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REDUCTIVE DECHLORINATION OF CHLORINATED AROMATICS

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Abstract:

A practical method has been found for the reduction of PCB's and chlorinated benzenes in a nonpolar solvent with formic acid, water, Pd/C and sodium carbonate. This reductive dechlorination can be run under atmospheric pressure and relatively mild conditions.

Introduction

Polychlorinated Biphenyls (PCB's) have been used for industrial applications as additives in dielectric, hydraulic and heat transfer fluids for several decades. They are now considered pollutants¹ and as a result, many techniques have been proposed to destroy PCB's including sodium metal reductions², high temperature incineration², and the ammonium formate catalytic hydrogenolysis described below.

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This report describes new conditions for the reductive dechlorination of PCB's which are useful in both preparative³ and environmental^{2,4} applications. The goal was to find an efficient and cost-effective process which was capable of reducing PCB's and other chlorinated aromatics in a nonpolar media such as transformer oil.

Reductive dechlorination of PCB's to biphenyl has previously been reported. Boyer, et. al.²⁵ have demonstrated this with a Pd catalyst using sodium hypophosphite as the reducing agent. They reported² that Aroclor[®] 1254 (registered trademark of Monsanto Company, St. Louis, MO), a commercial PCB mixture, was converted to biphenyl in yields \geq 95% when exposed to excess sodium hypophosphite (4 times the molar equivalent necessary to react with all aryl chlorine bonds) and 10% Pd-on-carbon at 90°C for 4 hours. Catalytic transfer hydrogenolysis with ammonium formate and Pd/C has also been successfully used to reductively dechlorinate PCB's. Catalytic transfer hydrogenation has been used as a means of reducing many different types of functionalized compounds.^{67,8,9,10} A report by Anwer and Spatola¹¹ claimed complete reductive dechlorination of Aroclor 1254 in less than 4 minutes using ammonium formate and 10% Pd/C in a methanol/tetrahydrofuran mixture at room temperature.

Herein we report that chlorinated aromatics and PCB's may be reduced to biphenyl under very mild conditions (Scheme 1). The reaction was typically run by adding an aqueous formic acid solution over 60 minutes to a stirred mixture of a chlorinated aromatic or PCB, sodium carbonate, 10% palladium-on-carbon and toluene at 90°C. It was later found that the formic acid addition time was important for the reduction of the PCB's. The formic acid and sodium carbonate were typically used in a molar excess of 4 to 5 times that required for reaction of all the aryl chloride functionalities. The level of palladium-on-carbon used was typically 2% of the weight of the chlorinated substrates and the concentrations of chlorine groups were typically 0.5N to 0.75N in toluene.



Results and Discussion

We have found that PCB's and chlorinated benzenes can be reacted in a nonpolar solvent (toluene) with formic acid, water, Pd/C and sodium carbonate to completely dechlorinate the aromatic rings. The principal organic product (benzene or biphenyl) was removed in the toluene phase while sodium chloride was the aqueous phase by-product. The process for chlorinated benzenes was quick and finished within 5 minutes after addition of the formic acid/water. Furthermore, each of the above listed components was required for the reaction to work well. Removal of the base, toluene or formic acid resulted in either no reaction or incomplete dechlorination.

Several reactions were run using 1,2,3,4-tetrachlorobenzene as a model for PCB's. Best results were obtained by slow addition of formic acid (1 hour) to a mixture of the tetrachlorobenzene, Pd/C, toluene, water and sodium carbonate in a 90°C oil bath. It was found that 5.0 minutes after the addition was complete, no detectable amounts of mono, di, tri or tetrachlorobenzenes were observed. Benzene and some very low levels of C_7H_{14} , C_8H_{16} , C_8H_{18} and two compounds with m/z

= 174 were all that were observable by GC/MS. The m/z = 174 peaks had electron impact spectra that were consistent with phenylmethylcyclohexane and cyclohexyltoluene. The C_7H_{14} electron impact mass spectrum was consistent with that of methylcyclohexane.¹²

We were able to follow the reaction by observing the stepwise loss of the chlorine from the various polychlorinated starting materials and intermediates. However, it was uncertain whether chloroaliphatics or chloroalkenes, resulting from the chloroaromatics, still remained. Therefore, we checked our products by both chloride-ion titration and GC/MS to insure that these were not present. Typically >98% of the expected chloride was found by chloride-ion titration for the 1,2,3,4-tetrachlorobenzene reactions, and no chloroaromatics or chlorohydrocarbons were detected by GC/MS.

It was also found that the time for complete reaction increased from 5 to 60 minutes when half the typical catalyst amount was used. Elimination of toluene, with all other factors the same, led to incomplete reaction. Exposure of a mixture of tetrachlorobenzene in water containing 10% Pd/C and an excess (4 to 5 times the molar equivalents of chlorine atoms) of sodium carbonate to an excess (4 to 5 times the molar equivalents of chlorine atoms) of formic acid afforded, after 15 minutes at 90°C, a partially dechlorinated product mixture. HPLC results indicated that the product mixture consisted of dichlorobenzene (~80%), trichlorobenzene (~10%) and a trace amount of benzene (<1%) 15 minutes after HCOOH addition was complete. Two other experiments monitored by HPLC in which no benzene was observed were the reactions run in the absence of sodium carbonate and Pd/C (after 5 h) and in the absence of sodium carbonate alone (after 20 hours).

A comparison of the ammonium formate and the sodium carbonate/formic acid reactions was done using the best conditions found for the latter. The results indicated that ammonium formate was slower than the sodium carbonate/formic acid when the reactions were done in toluene/water under similar conditions. The ammonium formate reduction was still not complete 20 minutes after its addition to the reaction mixture, while the sodium carbonate/formic acid was done 5 minutes after addition of the formic acid. The ammonium formate reaction was complete between 20 minutes and 2.5 hours.

We next turned our attention to reactions of PCB's under these same conditions. The formic acid addition time was cut nearly in half to 35 minutes for the reactions that employed Aroclor 1254 in place of the tetrachlorobenzene. It was found that addition times less than or greater than this caused a drop in overall dechlorination. Analysis indicated that the reaction was >95% complete 60 minutes after the formic acid addition; only traces of the chlorinated starting materials were detectable by GC/MS.

A major by-product of the Aroclor reduction was phenylcyclohexane. The molecular ion and electron impact fragmentation pattern¹² were consistent with phenylcyclohexane, and not an isomer containing two partially reduced rings. The presence of m/z = 91 was consistent with that expected for an aromatic hydrocarbon. Phenylcyclohexane may have resulted from reduction of biphenyl, or possibly from reduction of some or all of the double bonds prior to complete dechlorination. It could not be readily obtained from the solvent, and phenyltoluene was not used in the Aroclor 1254 experiments. The current data do not allow a mechanistic distinction to be made. The reduction of PCB's to phenylcyclohexane was not reported by Anwer and Spatola, but was reported by Boyer.

GC/MS also revealed that none of the observable peaks were hydrogenated PCB's which still had chlorine substitutents. Titration of the aqueous phase after workup detected 92% of the expected chloride.

We have demonstrated that a mixture of sodium carbonate, formic acid and palladium-on-carbon in an aqueous toluene system can be used to effectively reduce chlorinated aromatics and PCB's to their respective aromatic hydrocarbons and biphenyl. Phenylcyclohexane was also detected as a reduction product. The effects of temperature, pressure, catalyst type, catalyst loading and concentration effects on these reactions need to be further investigated.

Experimental Section General

Materials were used as received. Formic Acid (88%) was obtained from J.T. Baker or Fisher Scientific; 1,2,3,4-tetrachlorobenzene, 10% Pd/C and 4phenyltoluene were obtained from Aldrich Chemical Co.; toluene from E.M. Science; sodium carbonate from E.M. Science or Fisher Scientific and Arochlor 1254 from Accustandard Inc. (New Haven, CT). HPLC was done on a Shimadzu LC6A using A Zorbax[®]C8 column (Mac-Mod Analytical Inc., Chadds Ford, PA), eluted at 1.5 ml/minute with 90/5/5 acetonitrile/water/methanol at 37°C. GC analyses were done on a Shimadzu GC-14A heated from 60 to 190°C and eluted at 1.5 ml/minute. GC/MS was done on a JEOL SX-102 heated from 100 to 300°C/minute. GC and GC/MS were both done using a 30 m x 0.32 mm ID capillary column with 0.25µ film thickness of DB-5.

Chloride titrations were done using the Schoeniger Combustion Method and Compleximetric Titration of Bromine and Chlorine.¹³

Typical Reaction of 1,2,3,4-Tetrachlorobenzene with Formic Acid in the Presence of Pd/C and Sodium Carbonate

A three-necked 250 ml round bottom flask equipped with pressure equalizing dropping funnel, magnetic stirring bar, thermometer and condenser fitted with nitrogen inlet was initially charged with 10% Pd/C (0.2g), followed by water (0.2g, 11.1 mmol). Sodium carbonate (10.0g, 94.3 mmol) was added followed by toluene (25 ml), 1,2,3,4-tetrachlorobenzene (1.00g, 4.63 mmol, 18.5 equivalents of Cl) and 4-phenyltoluene (0.367g, 2.18 mmol, as an internal standard). The reaction mixture was heated to 90°C and then formic acid (88%, 4.00g, 76.5 mmol) diluted with water (4.00g, 0.222 mol) was added dropwise over 60 minutes. Samples (0.1 ml) were removed for analysis and diluted with 1.0 ml methylene chloride and analyzed by capillary GC. The sample was eluted using a temperature program described above. The reaction was monitored until none of the peaks for mono, di, tri or tetrachlorobenzenes were observable. Typically, the reaction was complete in ≤5 minutes after the 1 hour addition of the formic acid/water mixture. After cooling to room temperature, the toluene layer was decanted and 25 ml water was added to the residue with stirring to insure dissolution of the sodium chloride and other soluble inorganic materials. The water layer was then filtered, the residue was washed 2-3 times with 5 ml water each and the washes added to the water layer. The combined water layer was then weighed and analyzed for chloride ion via titration using the method described above. Results usually indicated complete removal of chloride within experimental error: 0.6453g Cl⁻ observed, 0.6577g Cl⁻ theoretical, 98.1% recovery of Cl. The organic layer was analyzed by GC and in some cases GC/MS to determine if any chlorine-containing species still remained. GC/MS revealed the presence of some hydrocarbons (C7H14, C8H16, C8H18, and two compounds with a m/z = 174. The m/z = 174 peak did not contain any chlorine atoms, nor did any of the other peaks in the GC trace.

Typical Reaction of Aroclor 1254 with Formic Acid in the Presence of Pd/C and Sodium Carbonate

A three-necked 250 ml round bottom flask equipped with pressure equalizing dropping funnel, magnetic stirring bar, thermometer and condenser fitted with nitrogen inlet was initially charged with 10% Pd/C (0.2g) followed by water (0.2g, 11.1 mmol). Sodium carbonate (8.0g, 75.5 mmol) was added followed by toluene (30 ml), Aroclor 1254 (1.00g, 15.2 equivalents of Cl assuming 54% Cl by weight) and 4-phenyltoluene (0.367g, 2.18 mmol, as an internal standard). The reaction mixture was heated to 90°C and then formic acid (88% in water, 3.60g, 68.9 mmol) diluted with water (5.0 ml) was added dropwise over 35 minutes. Samples (0.1 ml) were removed for analysis and diluted with 1.0 ml methylene chloride and analyzed by capillary GC. The reaction was monitored until none of the peaks for Aroclor 1254 were observable. Typically, the reaction was complete in 60 minutes after the 35 minute addition of the formic acid/water mixture. After cooling to room temperature, the toluene layer was decanted and 25 ml water was added to the residue with stirring to insure dissolution of the sodium chloride and other soluble inorganic materials. The water layer was then filtered, the residue was washed 2-3 times with 5 ml water each and the washes added to the water layer. The combined water layer was then weighed and analyzed for chloride ion via titration using the method described above. Results usually indicated complete removal of chloride within experimental error: 0.497g Cl⁻ observed, 0.540g Cl⁻ theoretical, 92.0% recovery of Cl. The organic layer was analyzed by GC and in some cases by GC/MS techniques to determine if any chlorine-containing species still remained. GC/MS revealed the presence of some hydrocarbons and trace levels of chlorinated aromatics. The major impurity had an m/z = 160 whose molecular ion and electron impact fragmentation pattern were consistent with phenylcyclohexane.

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