

Hydrogenolysis of Polychlorinated Biphenyls by Sodium Borohydride with Homogeneous and Heterogeneous Nickel Catalysts

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The hydrogenolysis (hydrodechlorination) of a series of pure PCB congeners with sodium borohydride was studied. In the absence of nickel compounds, very little reaction occurred, but in the presence of solid Raney-type nickel or in the presence of a soluble Ni(0)triphenylphosphine complex, extensive hydrogenolysis occurred at ambient temperatures in DMF. The selectivity of one congener versus another was studied and found to be low. The selectivity for 2-, 3-, and 4-chloro displacement from di- and trichlorobiphenyls in the presence of Ni(0) complexes, however, was found to be high. The selectivities are interpreted with respect to the known mechanism of oxidative addition of aryl halides with Ni(0) complexes.

Introduction

Aromatic chlorides are notoriously unreactive and long-lived once released into the biosphere. While aerobic bacteria can oxidize aryl halide compounds, such as polychlorinated biphenyls (PCBs) (1-4), these kinds of compounds tend to accumulate in anaerobic environments. In recent years, several studies have shown that anaerobic bacteria can cause bioremediation of PCBs by systematic hydrodechlorination until only the relatively innocuous mono- and dichlorobiphenyls remain (5-9). Studies of the metabolic pathways of these organisms are difficult with respect to culturing, isolating, and characterizing these air-sensitive bacteria (7, 10, 11). Isolation and characterization of the cell-free enzymes which effect hydrodechlorination in these "undefined anaerobic communities" has now been reported (10). The bacteria discovered to date are somewhat source specific in that they are selective for different halogens (Cl and Br) and for different isomers of the PCB congener mixture (6, 10-13). While Co- and Ni-containing porphyrins (corrinoids and Factor₄₃₀) have recently been suggested as likely catalysts or coenzymes in these anaerobic bacteria (10), and naturally occurring transition metal complexes appear to be involved for this reductive dechlorination (9, 14), the reaction is not yet completely understood.

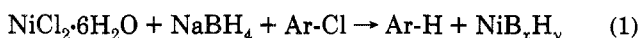
One of the distinctive variations observed with bacteria from different sources is that there is a preference for hydrogenolysis of PCB congeners to occur at specific structural positions, such that the 2-(ortho) chlorines in most congeners are found to be very unreactive, with the 3-(meta) chlorines often found to be the most reactive, although some recent reports have shown a specificity for the 2-(ortho) chlorines for some bacteria (5, 28). While this congener specificity has been extensively documented (5, 6, 8, 10, 12, 13), the question remains whether the selectivity observed is a result of bacterial source, enzyme and coenzyme variations, enzyme active-site structural differences, intrinsic PCB structural differences, or some combination of these. By examining PCB behavior in a model system reaction, which appears to mimic the biochemical route, it might be possible to find the intrinsic

structural requirements of PCB congeners for a similar abiotic reaction.

While there are few reactions which activate aromatic halogens toward displacement by hydrogen, the known systems are mainly those involving organometallic or photochemical/free-radical mechanistic pathways (15, 16). One of the best-studied systems may also have significant biochemical analogues: the nickel(0) tetrakis(phosphine) oxidative addition/reductive elimination reaction, which has been well-studied by Kochi et al. (17) and is outlined in Scheme 1.

The key step is that between the Π -complex and the cage pair. The reaction causes a gain of one electron to the aryl chloride to form a radical anion, followed by another one-electron transfer in a subsequent fast step to form the oxidative addition product. Previous work in our laboratory has shown that the resulting Ni(II) complexes can be reduced by NaBH₄ in DMF to yield dechlorinated aromatics at mild temperatures (18).

In the absence of phosphine ligands, Ni(II) salts are reduced to a colloidal "nickel boride" Raney nickel-type heterogeneous catalyst, effective for both alkene hydrogenation and aryl halide hydrogenolysis (19, 20):



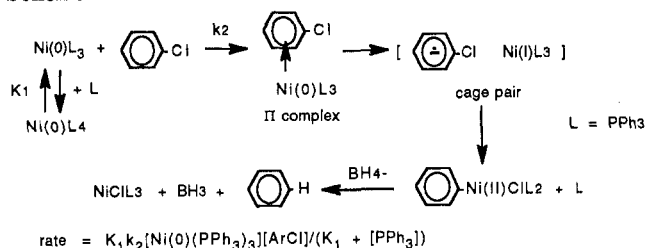
This paper reports the results of both the heterogeneous nickel boride and the homogeneous Ni(0)(PPh₃)₄ hydrogenolysis reactions of NaBH₄ in DMF with a series of mono-, di-, and trichlorobiphenyls. Pure PCB congeners with chlorines on only one biphenyl ring were synthesized and purified; 13 congeners were examined with respect to selectivity and relative rate of hydrogenolysis. The results are compared between the two nickel systems (heterogeneous and homogeneous) and to the previously reported anaerobic bacterial results.

Experimental Section

Synthesis. The three monochlorobiphenyls were purchased from Lancaster Chemical Co. and found to be 98.8% pure or better. Eleven pure congeners of the di- and trichlorobiphenyls with all chlorines on one phenyl ring were all synthesized. The synthesis were all accomplished by either the (a) decarboxylation of the benzoyl peroxide (21) or (b) deamination of the aniline derivative (the Cadogan Reaction) (22) in the solvent benzene. The yields from (a) were often poor (1-15%), but the purity was very high (98-99%). The yields from method (b) were somewhat better (5-20%), and the purity (greater than 97%) was about the same after vacuum sublimation.

Analysis. Capillary column gas chromatography was performed to determine preparative yields and purities, as well as to identify and quantify reaction products. A Hewlett-Packard 5890 GC fitted with a 25 m × 0.320 mm Ultra-1 column and flame-ionization detector (FID) was used for all analyses. Peak areas were determined by a Hewlett-Packard 3390 reporting integrator. UV-Vis

Scheme 1



spectroscopy was performed on the homogeneous Ni(0) complex with a Shimadzu Model UV-3101PC.

Nickel Boride Hydrogenolysis of PCBs. Nickel chloride hexahydrate (Mallinckrodt) was dissolved in DMF in a 10–15 mL round-bottom flask which had been previously flushed with nitrogen gas. The PCB congener was added, followed by sodium borohydride (Aldrich) solid or in DMF solution. The formation of an intermediate black suspension and some effervescence was always observed. GC analyses were then performed at regular intervals after quenching aliquots with 3% aqueous hydrogen peroxide and centrifuging the black solid.

(Triphenylphosphine)nickel(0) Complex Hydrogenolysis of PCBs. (a) *Zinc Dust Method.* The Tolman method (23) was used to prepare a solution of Ni(0)(PPh₃)₄. After excess zinc dust was filtered under nitrogen from hot toluene/hexane, the UV-Vis spectrum in DMF was determined to verify formation of the blood-red complex. The synthesis was repeated using an equivalent amount of sodium borohydride instead of zinc dust. The UV-Vis spectrum in DMF was the same. Aliquots of this solution were then transferred to a nitrogen sparged and flushed solution of the PCB congener in DMF. Additional sodium borohydride was then added as desired, and samples were withdrawn at regular intervals for GC analysis. The samples were quenched with excess aqueous 3% hydrogen peroxide before analysis.

(b) *In Situ Method.* Bis(triphenylphosphine)nickel(II) dichloride was prepared by the method of Venanzi (24). This yellow air-stable solid complex was dissolved in DMF to form an aqua-blue solution, 2 equivs of triphenylphosphine was added, the solution was flushed with nitrogen, and then sodium borohydride was added either as the solid or in a DMF solution (18). The UV-Vis spectrum of the red solution that formed after a few minutes confirmed the formation of the Ni(0) complex. For hydrogenolysis reactions, the PCB congener was added after the triphenylphosphine and before the sodium borohydride. GC analysis was performed as above.

(c) *Nickel Chloride Method.* A variation on the in situ method (b) above was performed with some reactions. Nickel chloride hexahydrate was dissolved in DMF, 4 equivs of triphenylphosphine was added, the solution was sparged and blanketed with nitrogen, the PCB congener was then added, and then sodium borohydride was added. A rusty-brown solution formed which changed to blood-red upon addition of a slight excess of sodium borohydride. GC analysis was performed as above.

Regardless of the source of nickel, the distinctive blood-red Ni(0) complex changed over the time of the reaction to a rusty-brown color followed by a change to a pale-green color. No precipitates were observed during the progress of the reaction. If carbon monoxide was substituted for nitrogen, no red complex was formed and no PCB hydrogenolysis occurred.

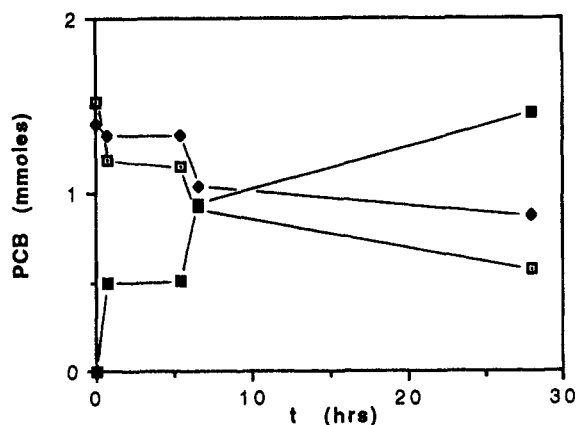


Figure 1. Intermolecular selectivity of dechlorination of 2- and 4-PCB by nickel boride. A solution of 7.5 mmol of NaBH₄ in 2.0 mL of ethanol was added dropwise to a solution of 3.0 mmol of NiCl₂·6H₂O, 1.52 mmol of 2-PCB, and 1.40 mmol of 4-PCB in 5.0 mL of DMF at room temperature and under nitrogen at *t* = 0 min. Additional NaBH₄ (7.5 mmol) was added at 5.5 h. Symbols: (□) 2-PCB, (◆) 4-PCB, and (■) BIPh.

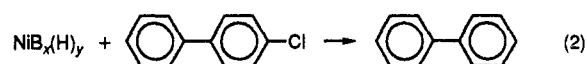
Results

Sodium Borohydride as Hydrogenolysis Reagent.

It had been previously observed in our laboratory (25) that NaBH₄ causes the hydrogenolysis (dechlorination) of mono- and dichlorobiphenyls without catalysts. Several experiments were performed with 2,4-dichlorobiphenyl and NaBH₄ in DMF (as the solvent). Reactions at both 25 and 50 °C were performed with small conversions to 2-chloro- and 4-chlorobiphenyl, with some biphenyl itself also being produced. However, the reaction was very slow under these conditions (15–20 h), and the dechlorination yields were small (1–5%), so this method of hydrogenolysis was not pursued.

Nickel Boride as Hydrogenolysis Catalyst. Nickel chloride solutions in ethanol, methanol, water, or DMF can be reduced by NaBH₄ to a black colloidal material known as “nickel boride”, which possesses a reactive form of hydrogen on the surface of the solid that is capable of causing both hydrogenation and hydrogenolysis reactions (19, 20), similar to the well-known “Raney” nickel heterogeneous catalysts.

The nickel boride surface hydrogen does readily hydrogenolyze aromatic halogens, including chlorine (eq 2).



The reaction was performed with a number of the mono- and dichlorobiphenyls to determine the stoichiometry and selectivity of this surface reaction. Although performing kinetics with this reaction is difficult, due to the heterogeneous nature of the catalyst, the dependence of the overall rate and yield of dechlorinated products was monitored with respect to the mole ratios of the reagents. These relationships can be seen in Figures 1 and 2. The dependence of both the amount of Ni and the amount of borohydride was studied, but the optimum ratio was not obvious. Even though both nickel chloride and sodium borohydride were present in significant excess, quantitative (100%) yield of biphenyl was seldom observed. The reasons for this may be the following: (1) Some NaBH₄ is consumed to reduce the Ni(II) salt to NiB_x(H)_y; the amount of NaBH₄ remaining after this occurs is then the

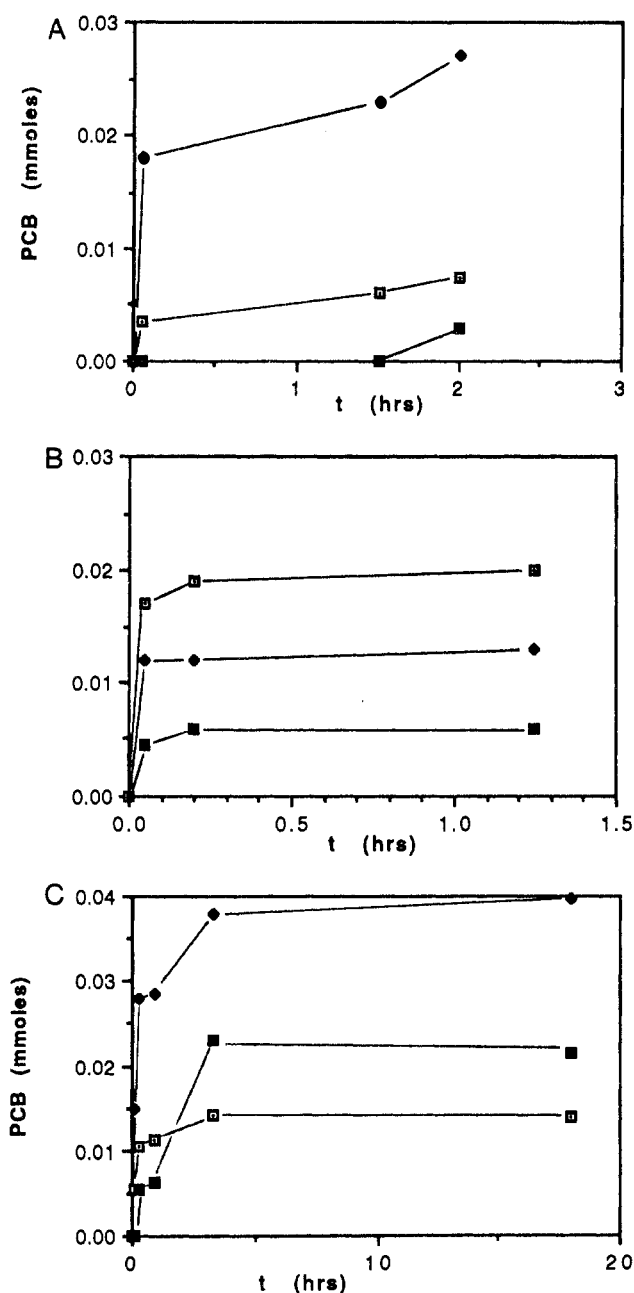
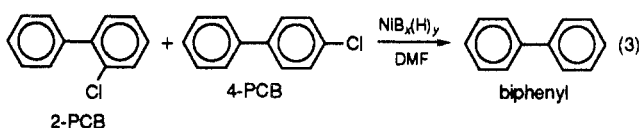


Figure 2. Selectivity of dechlorination of 2,4-PCB by nickel boride. (A) A solution of 0.75 mmol of NaBH_4 in 2.0 mL of ethanol was mixed with 0.30 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.15 mmol of 2,4-PCB in 5.0 mL of DMF dropwise at room temperature under nitrogen. Additional NaBH_4 (0.75 mmol) was added at 1.5 h. Symbols: (\square) 2-PCB, (\blacklozenge) 4-PCB, and (\blacksquare) BiPh. (B) A solution of 0.15 mmol of 2,3-PCB was reacted as in panel A. Symbols: (\square) 2-PCB, (\blacklozenge) 3-PCB, and (\blacksquare) BiPh. (C) A solution of 0.37 mmol of NaBH_4 in 2.0 mL of ethanol was added dropwise to a solution of 0.15 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.075 mmol of 3,4-PCB at room temperature and under nitrogen at $t = 0$ min. Additional NaBH_4 (0.37 mmol) was added at 0.87 h. Symbols: (\square) 3-PCB, (\blacklozenge) 4-PCB, and (\blacksquare) BiPh.

source of hydrogen for the hydrogenolysis. (2) The $\text{NiB}_x(\text{H})_y$ catalyst contains a significant amount of bulk (nonsurface) nickel metal which is not available for the hydrogenolysis reaction; the amount of nickel in this form is not known, since this depends upon particle size and porosity of the solid catalyst, and this information is difficult to determine. (3) The nickel boride that forms appears to catalyze the decomposition of NaBH_4 , as indicated by the observed effervescence of hydrogen gas.

Figure 1 indicates that this reaction is complex in terms of rates: there appears to be an initial fast reaction (during the formation of the nickel boride), which is then followed by a much slower hydrogenolysis.

In order to obtain a comparison between PCBs rates of reaction, relative rates were measured by performing the reaction under competitive conditions: equimolar mixtures of 2-PCB and 4-PCB were hydrogenolyzed with nickel boride. These two isomers yield the same product (biphenyl), so observing the decreases in concentration of each simultaneously would indicate whether there is a structural dependence for the hydrogenolysis (Figure 1):



This data indicates that the overall hydrogenolysis reaction has a slight preference for dechlorinating the 2-chloro position over the 4-chloro position by a factor of almost 2:1. This is the intermolecular selectivity.

If both the 2- and 4-positions are occupied by chlorine on the same aromatic ring of the same molecule (2,4-PCB), then it would be expected that three distinct products would be formed and could be independently observed by gas chromatography, 2-PCB, 4-PCB, and biphenyl:

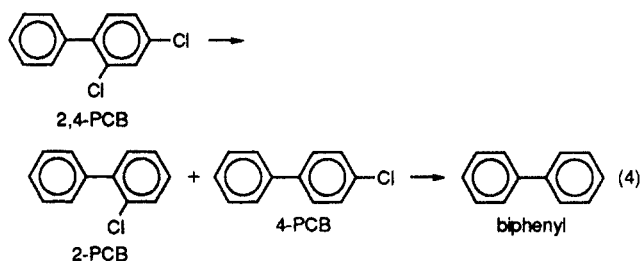
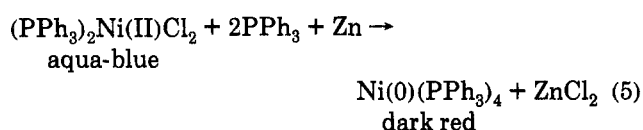


Figure 2A confirms this expectation and further shows that the 2-chloro position is more reactive than the 4-chloro position, by a factor of ca 4:1. This is the intramolecular selectivity. A similar study was done for 2,3-PCB and 3,4-PCB. The data for these are also shown in Figure 2B,C. The 2,3-PCB isomer shows a preference for reaction at the 3-chloro position vs the 2-chloro position (1.5:1), and the 3,4-isomer shows a preference for reacting also at the 3-position vs the 4-position (3:1). The intramolecular selectivities exhibit this trend: the less conformationally crowded 3-chloro is more reactive than the hindered 2-chloro, but 2-chloro is also faster than 4-chloro. The overall intramolecular selectivities for dechlorination of PCBs by nickel boride therefore are 3-chloro > 2-chloro > 4-chloro.

Tetrakis(triphenylphosphine)nickel(0) as Hydrogenolysis Reagent. A closely related catalyst system to the nickel boride heterogeneous catalyst described above is that of the soluble (homogeneous) Ni(0) complex tetrakis(triphenylphosphine)nickel(0) (17, 21). This blood-red complex can be made from bis(triphenylphosphine)nickel(II) dichloride (an air-stable complex) by the action of triphenylphosphine in acetonitrile, followed by reduction of nickel with zinc dust:



This complex is air sensitive [oxygen reoxidizes it to a

Table 1. Hydrogenolysis of 4-PCB by Ni(0)(PPh₃)₄ and NaBH₄ in DMF at 25 °C

[Ni(0)(PPh ₃) ₄] ₀ ^a (mM)	[NaBH ₄] ₀ (mM)	[4-PCB] ₀ (mM)	% BiPh	[BiPh]/ [Ni]	
Section A. Stoichiometry of Ni to 4-PCB					
2.4	69	13	54.8	2.96	
2.4	69	127	5.6	2.96	
4.8	66	121	11.3	2.98	
6.6	63	116	15.8	2.77	
Section B. Stoichiometry of NaBH ₄ to 4-PCB					
6.7 ^a	0	223	0.8		
6.7	55	111	16.2	2.7	
10.9	4.3	22.1	20.0 ^b		
12.8	14	16.6	41.0 ^b		
12	22	15.6	51.0 ^b		
Section C. Effect of the Source of Nickel					
4.5 ^c	5.8	10	<1		
4.4	8.5	10	3.6		
4.4	11.1	9.8	6.7		
4.3	13.6	9.6	11.5		
21 ^d	5.8	10	<1		
17	32.8	8.3	76.1		
Section D. Effect of PPh ₃					
[Ni(0)(PPh ₃) ₄] ₀ (mM)	[NaBH ₄] ₀ (mM)	[4-PCB] ₀ (mM)	% BiPh	PPh ₃ (mM)	[PPh ₃]/ [Ni]
5.1 ^c	161	23	13.9	3.1	2.6
3.9	132	18	28.6	7.8	4.0
11.8	23.8	26.7	11.5	47.2	6.0

^a Prepared by the zinc dust method; [PPh₃]/[Ni] = 4. ^b 7.1% (volume) ethanol added to the DMF solvent. ^c Prepared in situ from (PPh₃)₂Ni(II)Cl₂ and PPh₃ by the NaBH₄ method. ^d Prepared in situ from NiCl₂·6H₂O and 4 equivs of PPh₃ by the NaBH₄ method.

Ni(II) form] but is not sensitive to water or other hydroxylic solvents like alcohols. In our laboratory, it was found that NaBH₄ could serve as the reducing agent instead of the solid zinc dust, thus obviating the need to filter the resulting air-sensitive solution after the preparation (18). The hydrogenolysis behavior of this complex toward 4-chlorobiphenyl (4-PCB) is shown in Table 1.

Table 1A shows the stoichiometric relationship of the Ni(0) complex to the 4-PCB: as long as there is an excess amount of NaBH₄ present, the Ni(0) complex will hydrogenolyze up to three PCB bonds, but not more. This indicates that the Ni(0) complex is not a catalyst, but is rather a reagent in the reaction. It is apparently not reformed after the initial oxidative addition step which breaks the C-Cl bond. This may be due to the production of chloride ion and/or borane derivatives in the reaction, which could displace the stabilizing triphenylphosphine ligands. The stoichiometry of NaBH₄ can be seen in Table 1B, where no reaction occurred without some NaBH₄ being present, and the amount of hydrogenolysis depended on the amount of NaBH₄, in a proportional relationship.

The hydrogenolysis did not depend on the original form of the Ni, as can be seen in Table 1B,C. Whether NiCl₂·6H₂O, (PPh₃)₂Ni(II)Cl₂, or Ni(0)(PPh₃)₄ was used as the reagent, the results were about the same, as long as a mole ratio of 4:1 for PPh₃ to Ni was maintained. Without any PPh₃, nickel was simply reduced to nickel boride, as described above. When less than a 4:1 ratio existed, the hydrogenolysis yield was reduced, as can be seen in Table 1D. When more than the 4:1 ratio was employed, the complex was longer-lived, but the yield of biphenyl was reduced. This suggests that the Ni(0) complex is formed in a short time within (in situ) the

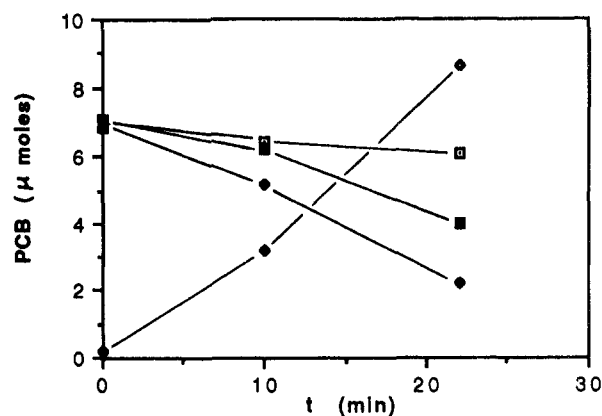


Figure 3. Dechlorination of 2-, 3-, and 4-PCB by Ni(0). A solution of 65 μmol of Ni(0)(PPh₃)₄ and 61 μmol of NaBH₄ in 1.0 mL of DMF was added to a 100-μL solution of 2-PCB, 3-PCB, and 4-PCB at room temperature under nitrogen at t = 0 min. Symbols: (□) 2-PCB, (◆) 3-PCB, (◻) 4-PCB, and (◇) BiPh.

Table 2. Intermolecular Selectivities for Dechlorination of PCBs by Ni(0)(PPh₃)₄ and NaBH₄

PCB congener	rate of dechlorination relative to 4-PCB ^a
2-	0.52 ± 0.03
3-	1.90 ± 0.13
4-	(1.00)
2,4-	0.7 ± 0.2 ^b
2,3-	10 ± 2
3,4-	1.6 ± 0.3 ^c
2,5-	1.0 ± 0.05
3,5-	2.5 ± 0.2
2,6-	0.7 ± 0.2
2,3,4-	^d
2,3,5-	1.5 ± 0.2
2,4,5-	2.3 ± 0.5
3,4,5-	5.1 ± 0.5

^a Measured as the rate of decrease of the congener vs the rate of decrease of 4-PCB, using mixtures of near-equimolar initial concentrations. ^b Measured as the rate of decrease of the congener vs the rate of decrease by 3-PCB, using mixtures of near-equimolar initial concentrations, normalized to 4-PCB by multiplying by 1.9. ^c Measured as the rate of decrease of the congener vs the rate of decrease of 2-PCB, using mixtures of near-equimolar initial concentrations, normalized to 4-PCB by multiplying by 0.52. ^d Not determined.

reaction system, immediately before hydrogenolysis, and that the reactive form is the trisphospine, formed by dissociation of the tetrakisphospine (17), as shown in Scheme 1. As with the nickel boride system, the relative rates of hydrogenolysis (the intermolecular selectivities) were determined by performing the hydrogenolysis under competitive conditions: an equimolar mixture of 2-, 3-, and 4-PCB was reacted with the nickel complex in the presence of NaBH₄. The results are shown in Figure 3. Here, the relative selectivities were found to be 3-PCB > 4-PCB > 2-PCB with a ratio of about 2:1:0.5. Notice that this order is not the same as for the nickel boride reaction, where the most crowded 2-PCB was faster than the 4-PCB.

The relative rates compared to a selected monochlorobiphenyl for the various dichlorobiphenyls and trichlorobiphenyls were determined in order to obtain the intermolecular selectivities for each congener. These are reported in Table 2.

The intramolecular selectivities were also determined. The selectivity data for these congeners is presented in

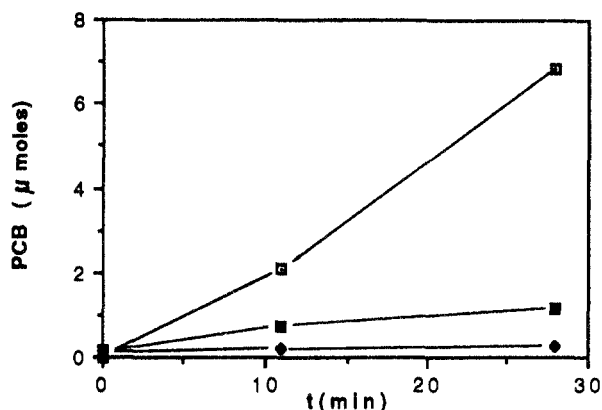


Figure 4. Dechlorination products from 2,4-PCB and Ni(0). Symbols: (□) 2-PCB, (◆) 4-PCB, and (■) BiPh. A 100- μ L solution of 2,4-PCB (23.3 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 75 μ mol of NaBH₄ in 2.0 mL of DMF at room temperature under nitrogen at $t = 0$ min:

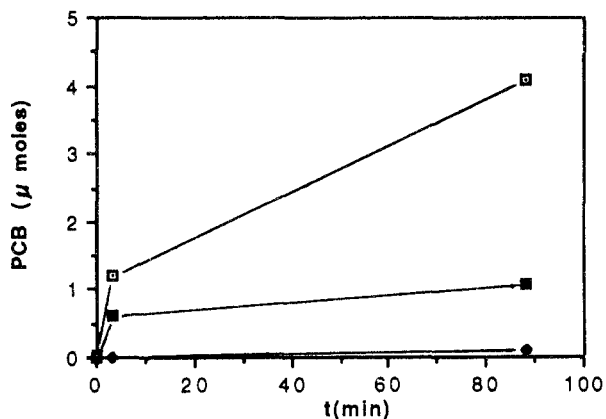
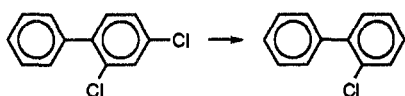
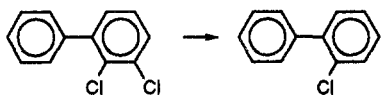


Figure 5. Dechlorination products from 2,3-PCB and Ni(0). Symbols: (□) 2-PCB, (◆) 3-PCB, and (■) BiPh. A 100- μ L solution of 2,3-PCB (21.9 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 79 μ mol of NaBH₄ in 2.2 mL of DMF at room temperature under nitrogen at $t = 0$ min:



Figures 4–11. The intramolecular selectivities are reported in Table 3.

The intermolecular selectivities showed little preference for one congener over another. For example, the 2,6-PCB is nearly as reactive as the 4-PCB congener and the 3,5-PCB is only slightly faster than the 4-PCB.

The intramolecular selectivities of the dichlorobiphenyls with the nickel(0) complex indicate that the most significant structural effect on reactivity is that 2-chloro is hydrogenolyzed much slower than either 3- or 4-chloro groups, while the 3-chloro is about the same or a bit faster than the 4-chloro position.

The selectivities of the trichlorobiphenyls with nickel(0) reveal a similar trend, where 2-chloro was always hydrogenolyzed slowest compared to chloro groups at either the 3- or 4-positions. In addition, the 3- and 4-chloro

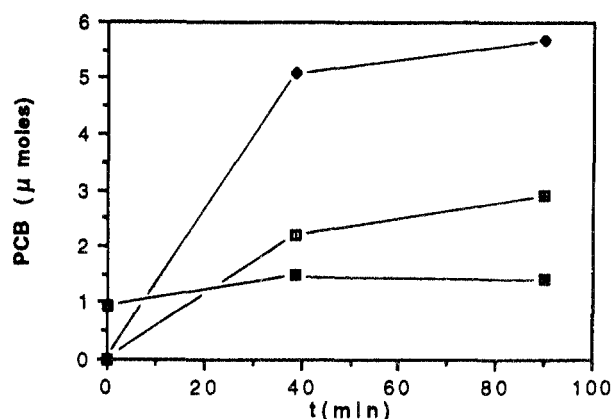


Figure 6. Dechlorination products from 3,4-PCB and Ni(0). Symbols: (□) 3-PCB, (◆) 4-PCB, and (■) BiPh. A 100- μ L solution of 3,4-PCB (30.1 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 63 μ mol of NaBH₄ in 1.1 mL of DMF at room temperature under nitrogen at $t = 0$ min:

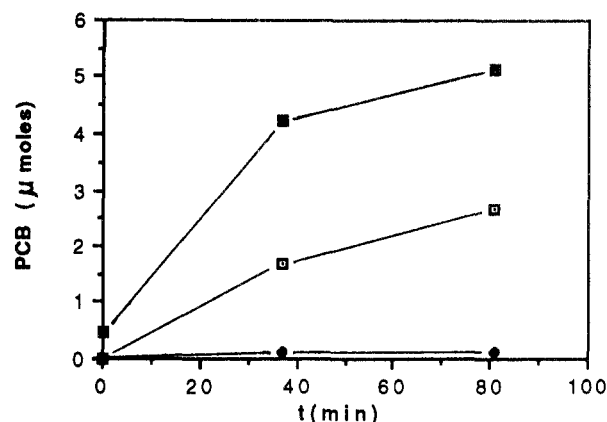
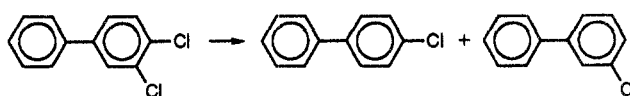
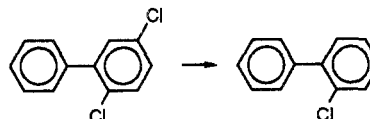


Figure 7. Dechlorination products from 2,5-PCB and Ni(0). Symbols: (□) 2-PCB, (◆) 3-PCB, and (■) BiPh. A 100- μ L solution of 2,5-PCB (18.6 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 94 μ mol of NaBH₄ in 2.3 mL of DMF at room temperature under nitrogen at $t = 0$ min:



groups were hydrogenolyzed at similar rates, but the least crowded chloro was always replaced first, regardless of whether it was at the 3- or 4-position, with very high selectivities (more than 50:1). In all cases of di- and trichlorobiphenyls, a significant amount of biphenyl was produced as soon as the reaction began, indicating that polyhydrogenolysis occurs as well as a stepwise sequential hydrogenolysis.

Discussion

Sodium borohydride, NaBH₄, which has been shown elsewhere to hydrogenolyze alkyl halides (26), will do the same reaction with aromatic halides (including PCBs), but only very slowly. This reaction may be similar to the

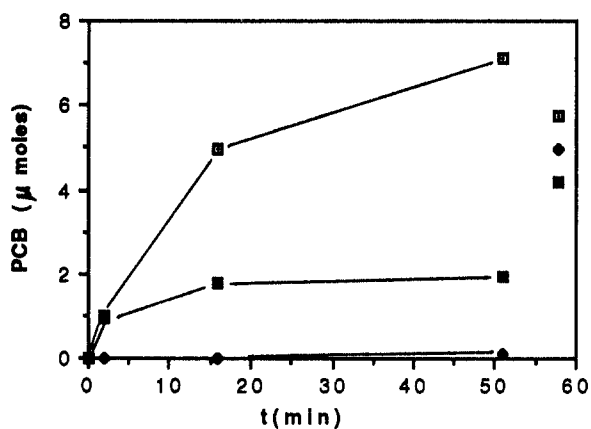


Figure 8. Dechlorination products from 2,3,4-PCB and Ni(0). Symbols: (□) 2,3-PCB, (◆) 2,4-, 3,4-, 2-, 3-, and 4-PCB, and (●) BiPh. A 100- μ L solution of 2,3,4-PCB (24.3 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 94 μ mol of NaBH₄ in 2.0 mL of DMF at room temperature under nitrogen at $t = 0$ min:

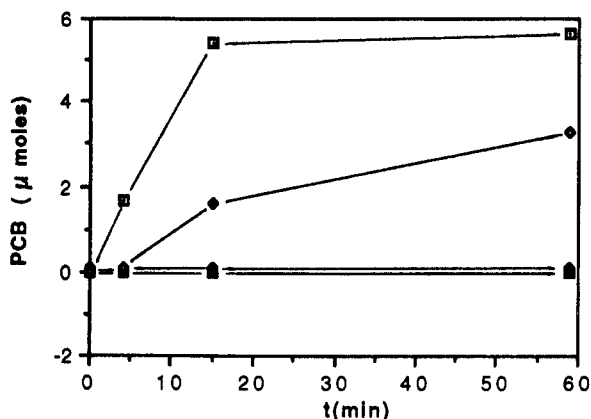
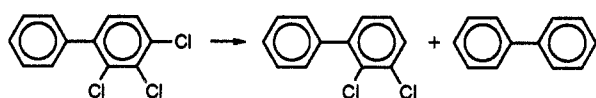
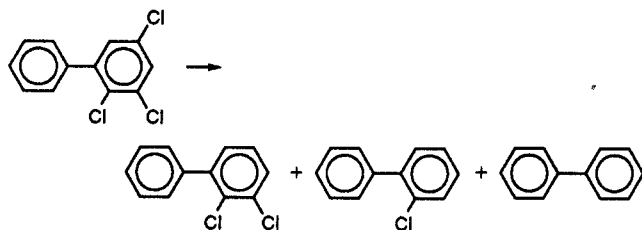


Figure 9. Dechlorination products from 2,3,5-PCB by Ni(0). Symbols: (□) 2,3-PCB, (◆) 3,5-PCB, (●) 2,5- and 3-PCB, and (◇) BiPh. A 100- μ L solution of 2,3,5-PCB (23.6 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 94 μ mol of NaBH₄ in 2.3 mL of DMF at room temperature under nitrogen at $t = 0$ min:



photochemical hydrogenolysis previously reported (27). Nickel boride is an effective catalyst for hydrogenolysis of PCBs, although the borohydride is apparently not always used very efficiently, since some decomposes to hydrogen gas during the reaction. However, the solid catalyst is renewable by adding excess borohydride, and high conversions of PCBs to biphenyl can be achieved. Because this is a heterogeneous catalytic system which depends on the surface area of the catalyst, the stoichiometry and kinetic parameters for the reaction are difficult to reproduce quantitatively.

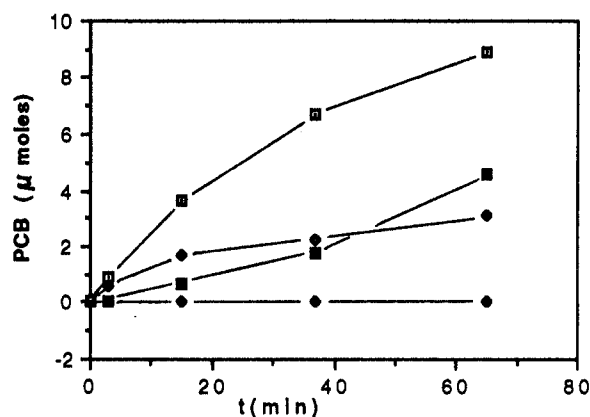


Figure 10. Dechlorination products from 2,4,5-PCB and Ni(0). Symbols: (□) 2,4-PCB, (◆) 3,4-, 2,5-, 3-, and 4-PCB, (●) 2-PCB, and (◇) BiPh. A 100- μ L solution of 2,4,5-PCB (26.2 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 94 μ mol of NaBH₄ in 2.3 mL of DMF at room temperature under nitrogen at $t = 0$ min:

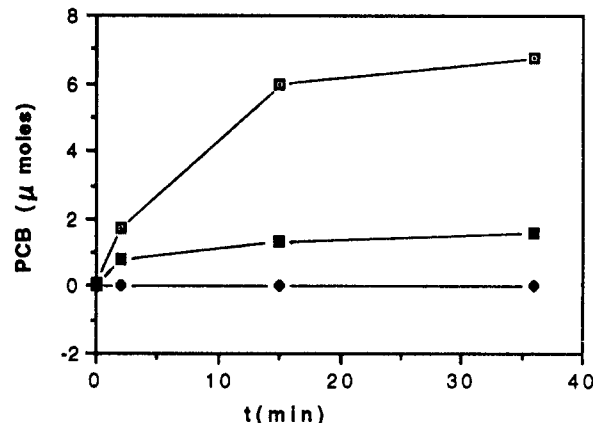
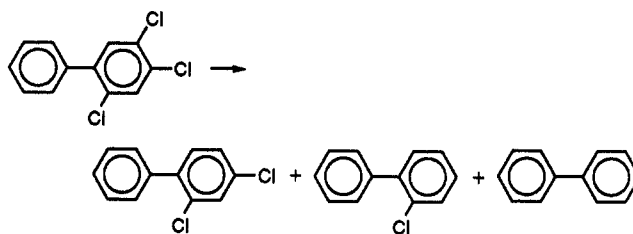
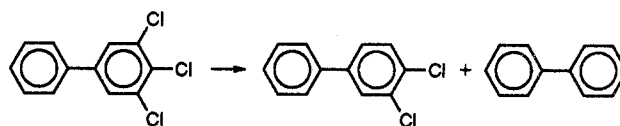


Figure 11. Dechlorination products from 3,4,5-PCB and Ni(0). Symbols: (□) 3,4-PCB, (◆) 3,5-, 3-, and 4-PCB, and (●) BiPh. A 100- μ L solution of 3,4,5-PCB (23.5 μ mol) in DMF was added to a solution of 51 μ mol of Ni(0)(PPh₃)₄ and 94 μ mol of NaBH₄ in 2.3 mL of DMF at room temperature under nitrogen at $t = 0$ min:



The most interesting result from the nickel boride hydrogenolysis reaction is that the more crowded (hindered) 2-chlorines are removed at a rate comparable to those at the 3- and 4-positions. Although the selectivity is not high (a rate range of only 2–4), the results are similar to a previously reported photochemical process (27) and at least one recent report of anaerobic dechlorination (28). The noteworthy thing is that these results are quite different than most of the anaerobic bacterial results (6–13) or the Ni(0) complex data discussed below, where the

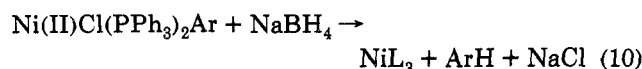
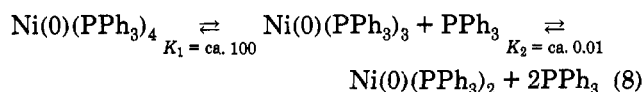
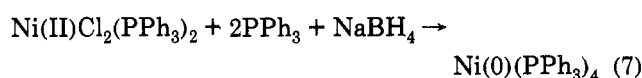
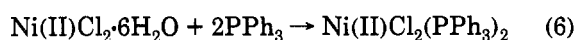
Table 3. Intramolecular Selectivities for Dechlorination of PCBs by Ni(PPh₃)₄ and NaBH₄

PCB congener	relative rate of dechlorination (relative positions) ^a
2,4-	25:1 (4- vs 2-)
2,3-	ca. 40:1 (3- vs 2-)
3,4-	2:1 (3- vs 4-)
2,5-	>50:1 (5- vs 2-)
2,3,4-	>100:1 (4- vs 2- or 3-)
2,3,5-	>100:1 (5- vs 2- or 3-)
2,4,5-	>100:1 (5- vs 2- or 4-)
3,4,5-	>100:1 (3- and 5- vs 4-)

^a Measured as the rate of formation of monodechlorinated congeners. In most cases, one main congener was formed in preference to all others, except for 3,4-PCB.

preferred position of hydrogenolysis is either the 3- or the 4-position.

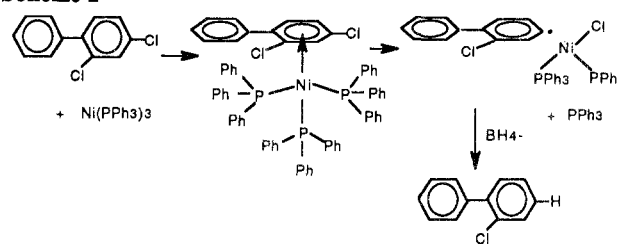
The Ni(0)(PPh₃)₄ complex is an effective and rapid-acting reducing agent for PCBs in DMF, but it is not a catalyst and is instead a stoichiometric reagent. One mole of the Ni(0) complex will hydrogenolyze up to 3 mol of aromatic C–Cl bonds to C–H bonds, but not more. No matter how much borohydride is added, the Ni(0) complex is apparently converted to some nonreactive form, although still soluble and not a nickel boride variation. The source of nickel seems to make little difference, since the reaction works equally well whether the nickel is introduced as the previously prepared Ni(0)(PPh₃)₄ complex or is prepared in situ by reduction of either Ni(II)Cl₂(PPh₃)₂ or even of Ni(II)Cl₂·6H₂O, as long as some triphenylphosphine (PPh₃) is present. The amount of triphenylphosphine is apparently important, since a mole ratio of phosphine to nickel of 3:1 is not as effective as a 4:1 ratio. Table 1, sections B and C, shows that enough borohydride to reduce Ni(II) to Ni(0) is needed and also that the amount of hydrogenolysis depends upon having an additional amount present to provide the hydrogen for hydrogenolysis. The reasons for this stoichiometry may be understood by the reactions outlined below:



Reactions 9 and 10 are the critical steps of this process which lead to the observed hydrogenolysis reactions, where Ar–Cl could be any aryl chloride, including any PCB congener. Previous work (17), supported by the current findings, has shown that the rate expression for Ni(II)Cl(PPh₃)₂Ar formation in reaction 9 has the following form: rate = $K_1 k_2 [\text{Ni(0)(PPh}_3)_3][\text{ArCl}] / (K_1 + [\text{PPh}_3])$

The two equilibria shown in eq 8 indicate the labile nature of the phosphine ligands in the crowded complex (17, 23) and suggest that the hydrogenolysis involves

Scheme 2



dissociation of the three phosphine ligands from the main form of Ni(0), the trisphosphine, resulting in the observed stoichiometry of 3:1. The nature of the final inactive form of nickel is not known, except that it is not the tris- or tetrakis-Ni(0)phosphine complex, nor is it Ni(II)Cl₂ or nickel boride. It is a soluble (homogeneous solution), pale-green complex formed under conditions where the oxidation state should still be low and likely still zero (0). The change of color from the original dark blood-red Ni(0)(PPh₃)₄ ($\epsilon = 3900$ at 500 nm) to an almost colorless form suggests the loss of all phosphine ligands.

The observed selectivities for the hydrogenolysis of PCBs must depend upon the mechanism of reaction 9. Reaction 9 has been shown to be a one-electron transfer from Ni(0) to the C–Cl bond of aryl chlorides, probably preceded by the formation of charge-transfer or π -complex, as shown in Scheme 1 (17).

Since the reaction causes a gain of one electron to the aryl chloride, a negative charge must form on the molecule during this step. The Hammett reaction parameters for this reaction have been determined and found to have a ρ value of 5.5, which indicates a very high negative charge concentration effect on the phenyl group during this process. Such a value precludes direct displacement of the phenyl group from the C–Cl bond by attack of Ni(0) on chlorine and supports coordination of Ni with the aryl ring during the electron-transfer reaction, i.e., π -complex formation (17).

The difference between the observed inter- and intramolecular selectivities may also be understood in the context of this mechanism. While the rate differences among 2-, 3-, and 4-chloro positions are not very great when the competition is between different molecules as intermolecular selectivities (e.g., 2-PCB vs 3-PCB), they are very high when these same positions are competing within the same molecule as intramolecular selectivities (e.g., 2,3-PCB). Coordination to form the π -complex should occur on the face of the planar phenyl rings, and the various isomers and congeners should not exhibit much difference at this stage, since the chloro groups are held at right angles to the incoming Ni(0) complex by the structure of the phenyl groups. When the electron is transferred to the C–Cl bond, the coordination with Ni must also change from the face-centered complex to a corner-coordinated cage pair or perhaps a σ -complex (Scheme 2). After this happens, severe crowding of neighboring chloro and phenyl groups in the PCBs with the remaining triphenylphosphine ligands of Ni would force selection of the least-crowded chloro group when more than one is available. This is exactly what is observed.

Conclusion

These results are somewhat different from those observed for anaerobic degradation of PCBs, although some

similarities can be found. For example, the very slow intramolecular reactivity of 2-(ortho)chloro groups with the Ni(0) complex in polychlorobiphenyls is very similar to that found for many anaerobic bacteria studied to date. Hudson River sediment (which contains such bacteria) can be incubated at 80 °C, still retain degradation activity, and dechlorinate PCBs at the 3-position in preference to the 2- or 4-positions. However, the native, unheated Hudson River bacteria react at both the 3- and 4-positions in preference to the 2-position (6, 29). It has also been suggested that anaerobic bacteria perform the dechlorination reaction through a sequential one-electron transfer (radical-type) process and, if so, this very likely occurs by a mechanism like the one described above, but this can only be confirmed when the bacteria have been cultured and specific enzymes have been identified (9, 10, 14).

Acknowledgments

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