing small amounts of Pd onto microscale iron particles and observed complete dechlorination of Aroclor 1254 and 1260 on the scale of a few minutes. In an effort to improve the analytical measurement of convoluted PCB mixtures, Doyle et al. [13] used a Mg/Pd bimetal to completely hydrodehalogenate Aroclor 1221 so that biphenyl is the only analyte. Using Mg as the base metal had the advantages of a larger reduction potential compared to Fe (−2.37 V and −0.44 V respectively vs. SHE) and eliminated the need to acid wash the iron prior to palladium deposition. Mg/Pd has been shown to degrade other halogenated compounds such as 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) [14], polychlorinated dibenzo-p-dioxins and naphthalenes [15], and chlorophenols [16] in a variety of solvents.

Elucidation of the mechanism, particularly the hydrogen source, of palladium catalyzed hydrodehalogenation on various substrates has been the focus of work by Ukisu and Miyadera [17], Agarwal [18], and DeVor et al. [19]. In each of the proposed mechanisms, the solvent is the hydrogen/hydride donor and the palladium facilitates the reaction by acting as an atomic hydrogen or hydride storage medium and transfer catalyst. DeVor et al. [20] showed reaction rate and mechanism changes depending on the solvent, and therefore proton source, being used. Based on this work, the studies presented here were designed to further investigate the source of the hydrogen in the reaction and the effects of various molecular substitutes on the reaction rate.

2. Methods

2.1. Materials and chemicals

Neat PCB standards were obtained from Accustandard and standard solutions were prepared by diluting the neat standards to the desired concentration with absolute ethanol from Pharmco-AAPER. Micro-scale magnesium (~4 μm) was obtained from Hart Metals, Inc. Ballmilling magnesium has been reported to increase its activity by cracking the passivated hydroxide/oxide surface layer and by changing the microstructure to create more surface defects [21,22]. Extensive testing has been conducted in our lab to optimize ballmilling parameters [23]. The study shown in Fig. 1 comparing ballmilled and unballmilled magnesium illustrates the vastly improved reactivity of the ballmilled magnesium. Comparing SEM images of the magnesium powder before and after ballmilling (Fig. 2) does not show a drastic change in particle size or shape. However the ballmilled particles appear to have a “cleaner” surface, free of irregular outcroppings of material. The magnesium was ballmilled by depositing 85 g of magnesium and 16 stainless steel ball bearings (1.5 cm diameter) in a stainless steel canister (inner

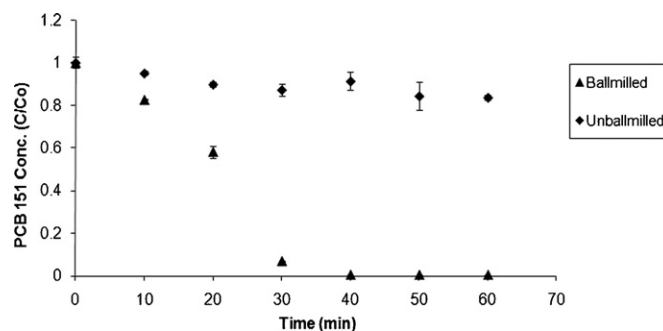


Fig. 1. Comparison studies of PCB-151 degradation using ballmilled Mg powder vs. Mg powder as received. The ballmilling process is an advantageous activation step for the Mg powder since it drastically increases the rate of dehalogenation of PCBs.

dimensions 5.5 cm diameter by 17 cm height) and milling on a Red Devil 5400 series paint mixer for 30 min.

Methanol, propanol, butanol, octanol, decanol, ascorbic acid, benzoic acid, phosphoric acid, formic acid, acetic acid, propionic acid, butyric acid, and valeric acid were all purchased from Fisher Scientific. All chemicals were used as received unless otherwise noted.

2.2. Experimental procedure

The following standard experimental procedure was used for all studies described in this paper including the ballmilled vs. unballmilled Mg study, the results of which are shown in Fig. 1. Modifications to this procedure were made based on the variable being tested in each separate experiment and are described in the corresponding text. Experiments were conducted in 20 mL vials with PTFE lined caps. Ballmilled Mg (0.25 g) and 5 mL of a 1.0 μg/mL PCB-151 in absolute ethanol solution were added. Next, glacial acetic acid (50 μL) was added and the vials were then placed on a Cole Palmer® EW-51401-06 adjustable shaker table operated at a 120 oscillations per minute, for the appropriate amount of time. Extraction of the PCBs was conducted by adding 5 mL of toluene to the vials and shaking vigorously by hand for 2 min. Of this miscible solution, 4 mL were drawn into a filtered syringe and then deposited in a centrifuge tube. Next, deionized water (2 mL) was added to facilitate separation of the ethanol/toluene mixture. Samples were centrifuged for 4 min and the toluene layer was then extracted for further analysis.

2.3. Analysis

Sample analysis was performed on a Perkin Elmer AutoSystem XL GC/ECD equipped with a Restek RTX®-5 column (30 m × 0.25 mm, 0.25 μm film thickness) and a temperature ramp from 120 °C to 300 °C. Degradation was measured by disappearance of the PCB-151 peak and confirmed (as opposed to adsorption to the Mg) by the appearance of lower chlorinated congeners.

3. Results and discussion

3.1. Choosing a hydrogen/proton donor

Studies were conducted to see if the incorporation of an acid into the reaction matrix would act as a suitable hydrogen/proton source in place of the noble metal in the bimetallic systems currently being used for PCB dechlorination. Since the acid would be coming into contact with micro-scale magnesium, acetic acid was initially chosen due to its weak acidity ($pK_a = 4.76$ at 25 °C) in order to minimize violent reaction. Initial tests using approximately 1% by

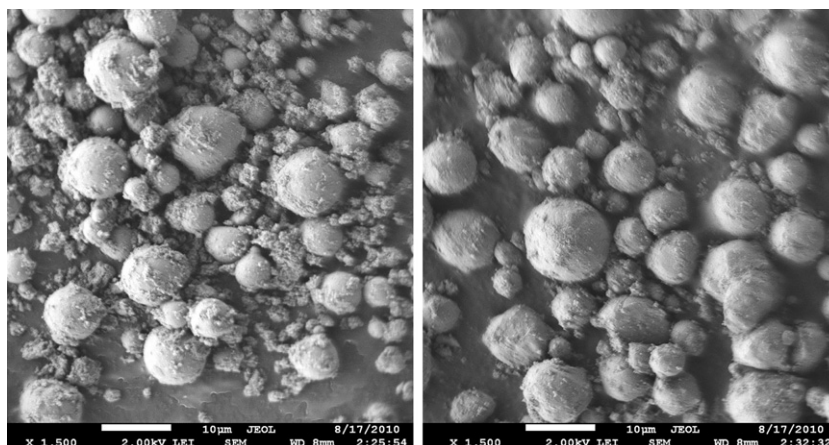


Fig. 2. SEM images of magnesium powder before (left) and after (right) ballmilling. Although the size and overall spherical shape of the particles remains generally unchanged, the surface of the ballmilled magnesium appears to have been stripped of some of the smaller agglomerated material.

volume of acetic acid yielded encouraging results. The first chlorine was removed from an entire 1.0 µg/mL PCB-151 sample in 40 min. Further degradation of the resulting lower chlorinated congeners was also seen within the 1 h timeframe of the study, as illustrated in Fig. 3. This pattern of byproducts was seen in all studies in which degradation was observed. The kinetic data for this standard reaction matrix is presented in all of the following graphs for reference. Tests of the reaction solution (filtered to remove any Mg powder) using wet litmus paper, indicate that upon addition of the acetic acid, the solution is slightly acidic with a pH of 4–5. By 1 min however the solution pH has risen to 7–8, likely due to the reaction of the acid with the Mg powder. Direct tests of the unfiltered solution are also initially slightly acidic then increase rapidly to a pH >10 due to the reaction of the Mg with the water on the litmus paper. This result agrees with experiments conducted by Agarwal [18] in aqueous systems using both Mg/Pd bimetal and Mg.

Based on the degradation seen in this first test, experiments were conducted to see if a mineral acid or an other organic acid would produce similar results. Phosphoric acid was chosen because it was assumed to be a suitable hydrogen donor and mineral acids such as phosphoric acid are often used to remove magnesium oxide/hydroxide layers from the bulk material thereby exposing the zero-valent subsurface and activating the metal [24]. Benzoic and ascorbic acids were chosen because their pK_a values are similar to acetic acid (Table 1) and due to their low toxicity. Fifty microliters of concentrated phosphoric acid was added to the sample vials just as acetic acid is added in the standard procedure and for the stud-

Table 1
pK_a values and masses of acids tested in these experiments.

Acid	pK _a	Amount used/5 mL EtOH
Acetic	4.75	53 mg
Phosphoric	2.12	84 mg of 85% H ₃ PO ₄
Ascorbic	4.10	39 mg
Benzoic	4.19	39 mg
Formic	3.75	61 mg
Propionic	4.87	50 mg
Butyric	4.81	48 mg
Valeric	4.82	47 mg

ies with ascorbic and benzoic acid a mass of acid equal to 1% of the mass of ethanol was dissolved (i.e. 0.04 g of acid for 5 mL of ethanol). The results of these studies are shown in Fig. 4. In each case, except for acetic acid, no degradation was observed. This result was unexpected since it was assumed that the availability of a proton was an important factor for the possibility of hydrodehalogenation to occur as well as the rate of that reaction.

Since experiments using a mineral acid with a much lower pK_a (phosphoric acid) and organic acids with similar pK_a values (ascorbic and benzoic) showed no degradation, pK_a appeared to either not be the determining or not the only determining property for an acid to produce the desired reaction in this matrix. In the next set of experiments, a series of structurally similar carboxylic acids were tested. Over the 1 h time period of this study no degradation was observed with any acid other than acetic acid (Fig. 5). It is worth not-

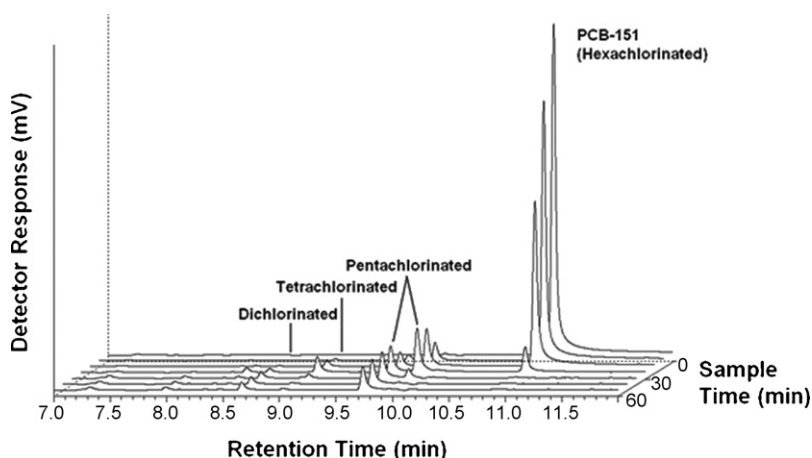


Fig. 3. Time resolved PCB-151 degradation chromatograms showing the typically observed dechlorination pattern seen in these studies.

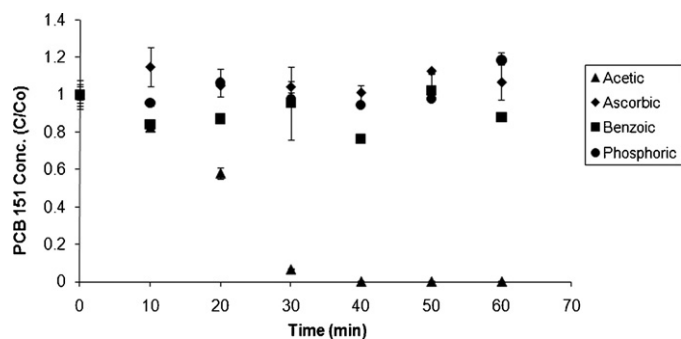


Fig. 4. Comparison of PCB-151 degradation using acids with similar pK_a values to acetic acid and phosphoric acid. In the case of ascorbic and benzoic acids the concentrations in solution were 0.04 g/5 mL of ethanol (i.e. the solvent volume of an individual sample) and for phosphoric acid samples 50 μ L of concentrated acid (85% solution in water) were added to each 5 mL sample.

ing that in an extended study (96 h) formic and propionic acid were able to degrade PCB-151 over a longer period of time with formic acid degrading 80% of the starting concentration of PCB-151 by day 4 and propionic acid degrading 100% by day 3. As in the 1 h study, no degradation was seen using either butyric or valeric acid over this extended time period. These results seem to invalidate the hypothesis that pK_a is correlated to reactivity. Paoprasert et al. [25] have reported that in carboxylate-metal complexes methylene groups act as insulators against electron transfer which may explain the decreased reactivity observed in the longer chain carboxylic acids.

3.2. Effect of Mg loading on PCB degradation

In the next study, the effect of varying the amount of Mg was observed. Previous work conducted in our lab had shown that in Mg/Pd bimetallic systems, as the amount of palladium present in the reaction matrix was increased, the reaction rates increased as well. The following study was designed to see if the same trend would be seen in matrices using only Mg. To determine this, Mg loadings of 0.05, 0.10, 0.15, 0.20, and 0.25 g were used. As can be seen from Fig. 6, virtually complete degradation of PCB-151 was achieved in 60 min in loadings as small as 0.05 g. While this may not be a surprising result based on molar amounts of the reactants in the 0.05 g study ($Mg \approx 2 \times 10^{-3}$ mol, $PCB-151 \approx 1 \times 10^{-8}$ mol, and acetic acid $\approx 9 \times 10^{-4}$), the amount of reactive Mg actually available for reaction is most likely limited by surface area and the extent of surface oxidation. While this paper makes no attempt to quantify either of these factors, it can be said that at loadings down to 0.10 g of magnesium, neither appears to have an effect on the reaction rate.

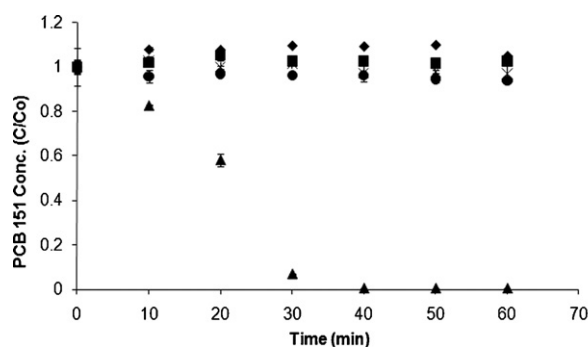


Fig. 5. Comparison of PCB-151 degradation using various, straight-chain carboxylic acids. For each sample 50 μ L of undiluted acid (>98% pure as received) was added to the reaction matrix.

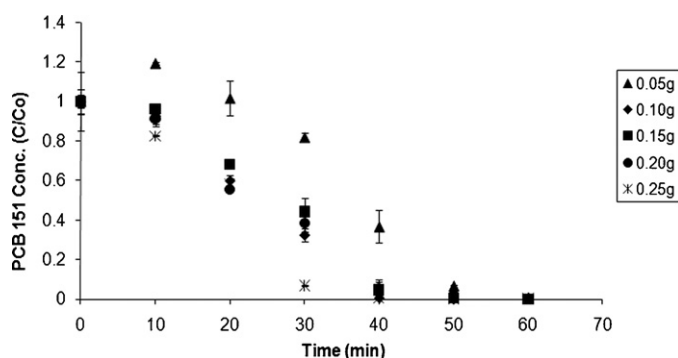


Fig. 6. Comparison of PCB-151 degradation using various loadings of Mg. Virtually no difference was seen in reaction rates with loadings as low as 0.10 g of Mg. At a loading of 0.05 g Mg the first decrease in the reaction rate can be seen. Even with this decreased reaction rate the concentration of PCB-151 is below the limit of detection by the end of the 60 min study.

3.3. Effect of varying acetic acid concentrations on PCB degradation

This study attempted to determine the effect of acetic acid concentration on the rate of PCB-151 dechlorination. Volumes of 0.5, 5.0, 25 and 50 μ L (approximately 0.01, 0.1, 0.5 and 1.0% by volume respectively) were added to the reaction matrix. Over the standard 1 h time period of the studies presented thus far, degradation was observed only in the samples with 50 μ L of acetic acid. However, the graph in Fig. 7 has been extended to 12 h to illustrate that samples containing 25 μ L of acetic acid showed 94% PCB-151 degradation by the second hour. Over the entire 96 h time period of this study virtually no degradation was seen in the samples containing 0.5 or 5.0 μ L of acetic acid. This data demonstrates a clear dependence of the reaction rate on the volume of acetic acid present in the reaction matrix. It may be the case that at these lower volumes there is not enough acid present to neutralize the $Mg(OH)_2$ layer and allow access to the reactive Mg^0 .

3.4. Effect of PCB concentration on degradation

In the fourth study, the concentration of PCB-151 was varied to see what effect this may have on the rate of degradation and to see if there is an upper limit to how much PCB-151 is capable of being degraded with the standard amounts of other reagents. As indicated by the data in Fig. 8, the standard acidified ethanol matrix was shown to be capable of degrading PCB-151 at least to the highest experimental concentration of 50 μ g/mL with relatively little change in the rate of degradation.

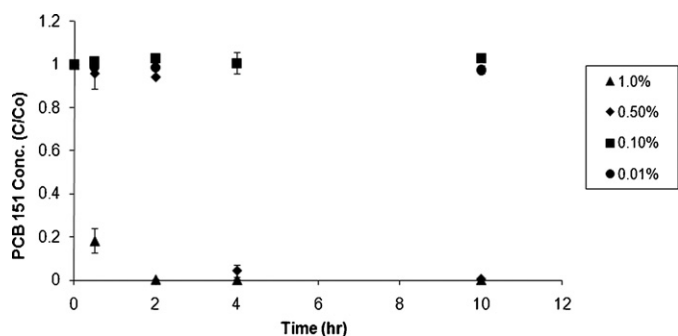


Fig. 7. Comparison of PCB-151 degradation with various volumes of acetic acid. The volume of acetic acid present in the reaction matrix has a definite effect on the rate/feasibility of the reaction.

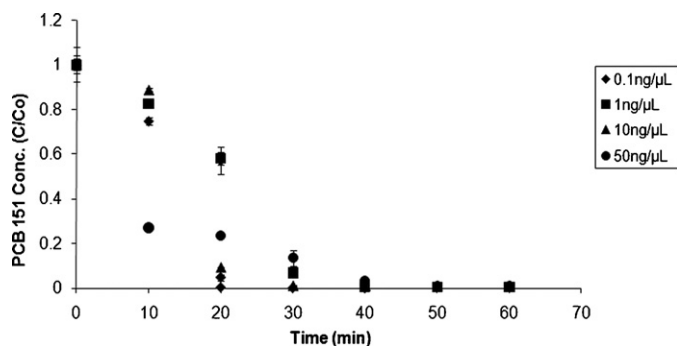


Fig. 8. Comparison of PCB-151 degradation using various starting concentrations of PCB-151.

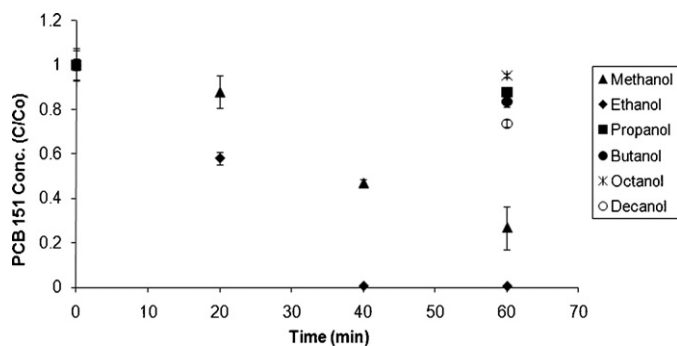


Fig. 9. Comparison of PCB-151 degradation rates using various straight-chain alcohol solvents. Methanol and ethanol were the only two solvents that showed significant degradation over a 1 h time period.

3.5. Effect of various straight chain alcohol solvents on PCB degradation

Previous studies in the literature [17–19] have indicated that the solvent was the hydrogen/hydride source in the reduction of PCBs. Based on our working hypothesis that the acid was now the hydrogen source, a study was designed to determine what if any effect the solvent would have on the reaction rate. In order to make comparisons to ethanol as close as possible, several straight chain alcohols were substituted as reaction solvents. Matrices using methanol, ethanol, propanol, n-butanol, n-octanol, and n-decanol as the solvent were all tested at 60 min. As Fig. 9 shows, only the samples with ethanol and methanol solvents showed significant degradation during the 60 min time period of the study. Therefore, in order to have a more detailed picture of the reaction rates in these two solvents, a second study was conducted with samples being taken at 20 min intervals. PCB-151 was degraded by 73% from its initial concentration in the methanol solvent and, as seen in previous studies using ethanol, the PCB-151 concentration is below the detection limit by 40 min. Interestingly, in the 60 min studies using n-butanol, n-propanol, n-octanol and n-decanol, it was decanol that showed the greatest reduction in PCB-151 concentration and was the only one of these solvents in which lower chlorinated byproducts were detected. A linear size/degradation rate relationship is not apparent.

4. Conclusion

This paper describes a magnesium, acetic acid, and ethanol matrix which is, to the best of our knowledge, a novel reaction matrix for the hydrodechlorination of PCBs. No appreciable decrease in the rates of degradation was seen in studies using as lit-

tle as 0.05 g of Mg or PCB-151 concentrations as high as 50 $\mu\text{g}/\text{mL}$. However the rate of reaction showed a strong dependence on the type and amount of acid used as well as the choice of solvent. In these experiments it was found that a volume of 50 μL of acetic acid in 5 mL ethanol solution yielded the best results. Neither phosphoric acid, which has been used to activate magnesium, nor organic acids with similar pK_a values were suitable substitutes for acetic acid. Steric effects were then considered since the ascorbic and benzoic acids used in the first study are much bulkier molecules, however a subsequent study with formic acid, which has both a lower pK_a and is a smaller molecule, showed a slower rate of degradation as well. Additionally the rate of reaction showed a strong dependence on which solvent is used, with methanol and propanol yielding much lower reaction rates than ethanol. Currently the exact roles of the acid and the solvent in the reaction are not fully understood.

A system using magnesium, acetic acid and ethanol has the potential to significantly reduce material expenses in comparison to similar systems using costly secondary metals such as palladium, platinum, gold, or silver. Additionally, the exclusion of a heavy metal eliminates recovery and regulation considerations for any *in situ* remediation techniques.

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