

Catalytic Dehalogenation of Highly Chlorinated Benzenes and Aroclors Using PdCl₂(dppf) and NaBH₄: Efficiency, Selectivity, and Base Support

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Reported herein is a convenient one-pot system that can dehalogenate highly chlorinated benzenes at room temperature with reasonable conversion rates using PdCl₂(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene) as catalyst, NaBH₄ as reducing agent, TMEDA (*N,N,N,N*-tetramethyl-1,2-ethylenediamine) as supporting base, and THF as solvent. Total conversion of substrate to less chlorinated isomers is achieved within 200 h when hexachloro-, pentachloro-, and tetrachlorobenzenes are used. Degradation to benzene is not achievable, but the efficiency shown in the partial dechlorination is encouraging. A pronounced selectivity is accomplished with removal of meta-substituted chlorines being preferred over ortho- or para-substituted Cl atoms. The sequence in which reagents are added is also critical, thus indicating a protective role of the base. The effectiveness of the method was tested on the PCB mixtures Aroclor 1242, 1248, and 1254. Dechlorination efficiency at 67 °C is satisfactory.

Introduction

Dechlorination of polychlorinated biphenyls (PCBs) and chlorinated benzenes as their model compounds has received considerable attention over the past few years. The problem is being tackled from various directions, including heterogeneous and homogeneous catalysis. A number of examples for heterogeneous catalytic systems using Pd on carbon can be found in the literature.^{1–5} In homogeneous catalysis, Pd is also the obvious metal of choice, since Pd complexes are among the most readily available, easily prepared and easily handled of transition metal complexes.⁶ Catalytic activities of complexes such as Pd(PPh₃)₄,^{7–9} Pd(PEt₃)₄,⁹ and Pd(dipp₂)₂¹⁰ have been reported. It has also been shown that NaBH₄ is an effective reducing agent which can be handled easily.^{11–15} While most of these methods have only been tested on

chlorinated benzenes, some of them have been demonstrated to dechlorinate PCBs as well.^{11,13–15,16}

However, some disadvantages are notable in many documented systems: only very few of the reported catalytic systems are effective at room temperature^{9,12,13} and most require the use of elevated temperatures, thus needing a high energy input. Moreover, a number of methods^{9,11,13–16} cannot be regarded as truly catalytic since more than 5 mol % of catalyst is used. Sometimes the “catalyst” is even employed in excess amounts, making it effectively a reagent. Other shortcomings include complicated quenching procedures,¹⁶ harsh conditions such as high pressure,^{10,17} catalysts which are difficult to prepare,¹² or the need to use multiphase systems.^{1–3}

It has been demonstrated in our laboratory that PdCl₂(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene) as catalyst with NaBH₄ as the reducing agent and TMEDA (*N,N,N,N*-tetramethyl-1,2-ethylenediamine) as the supporting base can effectively debrominate brominated benzenes and polybrominated biphenyls within minutes or a few hours. Complete debromination of polybrominated benzenes at room temperature could be achieved in 2 h (monobromobenzene) to 7 h (hexabromobenzene).¹⁸ Polybrominated biphenyls can be debrominated in 4 min (monobromobiphenyl), 10 min (dibromobiphenyl), and 40 h (decabromobiphenyl).¹⁹

In this paper we report the efficiency of this system toward 11 isomers of polychlorinated benzene and the PCB mixtures Aroclor 1242, 1248, and 1254. The site selectivity of the dechlorination reactions is examined. The effects of reaction atmosphere, namely air or inert

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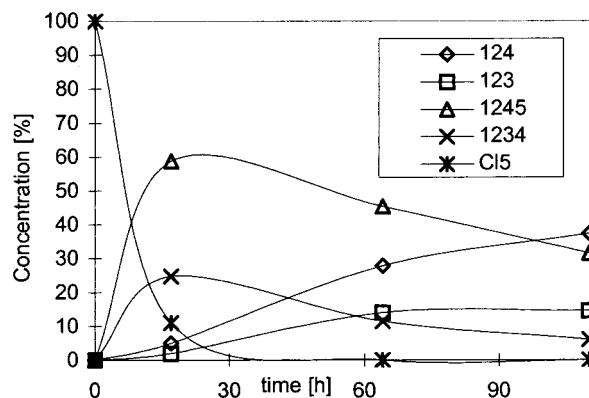


Figure 1. Dechlorination of pentachlorobenzene at room temperature. 124 = 1,2,4-trichlorobenzene, etc.

gas, temperature (rt or 67 °C), and order of addition of reagents are also investigated and discussed.

Results and Discussion

General. When chlorinated benzenes are mixed with NaBH_4 in the presence of catalytic quantities of PdCl_2 -(dppf), dechlorination occurs. The performance of the catalyst can be considerably enhanced by adding a nitrogen-base such as TMEDA.¹⁸



The formation of the adduct $\text{TMEDA} \cdot 2\text{BH}_3$ has been verified by GC/MS.¹⁸ When Et_3N is used as the base, the analogue $\text{Et}_3\text{N} \cdot \text{BH}_3$ is formed. However, the yields are lower than those with TMEDA.

Figure 1 shows a typical reaction of pentachlorobenzene being degraded to tetra- and trichlorobenzenes. The dechlorination proceeds sequentially to monochlorobenzene (formed after ~160 h, not shown in the figure). It could take more than a week for the substrate to degrade quantitatively to monochlorobenzene. No conversion to benzene is observed. This is not unexpected as the present catalytic system is ineffective toward monochlorobenzene. The selectivity of the reaction is also notable. For example, pentachlorobenzene preferentially gives 1,2,4,5-tetrachlorobenzene and then 1,2,4-trichlorobenzene (Figure 1).

The degradation of hexachlorobenzene, pentachlorobenzene, and all possible isomers of tetra-, tri-, and dichlorobenzene (except 1,2,3,5-tetrachlorobenzene, which is not easily available commercially) was tested using similar conditions. The breakdown²⁰ of these substrates versus time at room temperature (28 °C) is shown in Figure 2. In general, the more chlorinated benzenes react much faster than the less chlorinated derivatives, with monochlorobenzene showing negligible activity. A high degree of chlorination would deplete the aromatic ring of electron density and make the carbon centers more susceptible to nucleophilic attack. Accordingly, oxidative addition with a low-valent Pd center is expected to be facile. Such rate enhancement provides direct evidence for the rate-determining role of the oxidative addition reaction. It is remarkable that hexachloroben-

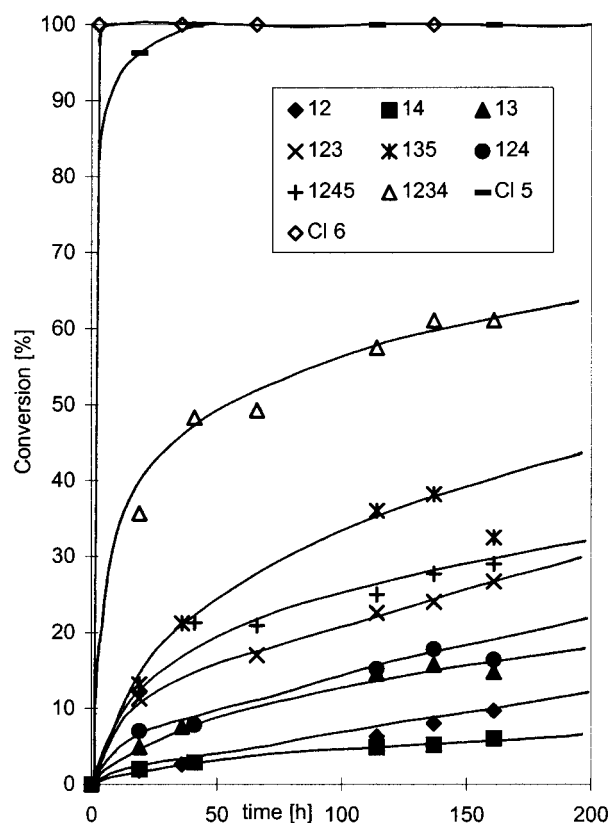


Figure 2. Dechlorination of different substrates at room temperature. 12 = 1,2-dichlorobenzene, etc.

zene can undergo complete degradation to pentachlorobenzene within minutes. After ~40 h of stirring, even pentachlorobenzene can breakdown completely to tetrachlorobenzenes and lower chlorinated derivatives. These results demonstrate the high efficiency of our catalyst.

Effect of Higher Temperature. Figure 3 shows the same series of reactions carried out at the reflux temperature of THF (67 °C). The increase in temperature increases the rate of decomposition and the yield in all reactions. Under these thermal conditions, both tetrachlorobenzenes and even 1,2,3- and 1,2,4-trichlorobenzene approach completion of the first dechlorination step within 200 h. However, monochlorobenzene remains intact. Since the reproducibility for the lower chlorinated isomers is rather poor, the observed inconsistencies in reactivity order (e.g., 1,2-dichlorobenzene reacts faster than 1,4-dichlorobenzene at room temperature but slower at 67 °C) are probably not significant. While higher temperatures naturally would lead to higher yields, a compromise between energy input and reaction time needs to be sought. With pentachlorobenzene and hexachlorobenzene as substrates, the difference between room temperature and 67 °C is not very pronounced, so that heating is unnecessary. For less chlorinated benzenes, however, a higher temperature is desirable to shorten the reaction time to an acceptable level.

Regardless of temperature and substrate, the first dechlorination step is inevitably the fastest, with the others being subsequently slower. Whereas the dechlorination of hexachlorobenzene to pentachlorobenzene at reflux temperature can be accomplished in less than 3 h and the removal of the first chlorine in pentachlorobenzene in about 17 h, the subsequent steps are increasingly slower. While it takes at least 40 h to convert tetrachlo-

(20) Expressed in terms of percent conversion of the substrate to various lower chlorinated derivatives.

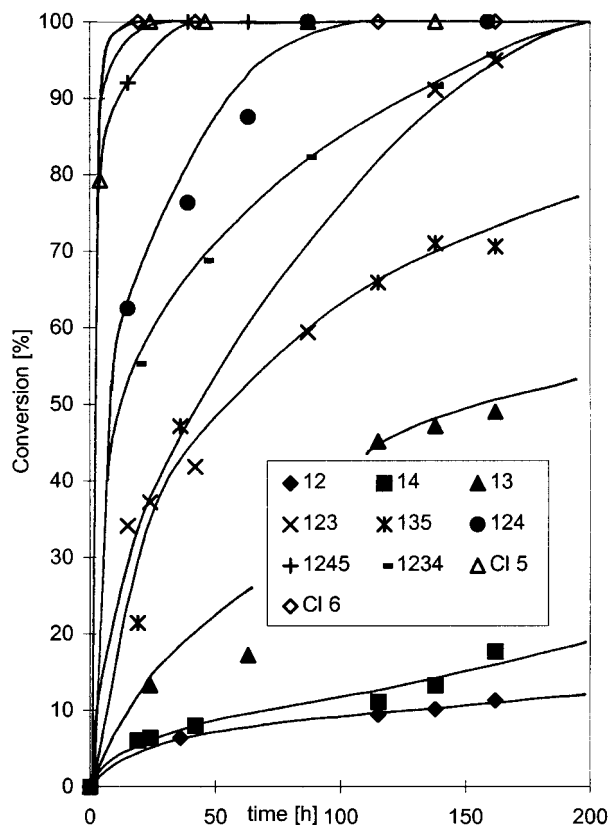


Figure 3. Dechlorination of different substrates at 67 °C. 12 = 1,2-dichlorobenzene, etc.

robenezene to trichlorobenzene, and at least 90 h for trichlorobenzene to decompose to dichlorobenzene, dichlorobenzene itself cannot be converted completely to monochlorobenzene in 200 h and monochlorobenzene does not react at all. With the above in mind, it is not surprising that regardless of the substrate used mixtures of roughly the same composition can be obtained after a prolonged reaction time.

Effect of Atmospheric Oxygen. It can be shown that the yields of the dechlorination reactions are much lower when the reactions are carried out in air instead of argon or nitrogen. Reactions with 1,2,3-trichlorobenzene as a model substrate were carried out under both atmospheres in "closed" and "open"²¹ systems. Regardless whether the system is closed or open, the reaction is significantly more effective under argon. With argon atmosphere, conversion of substrate reaches 25% after 150 h, as compared to only 5% under air. It is understandable that an inert gas protects the active catalyst better in view of the involvement of a low-valent Pd(0) complex in the catalytic cycle. However, there is no significant difference in reaction yields between an open or closed system.

The dechlorination efficiency also depends on the amount of catalyst used. For example, the yield drops by ca. 30% when only half of the usual catalyst amount is used. Some catalyst decomposition is inevitable,

(21) "Open" means a continuous flow of inert gas (usual conditions), whereas "closed" means a static atmosphere which is not strictly pressure-controlled. The latter was performed to check if there were any volatile products (especially benzene) in the reaction. Although the Schlenk tube was generally isolated from the gas source, it was periodically opened to release any excess pressure. Loss of pressure was also inevitable during sample taking.

Table 1. Selectivity

substrate			
1,2,3-TCB ^a	1,2-DCB (%)	1,3-DCB (%)	
expected ^b	67	33	
observed ^c	90	10	
Stiles ^d	45	55	
substrate			
1,2,4-TCB	1,2-DCB (%)	1,3-DCB (%)	1,4-DCB (%)
expected	33	33	33
observed	40	20	40
Stiles	5	20	75
Marques et al. ^e	50	30	20
Zhang et al. ^f	70	20	10
substrate			
1,2,3,4-TeCB	1,2,3-TCB (%)	1,2,4-TCB (%)	
expected	50	50	
observed	50	50	
Stiles	10	90	
substrate			
PeCB	1,2,3,4-TeCB (%)	1,2,3,5-TeCB (%)	1,2,4,5-TeCB (%)
expected	40	40	20
observed	30	0	70

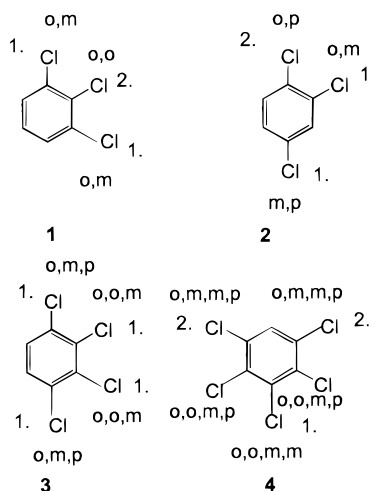
^a DCB = dichlorobenzene, TCB = trichlorobenzene, TeCB = tetrachlorobenzene, PeCB = pentachlorobenzene. ^b From statistical probability. ^c At highest yield of main product; averages of several runs, uncertainty 5%. ^d See ref 12. ^e See ref 3. ^f See ref 25.

especially when the reaction is carried out in air, and hence the catalyst activity generally decreases with time.

Selectivity. The product distribution ratios in the reactions involving 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene at the first dechlorination step are summarized in Table 1. The statistically expected ratios are included for reference. While the observed yields are in agreement with the statistically dictated values when 1,2,3,4-tetrachlorobenzene is the substrate and to a lesser extent when 1,2,4-trichlorobenzene is used, a very pronounced selectivity can be observed when 1,2,3-trichlorobenzene or pentachlorobenzene is degraded. 1,2,3-Trichlorobenzene gives predominantly 1,2-dichlorobenzene whereas pentachlorobenzene degrades to 1,2,4,5-tetrachlorobenzene as the major and 1,2,3,4-tetrachlorobenzene as the minor product. There is no evidence for the formation of 1,2,3,5-tetrachlorobenzene.

Comparing the two trichlorobenzenes, a strong selectivity *against* the formation of 1,3-dichlorobenzene is apparent. A closer examination of the product distribution in relation to the orientation of the chlorine atoms reveals that those Cl atoms which are in a meta position with respect to other Cl atoms are preferentially removed (Scheme 1). For example in 1,2,3-trichlorobenzene (**1**), the Cl atoms at positions 1 and 3 are removed preferentially, since both are meta to each other. Similarly, 1,2,4-trichlorobenzene (**2**) loses the Cl atoms at sites 2 and 4 with equal ease since both have one meta substituent. Thus we are also able to explain the absence of any notable selectivity in 1,2,3,4-tetrachlorobenzene (**3**) in which all Cl atoms are in a meta position to *one* other Cl atom. In pentachlorobenzene (**4**), atoms 1, 3, and 5 (*two* meta substituents) are favored over atoms 2 and 4 (*only one* meta substituent) so strongly that no 1,3,4,5-tetrachlorobenzene is formed at all. The preference for 1,2,4,5-tetrachlorobenzene over 1,2,3,4-tetrachlorobenzene as a

Scheme 1



product is presumably thermodynamic in origin and cannot be explained along these lines.

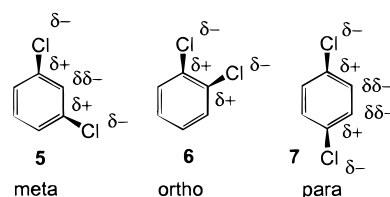
The observed site selectivity in favor of meta-directing substitution of Cl with H is an interesting phenomenon which is not encountered in the common aromatic substitutions.

Our catalytic system also did not give the product distribution found by other researchers. For example, in the degradation of 1,2,3-trichlorobenzene, Stiles¹² used nickel(II) complexes of tetraazacycles as catalysts, reporting a near-even distribution of 1,2- and 1,3-dichlorobenzene, whereas our system gives predominantly (90%) 1,2-dichlorobenzene. On the other hand, we obtained an even distribution of 1,2,3- and 1,2,4-trichlorobenzene from 1,2,3,4-tetrachlorobenzene when Stiles found 90% of 1,2,4-trichlorobenzene (Table 1).

Our observed site selectivity may be explained in terms of electron density factors which are pertinent to the catalytic mechanism. In this mechanism, oxidative addition of Ar-Cl (Ar = aryl) on the zerovalent Pd giving Pd(Ar)Cl(dppf) represents a key step which is not only rate determining but controls the site selectivity. The ability for [Pd⁰(dppf)] to undergo oxidative addition with aryl halides has been established.²² We have also isolated and structurally characterized similar oxidative addition products.²³ The significantly higher reactivity of polychlorobenzene compared to that of the lower chlorobenzenes in our catalytic mixtures is also consistent with this proposed key step. Oxidative addition of an aryl halide to a Pd(0) species is also an important step in many known catalytic processes, such as in the Heck reaction, Pd-catalyzed carbonylation, or Stille coupling.²⁴

The strong inductive effect of Cl substituents depletes the ring of electron density, polarizes the C-Cl bond, and makes it more susceptible to oxidative addition (Scheme 2). Such polarization causes uneven electron distribution, creates alternating charges, and activates the C-Cl bonds toward oxidative addition. When the ring is highly substituted, the carbon centers are very electrophilic and

Scheme 2



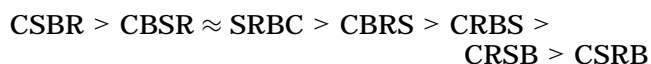
hence are susceptible to oxidative attack. The facility of the attack therefore could depend on the charge distribution on the ring, i.e., an alternating distribution of δ⁺ (electrophilic) and δ⁻ (nucleophilic) sites is therefore most favorable. Such alternating charges are formed when two chlorine atoms are meta to each other (5 in Scheme 2) so that the electrophilicities of the two carbon centers are mutually reinforced.

On the other hand, an electron-withdrawing substituent in an ortho or para position (6 and 7 in Scheme 2) would give rise to neighboring C atoms having the same and thus repelling charges. This would dilute the electrophilicity and destabilize the attack.

The observed selectivity is therefore a phenomenon arising from the preferential addition of the Pd(0) species (9) into electron-poor bonds.

A steric effect, which is governed by a preferential attack on the sterically least crowded C-Cl bond, such as reported by Marques et al.³ or Zhang et al.²⁵ (Table 1) is not found in our system. Such steric factors would favor the formation of 1,2-dichlorobenzene (from 1,2,4-trichlorobenzene), 1,2,3-trichlorobenzene (from 1,2,3,4-tetrachlorobenzene) and 1,2,3,4-tetrachlorobenzene (from pentachlorobenzene), which is not observed in our case. The selectivity reported by Stiles¹² for a radical mechanism which is linked to the dissociation of the radical anion RX⁻ is also not in agreement with ours.

Effect of the Order of Reagent Addition. Our earlier work on the bromo derivatives^{18,19} suggested that the dehalogenation efficiency is also critically dependent on the order in which the reagents are added together. As this phenomenon has some mechanistic implications, we have extended the study to this system. Although a number of permutations are possible, only a few are conceptually and mechanistically sound. We have chosen those in which the solvent and catalyst are added together in the beginning, except in the case of order "SRBC" (see explanation below), where the catalyst is "given the choice" with what to react first. Surprisingly, considerable differences were observed (Figure 4). The best results were obtained when the reactants were added in the order THF, catalyst (C), substrate (S), base (B), and reducing agent (R). Using pentachlorobenzene as a model substrate, the dechlorination efficiency is found to decrease as follows (the solvent is always added first):



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From this general trend, it can be concluded that the base has to be added before the reducing agent in order to obtain good yields. This complements the earlier observation that the catalytic performance is significantly enhanced when a base is present. The essential influence

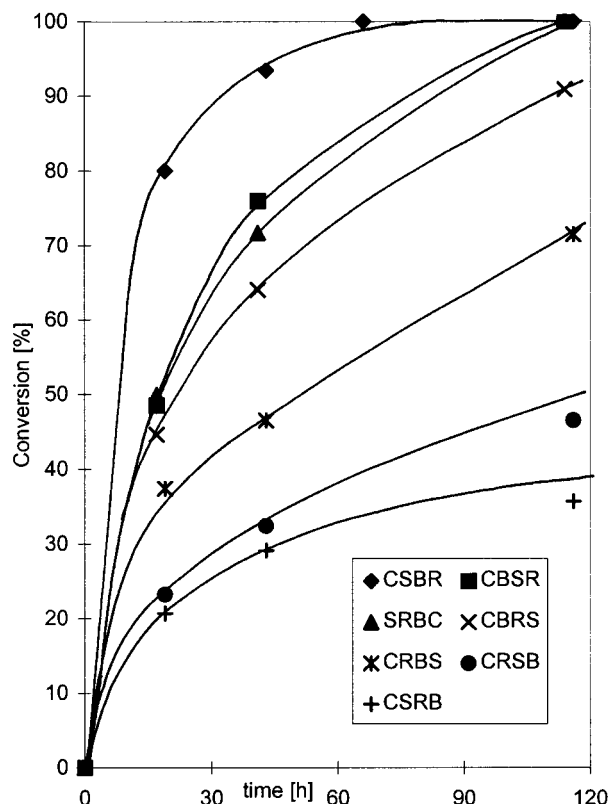
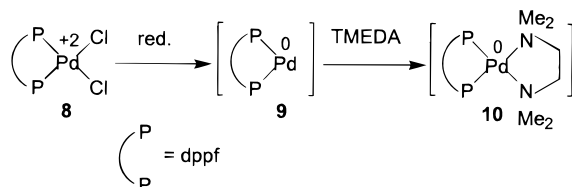


Figure 4. Effect of changing the sequence in which reagents are added. Substrate pentachlorobenzene, rt. C = catalyst, S = substrate, B = base, R = reducing agent.

Scheme 3



of a base on a coupling vs reductive dehalogenation process has been recently described.²⁶

We can propose that the base is weakly coordinated to the electronically unsaturated active catalytic species $[\text{Pd}^0(\text{dppf})]$ (**9**), thus forming the intermediate $[\text{Pd}(\text{dppf})(\text{TMEDA})]$ (**10**) (Scheme 3). This coordination is strong enough to protect the Pd(0) species from decomposition (to Pd metal) but weak enough as not to inhibit oxidative addition. Such stabilization is crucial in the dechlorination mechanism since the oxidative addition step is rate determining, so the lifetime of the active catalyst must be long enough to allow this step to occur. This is supported by our experimental observation that a black precipitate of Pd metal is formed when the base is added late.

Another possible function of the base is the observed formation of the adduct $\text{TMEDA} \cdot 2\text{BH}_3$. This provides an extra drive for the release of the nucleophilic H^- from BH_4^- and promotes the hydride transfer. The adduct could also serve as a hydride source itself. The reducing ability of amine– BH_3 adducts has been reported.²⁷

(25) Zhang, Y.; Liao, S.; Xu, Y. *Tetrahedron Lett.* **1994**, 35, 4599.

(26) Murata, M.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, 62, 6458.

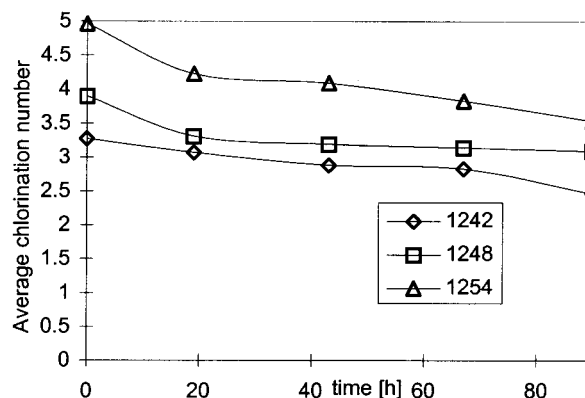


Figure 5. Dechlorination of different PCB mixtures at 67 °C. (1242 = Aroclor 1242, etc.). For definition of “average chlorination number” see footnote 28.

Furthermore, the base may also lead to intermolecular elimination of HCl by scavenging it from the system.

Our use of tertiary amines in promoting catalytic dechlorination has several precedents. Ferrughelli et al.¹⁷ reported the use of NEt_3 to neutralize HCl formed during the activation of the catalyst $[(\text{C}_5\text{Me}_5)\text{RhCl}_2]_2$ by H_2 . Liu et al.¹⁴ have examined a variety of bases and their combinations in a system containing Cp_2TiCl_2 and NaBH_4 , which probably has a radical mechanism. The best combination of bases was found to be pyridine/*N,N*-dimethyloctylamine (1:1). NaBH_4 forms the adduct $\text{NR}_3 \cdot \text{BH}_3$ with the aliphatic amine, while pyridine is proposed to coordinate to the active Ti species.

Another striking result from our experimentation with the order of reagent addition is that, at least in some cases, the selectivity changes significantly with the order. For example, under the usual circumstances (order CSBR), pentachlorobenzene produces 30% 1,2,3,4-tetrachlorobenzene and 70% 1,2,4,5-tetrachlorobenzene. Small deviations can be observed with orders CBSR (45% 1,2,3,4-TeCB, 55% 1,2,4,5-TeCB) and CSRB (55% 1,2,3,4-TeCB, 45% 1,2,4,5-TeCB), but order SRBC completely reverses the situation, leading to an excess of 1,2,3,4-TeCB (80%) over 1,2,4,5-TeCB (20%). The reasons for this change in selectivity are unclear and subject of further investigations.

Dechlorination of Aroclors. Our success in the dehalogenation of polychlorinated benzenes prompted us to test our catalytic system on a few commercially available Aroclors. The dechlorination efficiencies (expressed as decrease in average chlorination number²⁸) of the PCB mixtures Aroclor 1242, 1248 and 1254²⁹ at reflux temperature are shown in Figure 5. As expected, mixtures that contain higher chlorinated congeners react faster. Although dechlorination also works at room temperature, the rate of degradation significantly increases under thermal conditions. After ~4 days at 67

(27) Andrews, G. C.; Crawford, T. C. *Tetrahedron Lett.* **1980**, 21, 693.

(28) The average chlorination number is obtained as follows: $\text{ACN} = [\text{conc \% monochloro} + (\text{conc \% dichloro}) \times 2 + (\text{conc \% trichloro}) \times 3 + \dots] / 100$. Percentage yields were obtained by GC, the retention time windows of the different chlorination levels estimated by GC/MS. We are aware that there are overlaps between these regions, so the calculated ACNs are only approximate, but sufficient for this comparison.

(29) Main components: Aroclor 1254 tetrachloro, pentachloro, and hexachloro; Aroclor 1248 trichloro, tetrachloro and pentachloro; Aroclor 1242 dichloro, trichloro, and tetrachloro.

°C, the average chlorination numbers of Aroclor 1242, 1248, and 1254 decrease from 3.27, 3.90, and 4.96 to 2.46, 3.09 and 3.53, respectively. All possible isomeric products are formed, traces of biphenyl can be detected after 90 h or less. This performance is better than, for example, that reported by Roth et al.³⁰ for a system using Ni(PPh₃)₄ and NaBH₄.

Recovery of Catalyst. We have also succeeded in recovering a substantial portion of the metal from the catalytic reaction. With test mixtures containing all the usual ingredients but the less expensive PdCl₂(PPh₃)₂ as catalyst, we have reproducibly recovered 40% of the metal from the reaction residue. A simple treatment includes an aqueous washing of the vacuum-dried residue, followed by digestion with *aqua regia*. Gradual introduction of concentrated HCl gives essentially H₂PdCl₆ which readily yields K₂PdCl₄ when treated with excess KCl. PdCl₂(dppf) can be easily obtained from K₂PdCl₄. Such recycling of a precious metal would enhance the value of this process in any potential industrial application.

Conclusion

We have demonstrated that a catalyst system containing PdCl₂(dppf) and NaBH₄ can efficiently dechlorinate higher chlorinated benzenes in THF at room temperature when TMEDA is used as the supporting base. Within 200 h, complete degradation of substrate to a mixture of lower chlorinated isomers (including monochlorobenzene, but not benzene) is accomplished at room temperature (for hexa- and pentachlorobenzene) and at 67 °C (for hexa-, penta-, 1,2,4,5-tetra-, 1,2,3,4-tetra-, 1,2,4-tri-, and 1,2,3-trichlorobenzene). These conditions are mild compared to many reported systems. The present catalytic system also shows encouraging dechlorination activity toward PCB mixtures. Again, the conditions used are significantly milder than the incineration conditions currently in practice. It is notable that a high level of chlorination leads to high rates and yields. This catalytic approach therefore complements well the biodegradation approach which generally works better for the lower chlorinated congeners. As toxicity of chlorobenzenes and PCBs increases with higher chlorine content, a system which works best for higher chlorinated aromatics is clearly an advantage.

A pronounced selectivity can be observed for the chlorinated benzenes with meta-substituted Cl atoms being removed preferentially. This is probably linked to electronic factors governing the ease of oxidative addition. The observed site selectivity is unique and could be used to prepare isomers that are not easily accessible by common synthetic routes.

We propose a catalytic cycle involving oxidative addition, hydride transfer, and reductive elimination with the first as the rate-determining step. A bidentate basic ligand like TMEDA can enhance the performance of the catalyst, through the formation of [Pd(dppf)(TMEDA)] and TMEDA·2BH₃, for example.

Although the conversion rates for the lower chlorinated species are still unsatisfactory, this catalytic system can serve as a starting point for further investigations. Preliminary results show that a change in solvent can further improve the dechlorination rates and yields.

(30) Roth, J. A.; Dakoji, S. R.; Hughes, R. C.; Camody, R. E. *Environ. Sci. Technol.* **1994**, *28*, 80.

Current efforts are directed along these lines, especially toward the ultimate target of degradation of PCBs to biphenyl.

Experimental Section

All reactions were carried out under argon or oxygen-free nitrogen except where otherwise stated. Standard Schlenk techniques were used. Dppf³¹ and PdCl₂(dppf)³² were synthesized according to literature methods. Chlorinated benzenes were obtained from Aldrich; PCB mixtures came from AccuStandard (Aroclor 1242 and 1254) and Chem Service (Aroclor 1248).

In a typical reaction, the substrate (1 mmol) was dissolved in freshly degassed THF (20 mL) together with PdCl₂(dppf)·CH₂Cl₂ (0.037 g, 0.045 mmol), forming an orange solution. Upon addition of of TMEDA (2 mL, 13.4 mmol, excess), the solution turned deep red.³³ Addition of NaBH₄ (0.19–1.14 g, 0.19 g (5 mmol) per mmol of "Cl") led to a further deepening in color, followed by effervescence, during which the suspension (NaBH₄ is only slightly soluble in THF) slowly turned brown-black.

The suspension was stirred for several days (at room temperature or 67 °C) under inert atmosphere (argon or oxygen-free nitrogen) and atmospheric pressure. Samples of ca. 0.5 mL were withdrawn periodically by filtering through a Teflon delivery tube. After addition of a standard solution (known concentration of anthracene in THF), the sample was diluted to 10 mL with THF and analyzed with a HP 5890 series II gas chromatograph (column HP1, cross-linked methyl silicone gum, 25 m × 0.32 mm × 0.52 μm film thickness). CG-program: 32 °C, keep for 5 min, heat at 10 °C/min to 260 °C, keep for 1 min. The injector was held at 200 °C and the FID detector at 250 °C.

Sample filtering and diluting was shown to be sufficient to quench the reaction. GC/MS (Shimadzu QP5000) was used to confirm peak identity.

Concentration ratios obtained by the area ratio method (assuming equal FID-sensitivity for all substrates) are almost identical to those obtained by internal calibration. When anthracene was used as the internal standard, (FID sensitivity = 1), the sensitivities of chlorinated benzenes varied only from 0.51 (hexachlorobenzene) to 0.63 (benzene). No internal standard was used for the analysis of Aroclors, which is justified since relative molar response factors for PCB congeners have been reported to range from 0.94 to 1.09.³⁴

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