



Dechlorination of polychlorobiphenyls using NaBH_4 and $\text{NaBH}_4/\text{LiCl}$ at 120–310°C in glyme solvents

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Abstract

High temperature PCB dechlorination (Aroclor 1016) occurred using NaBH_4 alone in tetraglyme at 290–310°C within 2 h in a sealed tube. Aroclor 1016 dechlorination was also quantitatively achieved using $\text{NaBH}_4/\text{LiCl}$ /glyme solvents (di-, tri-, or tetraglyme) at 125–135°C. The best results were obtained by prestirring NaBH_4 , LiCl and the glyme solvent at room temperature before heating at 125–135°C. At equivalent conditions, PCB dechlorination rates were found to depend on solvent in the order: tetraglyme > triglyme > diglyme. At 130°C, Aroclor 1016 can be dechlorinated in $\text{NaBH}_4/\text{LiCl}$ /tetraglyme in 4 h. 2-Chlorobiphenyl and 2,2'-dichlorobiphenyl were the least reactive congeners in dechlorinations with $\text{NaBH}_4/\text{LiCl}$ in diglyme. Competitive dechlorinations with $\text{NaBH}_4/\text{LiCl}$ in diglyme showed 3-chloro- and 4-chlorobiphenyl reacted faster than 2-chlorobiphenyl at 130°C. The reactions were clean with no solvent decomposition in the range of 120–162°C. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorinated organic molecules, especially, PCBs, represent a major environmental problem [1]. PCBs are harmful to both human health and wildlife. Because of these concerns, the development of methods for both the destruction and disposal of PCBs and other chlorinated aromatic compounds has been intensely studied. Over the past several decades, dehalogenations of PCBs and related chlorinated organic compounds have been carried out by many methods such as incineration [2,3], wet air oxidation [4], catalytic dehydrochlorination [5],

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sodium-based reduction [6,7], reaction with superoxide [8], photolysis in the presence of hydrogen donors [9], transition metal-promoted borohydride or alkoxyborohydride reductive dechlorination [10,11], electrolytic reduction [12], nickel-catalyzed hydrogenolysis [13], silylhydride dechlorination [14], amine-promoted titanium complex-catalyzed borohydride dechlorination [15], iron-promoted dechlorination [16], and thermolysis over solid bases like CaO/Ca(OH)₂ [17]. However, none of these techniques has been widely adopted commercially for environmental remediation applications due to one or more limitations of each method. For example, incineration of concentrated chlorinated organic compounds requires special treatments to remove the HCl generated [18]. HCl corrodes the equipment if not removed. In addition, incineration of PCBs and other chlorinated organics often produces more toxic compounds (e.g. dioxins) if it is not carefully controlled. Erickson et al. [19], for instance, reported that combustion of PCBs lead to the formation of small amounts of the most highly toxic polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs). Many of the methods noted above seem impractical for commercial PCB remediation or the remediation of other chlorinated aromatic contaminated materials (such as soils). Thus, other effective methods for dechlorination of PCBs and related chlorinated organic molecules are needed before incineration can be safely carried out.

Recently, Commodor Solutions Technology Inc. (previously Sandpiper Corporation) [20,21] and our group [22–25] have pioneered the ambient temperature, solvated-electron reduction of PCBs, both neat and in wet soils, using Ca/NH₃ and Na/NH₃. In this technique, wet soils were slurried in liquid NH₃ and then either calcium or sodium metal was dissolved. The solvated electrons formed dechlorinated PCBs to biphenyl at far faster rates than the solvated electrons were consumed by water. While this method exhibits promise for environmental remediation, it does require a reaction vessel which contains the autogeneous pressure of ammonia. There remains a need to develop reasonably inexpensive methods to dehalogenate PCBs at ambient pressure using reasonably inexpensive reducing agents and readily applied temperatures. NaBH₄ is a fairly low cost reducing agent with four reducing equivalents per mole, a low molecular weight (38) and ready industrial availability. NaBH₄ and KBH₄ are available in multiton quantities from Rohm and Haas Inc. Thus, we decided to explore its potential in PCB dechlorinations. Sodium borohydride is not known to dechlorinate chloroaromatic compounds [26], except when using transition metal catalysts [13,15]. Despite the fact that NaBH₄ is very thermally stable, its use at high temperatures (120–350°C) has largely been neglected by organic chemists. Instead, a large variety of more expensive and reactive hydrides (e.g. LiAlH₄, NaBHET₃, LiB(NR₂)H₃, NaBH₂(OCHCH₂OCH₃)₂, etc.) have been extensively investigated and applied in functional group reductions [27–40]. Some of these hydrides, such as LiAlH₄, are quite dangerous, and some are more shock sensitive than NaBH₄. Others, like the lithium aminoborohydrides, while more stable (air-stable, thermally stable), are expensive. Therefore, in this study, the reactivity of NaBH₄ at high temperatures was explored where very little information has been published about its reactivity.

We have recently studied the dechlorination of 4-chlorobiphenyl using NaBH₄ in various high boiling inert solvents at elevated temperatures. 4-Chlorobiphenyl was successfully dechlorinated using NaBH₄ at 290–310°C or NaBH₄/LiCl at 120–162°C in glyme solvents [41]. It was shown that lithium borohydride, formed in situ by mixing sodium borohydride and a lithium halide (LiCl or LiBr) in glymes, was a very powerful dechlorinating agent.

For instance, dechlorination of 4-chlorobiphenyl was accomplished at 120–135°C over lithium borohydride (generated in situ by mixing sodium borohydride and lithium chloride or lithium bromide). Curiously, the rate of this dechlorination was significantly enhanced when the reaction mixture was stirred at room temperature for about 20 min before being heated. This method is simple and avoids the need to use a transition metal system such as Ni(0) to carry out dechlorination. Furthermore, it should be environmental friendly. In addition, the cost of using the combination of sodium borohydride and a lithium halide is much less expensive than using commercial lithium borohydride. We now report that the commercial PCB mixture, Aroclor 1016, is readily dechlorinated under these same conditions. This represents a rather simple method to dispose of bulk PCB wastes.

2. Materials and methods

2.1. Materials

The PCB mixture (Aroclor 1016) was obtained years ago from Monsanto Company. NaBH₄, LiCl, diglyme, triglyme and tetraglyme were obtained from Aldrich Chemical Company. 2-Chlorobiphenyl, 3-chlorobiphenyl and 4-chlorobiphenyl were purchased from Lancaster Chemical Company. 2,2'-Dichlorobiphenyl was purchased from Chem Service Inc.

2.2. Apparatus

A gas chromatograph (FID) equipped with a fused-silica bonded-phase capillary column (30 in., 0.25 mm i.d., DB-5) was employed to analyze reaction samples. GC–MS was utilized versus authentic standards when product identification was ambiguous based on GC analysis.

2.3. General sampling procedures

Most experiments were conducted in three-necked reaction flasks, equipped with a thermometer, a condenser, a magnetic stirring bar and a septa, under a nitrogen atmosphere. Docosane was the internal standard (IS) during Aroclor 1016 dechlorinations since it did not overlap with any PCB congener or product peaks in this reaction system. Samples were collected using microliter syringes which contained Teflon-coated plungers with Teflon-coated tips. Multiple injections established excellent repeatability. Samples (0.1–0.4 ml) of each reaction mixture were collected as a function of time during the reaction, quenched with diluted H₂SO₄, extracted with 2 ml of CH₂Cl₂ and then analyzed by GC and GC/MS.

Aroclor 1016 was weighed into Pyrex glass tubes (10 mm i.d., 12 in. long), followed by charging preweighed amounts of NaBH₄ and docosane (IS). Then a specified volume of tetraglyme was added; the tubes were sealed and placed into cylindrical metal tube shields. The annular space between the tube and shield was filled with sand. Then the tubes were placed in an oven preheated to the specified temperature (290–310°C). At the various reaction times, the metal tubes were removed, cooled to room temperature and then to

liquid nitrogen temperature and opened. The solidified reaction mixture was melted and an aliquot (0.1–0.2 ml) was withdrawn by a microsyringe. Aliquots were neutralized with diluted H_2SO_4 , extracted with 2 ml CH_2Cl_2 , and analyzed by GC.

2.4. Dechlorination of Aroclor 1016 using NaBH_4 in di-, tri-, and tetraglyme

A clean 25 ml, oven dried, three-necked flask equipped with a silicone rubber stopper, a thermometer, a magnetic stirring bar and a reflux condenser was used. NaBH_4 (0.384 g, 10 mol) was added to a stirred solution of diglyme (6 ml, 42 mol), Aroclor 1016 (0.1287 g, 0.5 mol), docosane (IS, 14 mg) at 162°C (reflux). Aliquots (0.1 ml) of the reaction mixture were withdrawn by a syringe at appropriate time intervals, quenched with dilute H_2SO_4 , extracted with CH_2Cl_2 and analyzed by GC. The GC temperature program and conditions employed in the analyses were: 30 in., DB-5 capillary column, FID detector; 140°C , 2 min, with subsequent heating at $5^\circ\text{C}/\text{min}$ to 250°C , followed by heating at $30^\circ\text{C}/\text{min}$ to 300°C where it was held for 10 min. About 65% of the Aroclor 1016 disappeared after 180 h when NaBH_4 alone was used in diglyme at 162°C (Table 1, entry 1).

Table 1
Dechlorination of Aroclor 1016 using NaBH_4 in di-, tri-, and tetraglyme

Entry	Reagents ratios (mol) ^a	Temperature ($^\circ\text{C}$)	Time (h)	Dechlorination (mol%) ^b
1	Substrate/ NaBH_4 /diglyme (1/20/84)	162	8	10
			48	37
	Cl/ NaBH_4 /diglyme (1/6.7/28)		96	54
			180	65
2	Substrate/ NaBH_4 /triglyme (1/20/66.4)	216	8	39
			16	57
	Cl/ NaBH_4 /triglyme (1/6.7/22)		48	86
			96	99
3	Substrate/ NaBH_4 /tetraglyme (1/20/54.4)	275	8	43
			16	51
	Cl/ NaBH_4 /tetraglyme (1/6.7/18)		48	56
			96	57
4 ^c	Substrate/ NaBH_4 /tetraglyme (1/10/54.4)	290	1	61
			2	80
			Cl/ NaBH_4 /tetraglyme (1/3.3/18.1)	
5 ^c	Substrate/ NaBH_4 /tetraglyme (1/15/27.2)	310	1	88
			2	99
			Cl/ NaBH_4 /tetraglyme (1/5/9.1)	

^a Substrate refers to the moles of Aroclor 1016 chlorinated biphenyl molecules present vs. the other reagents. Cl refers to the moles of chlorine atoms (present in the Aroclor 1016) vs. the moles of other reagents.

^b Dechlorination (mol%) refers to the total moles of chlorine atoms removed as a percentage of the total chlorine present in the Aroclor 1016 used in the specified reaction. Biphenyl was the only complete dechlorination product detected.

^c The reaction was conducted in a sealed tube.

The same reagent-to-substrate ratio and procedure as entry 1 of Table 1 were used except that triglyme was used instead of diglyme. A 99% of the Aroclor 1016 had reacted after 96 h (Table 1, entry 2).

The same reagent-to-substrate ratio and procedure as entry 1 in Table 1 were used except that tetraglyme was used instead of diglyme. A 57% Aroclor 1016 had reacted after 96 h (Table 1, entry 3).

Aroclor 1016 (0.0644 g, 0.25 mol) was weighed into a Pyrex glass tube (10 mm i.d., 12 in. long), followed by charging NaBH_4 (0.096 g, 2.5 mol). Then tetraglyme (3 ml, 13.6 mol) and docosane (IS, 7 mg) were added; the tube was sealed and placed into a cylindrical metal tube shield and the annular space between the tube and shield was filled with sand. Then the tube was placed in an oven preheated to 290°C and heated for 2 h. The glass tube was then removed from the shield, cooled to liquid nitrogen temperature and opened. The opened tube was allowed to warm to liquify the solidified reaction mixture. An aliquot (0.05 ml) of this liquid was withdrawn by a microsyringe, transferred to a separatory funnel, neutralized with diluted H_2SO_4 and extracted with CH_2Cl_2 and analyzed by GC. The GC temperature program and conditions employed in the analysis were the same as above for entry 1, Table 1. Removal of 80% of the chlorine occurred within 2 h (Table 1, entry 4).

This experiment was conducted by the method described as above for entry 4, Table 1 using Aroclor 1016 (0.1287 g, 0.5 mol), NaBH_4 (0.288 g, 7.5 mol), tetraglyme (3 ml, 13.6 mol) and octadecane (IS, 14 mg). The tube was placed in an oven preheated to 310°C. Substrate dechlorination reached 99% in 2 h (Table 1, entry 5).

2.5. Dechlorination of Aroclor 1016 by $\text{NaBH}_4/\text{LiCl}$ in di-, tri-, and tetraglyme

This experiment was conducted by the method described above for entry 1, Table 1 using LiCl (0.254 g, 6 mol), NaBH_4 (0.230 g, 6 mol), diglyme (6 ml, 42 mol), Aroclor 1016 (0.1287 g, 0.5 mol), and docosane (IS, 14 mg) at 162°C (reflux). A 98% of the Aroclor 1016 had reacted after 96 h (Table 2, entry 1).

The same stoichiometry described above for entry 1 (Table 2) was used except that the reaction mixture was prestirred at room temperature for 20 min before heating at 160°C. A 98% of the Aroclor 1016 had reacted after 48 h (Table 2, entry 2).

The same reagent-to-substrate ratio and procedure described for entry 1 (Table 2) were used except heating was carried out at 130°C. A 99% of the Aroclor 1016 had reacted after 16 h (Table 2, entry 3).

The same reagent-to-substrate ratio and procedure in entry 1 (Table 2) were used except that triglyme was used instead of diglyme. A 99% of the Aroclor 1016 had reacted after 6 h. (Table 2, entry 4).

The same reagent-to-substrate ratio and procedure as described in entry 1 (Table 2) were used except that tetraglyme was used instead of triglyme. A 99% of the Aroclor 1016 had reacted after 4 h. (Table 2, entry 5).

2.6. Dechlorination of 2-chloro-, 3-chloro-, and 4-chlorobiphenyl in diglyme

A clean 25 ml, oven dried, three-necked flask equipped with a silicone rubber stopper, a thermometer, a magnetic stirring bar and a reflux condenser was used. LiCl

Table 2
Dechlorination of Aroclor 1016 by NaBH₄/LiCl in di-, tri-, and tetraglyme

Entry	Reagents ratios (mol)	Temperature (°C)	Time (h)	Dechlorination (mol%) ^a
1	Substrate/NaBH ₄ /LiCl/diglyme (1/12/12/84) Cl/NaBH ₄ /LiCl/diglyme (1/4/4/28)	162	1	6
			24	57
			48	77
			96	98
2 ^b	Substrate/NaBH ₄ /LiCl/diglyme (1/12/12/84) Cl/NaBH ₄ /LiCl/diglyme (1/4/4/28)	162	1	16
			24	78
			48	98
3 ^{b,c}	Substrate/NaBH ₄ /LiCl/diglyme (1/12/12/84) Cl/NaBH ₄ /LiCl/diglyme (1/4/4/28)	130	1	24
			4	40
			8	75
			16	99
4 ^b	Substrate/NaBH ₄ /LiCl/triglyme (1/12/66.4) Cl/NaBH ₄ /LiCl/triglyme (1/4/4/22)	130	1	42
			4	95
			6	99
5 ^b	Substrate/NaBH ₄ /LiCl/tetraglyme (1/12/12/54.4) Cl/NaBH ₄ /LiCl/tetraglyme (1/4/4/18.1)	130	1	64
			4	99

^a Dechlorination (mol%) refers to the total moles of chlorine atoms removed as a percentage of the total chlorine present in the Aroclor 1016 used in the specified reaction. Biphenyl was the only complete dechlorination product detected.

^b The reaction mixture was stirred at room temperature for 20 min before being heated to the indicated reaction temperature. These conditions are in the optimum range found, so far, for this reaction.

^c This reaction was repeated using LiBH₄ and NaCl in a mole ratio of substrate/LiBH₄/LiCl/diglyme of 1/12/12/84. After 8 and 16 h, respectively, the mol% dechlorination values were 77 and 99%.

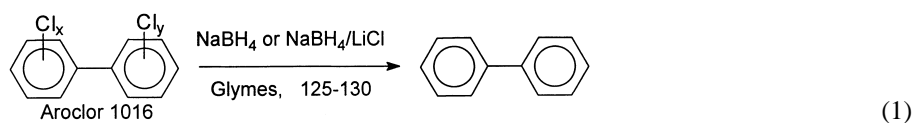
(0.106 g, 2.5 mol) and NaBH₄ (0.096 g, 2.5 mol) were added to a solution of diglyme (3 ml, 21 mol), 2-chlorobiphenyl (0.0236 g, 0.125 mol), 3-chlorobiphenyl (0.0237 g, 0.125 mol), 4-chlorobiphenyl (0.0238 g, 0.125 mol), octadecane (IS, 25 μl). The reaction mixture was prestirred at room temperature for 20 min before heating at 130°C. Aliquotes (0.1 ml) of the reaction mixture was withdrawn by a syringe at appropriate time intervals, quenched with dilute H₂SO₄, extracted with CH₂Cl₂ and analyzed by GC. The GC temperature program and conditions employed in the analyses were: 30 in., DB-5 capillary column, FID detector; initial temperature of 140°C, with subsequent heating at 10°C/min to 160°C where it was held for 5 min followed by heating at 30°C/min to 300°C where it was held for 15 min. After 9 h, 82% of the 2-chlorobiphenyl was dechlorinated compared to 94% dechlorination of 3-chlorobiphenyl and 96% dechlorination of 4-chlorobiphenyl.

3. Results and discussion

3.1. Dechlorination of Aroclor 1016 using NaBH_4 Or $\text{NaBH}_4/\text{LiCl}$ in di-, tri-, and tetraglyme

Aroclor 1016, the least reactive of the commercial PCB mixtures, was dechlorinated in several NaBH_4 /glyme systems. Example conditions and representative results are summarized in Table 1. Only 65% of the chlorine was removed from Aroclor 1016 after reacting with NaBH_4 alone for 180 h in diglyme at 162°C (reflux) (Table 1, entry 1). A slight rate enhancement occurred when triglyme was used at 216°C (reflux) (entry 2). Slow dechlorination appeared to take place in tetraglyme at 275°C (reflux) (entry 3). Actually, dechlorination is occurring faster than is apparent in Table 1, but the NaBH_4 is being consumed by competitive side reactions of NaBH_4 with solvent. GC/MS and GC analyses of the reaction mixture showed byproducts arising from the solvent. A similar distribution of these same products was found when NaBH_4 and tetraglyme were heated at 275°C . Thus, it seemed like increasing the temperature beyond 200°C would not be productive. The identity of the solvent breakdown products above 200°C was not carried out. However, we discovered that, at 290 and 310°C , much faster Aroclor 1016 dechlorination took place in sealed tubes using NaBH_4 in tetraglyme. Removal of 80% of the chlorine had occurred at 290°C (NaBH_4/Cl ratio of 3:3) within 2 h (entry 4). Substrate dechlorination reached 88% in 1 h and 99% in 2 h employing NaBH_4 /tetraglyme at 310°C (NaBH_4/Cl ratio of 5, entry 5). Fig. 1 shows the gas chromatogram of Aroclor 1016 (a) before and (b) after this treatment.

Biphenyl was the final dechlorination product observed in all of these NaBH_4 dechlorinations (Eq. (1)). No alkoxybiphenyls were observed. No hydrogenation products were produced. The least reactive PCB congeners were 2-chloro- and 2,2'-dichlorobiphenyl but these steadily reduced to biphenyl under these conditions. This was verified by examining the GC and GC/MS analyses as a function of reaction time. The more highly chlorinated congeners disappeared more rapidly. Careful analyses of the GC results showed the relative rates of chlorine loss from the most highly chlorinated congeners was no more than six times faster than congeners with only one chlorine per ring. The only exception were the 2-chloro- and 2,2'-dichloro-congeners which were slower by a factor greater than 10.



LiBH_4 is a stronger reducing agent than NaBH_4 . The lithium cation is a rather strong Lewis acid and it can coordinate to atoms with lone electron pairs. We speculated that Li^+ may serve to complex chlorine atoms in PCBs thereby serving to “pull” away Cl^- anions during nucleophilic attack of hydride at an aromatic ring. It was found that addition of LiCl to NaBH_4 /glyme sharply increased the dechlorination rates while also enhancing the rate of side reactions with solvent which also consumed borohydride. For example, Aroclor 1016 was 98% dechlorinated after 96 h in diglyme at 162°C with a 12-fold excess of $\text{NaBH}_4/\text{LiCl}$ (1:1) (entry 1, Table 2). This was significantly faster than the 65% dechlorination obtained in 180 h using a 20-fold NaBH_4 excess without LiCl (entry 1, Table 1). The in situ formation

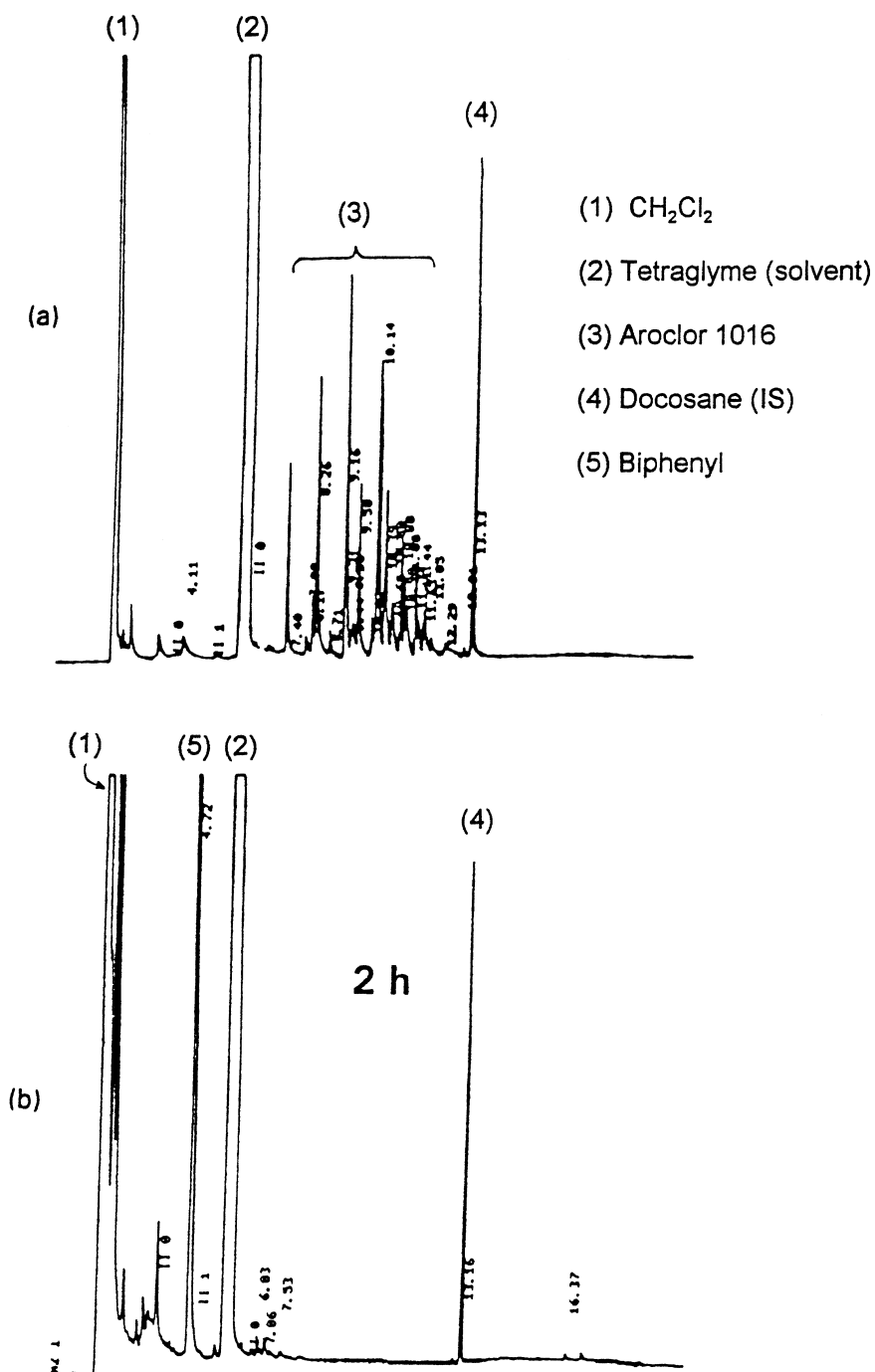


Fig. 1. The gas chromatograms of Aroclor 1016 (a) before and (b) after treatment (for 2 h) with NaBH₄/tetraglyme in a sealed tube at 310°C.

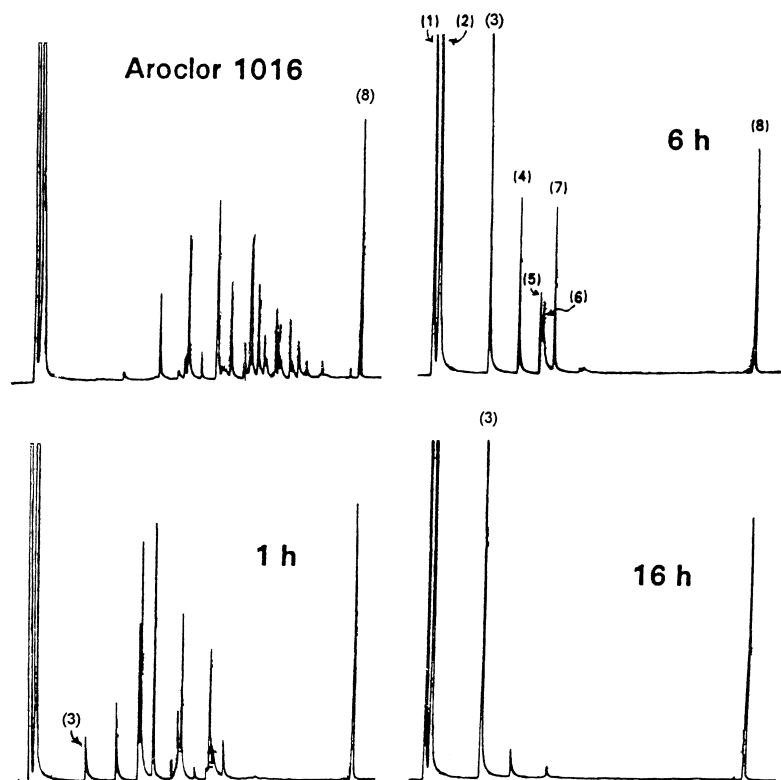


Fig. 2. The gas chromatograms of Aroclor 1016 before and after treatment with $\text{NaBH}_4/\text{LiCl}/\text{diglyme}$ for periods of 1, 6, and 16 h at 130°C . (The peak numbers stand for: (1) CH_2O_2 ; (2) diglyme; (3) biphenyl; (4) 2-chlorobiphenyl; (5) 3-chlorobiphenyl; (6) 4-chlorobiphenyl; (7) 2,2'-dichlorobiphenyl and (8) docosane (IS)).

of lithium borohydride [42,43] and the improved solvation of Li^+ by glymes might also increase rates of dechlorination by promoting the formation of more the reactive 'free' BH_4^- anions as opposed to less reactive contact or solvent-separated ion pairs. The borohydride solubility is also increased by the more effective solvation of the lithium versus the sodium cation.

A significant improvement in dechlorination was observed when the $\text{NaBH}_4/\text{LiCl}/\text{diglyme}$ reaction mixture was prestirred at room temperature for 20 min before heating at 162°C (compare entry 2 with entry 1, Table 2). Remarkably, a further increase in PCB conversion to biphenyl occurred when the reaction temperature was lowered to 130 from 162°C (entry 3 versus 2, Table 2). Dechlorination was 99% completed in 16 h at 130°C . Fig. 2 shows the gas chromatograms of Aroclor 1016 before and after treatment with $\text{NaBH}_4/\text{LiCl}/\text{diglyme}$ at 130°C as a function of time. Close examination of these peak arrays clearly illustrated that the more highly chlorinated congeners (higher retention times) disappeared more rapidly than the less chlorinated peaks. After 16 h, only very small amounts of two components remained undechlorinated. These components were identified as 2-chlorobiphenyl

and 2,2'-dichlorobiphenyl by GC and GC–MS versus authentic standards. At these lower temperatures (120–160°C) no byproducts due to solvent decomposition were formed.

The use of NaBH₄/LiCl was compared to the use of LiBH₄/NaCl at the same stoichiometry and reaction conditions (see Table 2, entry 3, footnote b). Within experimental error, the results were the same. Studies of LiBH₄ alone were not carried out during this work. However, after submission of this work for publication, we learned that LiBH₄ in THF will become available in commercial quantities from Rohm and Haas Co. in 2001, suggesting that it might be easily added to glymes followed by THF removal by distillation. This would allow use of LiBH₄ at higher temperatures.

The effect of changing the solvent from diglyme to triglyme and tetraglyme in the NaBH₄/LiCl dechlorinations was investigated using the room temperature premixing procedure followed by heating. Dechlorination of Aroclor 1016 was faster (99% chlorine loss in 6 h) in triglyme at 130°C than in diglyme (75 and 98% chlorine loss in 8 and 16 h, respectively) when compared at equivalent conditions: 130°C, NaBH₄/Cl = 4 (Table 2, entry 4 versus 3). A further rate increase occurred at the same conditions using tetraglyme (Table 2, entry 5 versus 4). In only 4 h, 99% of the chlorine had been removed at 130°C. The fact that dechlorination was faster in both tetraglyme and triglyme than in diglyme (entries 4 versus 3, 5 versus 4, Table 2) at these conditions is a very interesting observation. Perhaps, tetraglyme solvates lithium and sodium cations more favorably (less increase in entropy for six oxygens to coordinate Na; chelate effect) which may increase NaBH₄ solubility or more effectively solvent-separate the ion pairs, thereby increasing the reactivity of the borohydride anion. The optimum conditions for PCB dechlorination with NaBH₄/LiCl appear to be 125–140°C in tetraglyme.

It is worth emphasizing that no alkoxyborohydride species were involved in these dechlorinations in the lower temperature range (120–162°C). Chloride is replaced by hydride. Thus, alkoxide ions, which might result from hydride attack on the solvent, are not involved in nucleophilic aromatic substitutions which replace chloride. Evidence for this conclusion comes from the lack of observing products resulting from solvent cleavage. No CH₃OH, CH₃OCH₂CH₂OH, or CH₃OCH₂CH₂OCH₂CH₂OH were observed in the glyme solvents after various exposures to NaBH₄/LiCl in separate reactions or in the dechlorination reactions. So, the effective reducing agent in this dechlorination method should be BH₄[−] itself or BH₄[−] activated by the LiCl. This is quite different from metal-catalyzed alkoxyborohydride dechlorination, where stoichiometric amounts of other metal agents (e.g. Ni) was needed [10,11]. Furthermore, it is important to emphasize that this dechlorination media was quite simple compared to Schwartz's approach [15] which required the addition of titanium catalyst, pyridine and *N,N*-dimethyloctylamine to NaBH₄/triglyme.

3.2. Dechlorination of 2-chloro-, 3-chloro-, and 4-chlorobiphenyl using NaBH₄/LiCl in diglyme

Approximate relative dechlorination rates of three monochlorobiphenyl isomers were studied to determine which is the least reactive under the conditions studied. 2-Chlorobiphenyl was more rapidly dechlorinated than 4-chlorobiphenyl using NaBH₄ in the presence of a nickel boride catalyst at ambient temperature in DMF [13]. However, the reactivity order was 3-PCB > 4-PCB > 2-PCB when tetrakis(triphenylphosphine)Ni(0) was employed as

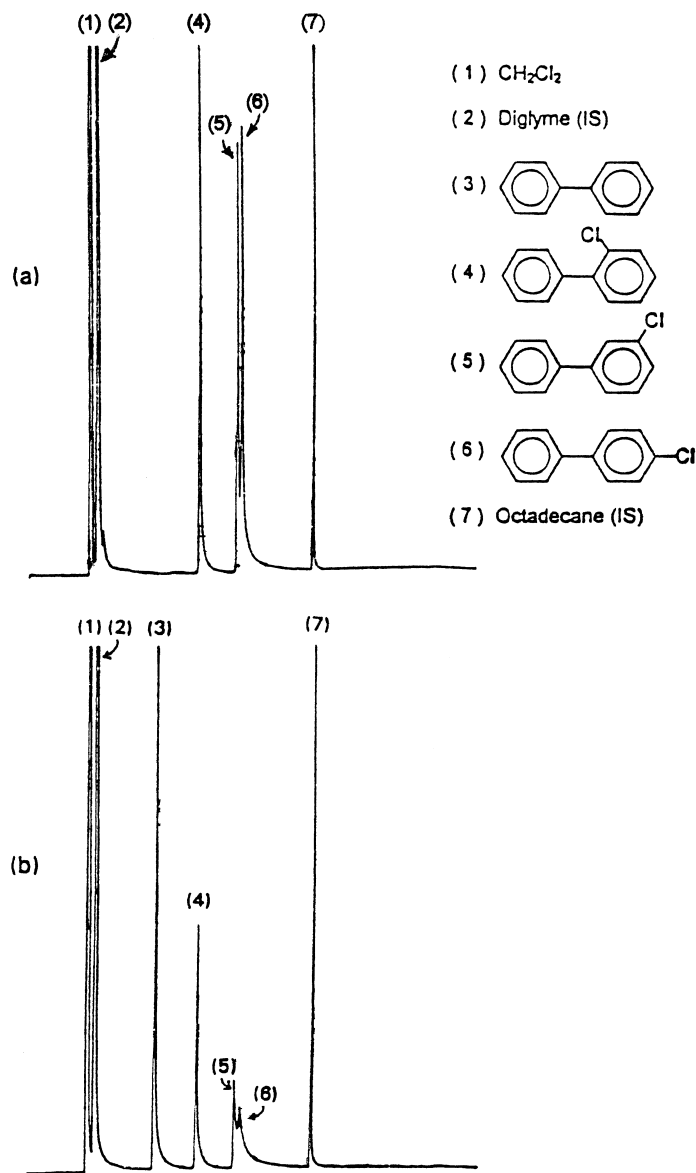


Fig. 3. The gas chromatograms of an equimolar mixture of 2-PCB, 3-PCB, and 4-PCB: (a) before and (b) after treatment with $\text{NaBH}_4/\text{LiCl}/\text{diglyme}$ at 130°C for 1 h.

the catalyst at the same conditions [13]. Competitive dechlorinations were performed on equimolar mixtures of 2-PCB, 3-PCB, and 4-PCB using $\text{NaBH}_4/\text{LiCl}$ in diglyme at 130°C . These three isomers yield biphenyl (Eq. (2)), so the relative rates were determined by following the disappearance of each isomer by GC. Fig. 3 shows the gas chromatograms of

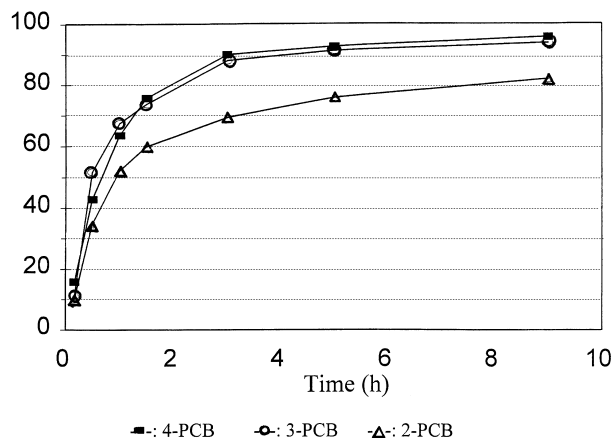
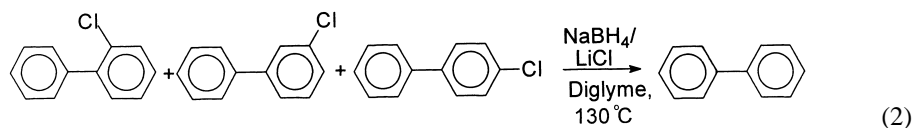


Fig. 4. Relative dechlorination rates of 4-, 3-, and 2-chlorobiphenyl in $\text{NaBH}_4/\text{LiCl}/\text{diglyme}$ (6.6/6.6/12) at 130°C .

the monobiphenyls (a) before and (b) after treatment for 1 h. These results are graphically illustrated in Fig. 4.



A slight preference exists for dechlorinating the 4- and 3-chloro positions versus the 2-chloro position (Fig. 4). Thus, 2-chlorobiphenyl was the least reactive of these isomers in dechlorinations with $\text{NaBH}_4/\text{LiCl}$ in diglyme.

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