



# Complete and truly catalytic degradation method of PCBs using Pd/C–Et<sub>3</sub>N system under ambient pressure and temperature

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**Abstract**—Since PCBs are persistent toxic pollutants and do not degrade easily, the development of a safe and perfect methodology for destruction of such remains is of great importance. We have found that the catalyst activity of Pd/C toward the hydrodechlorination of PCBs was outstandingly activated by the addition of triethylamine. PCBs could be thoroughly dechlorinated under ambient temperature and pressure, and no product other than biphenyl has been detected by GC/MS. © 2002 Elsevier Science Ltd. All rights reserved.

Polychlorinated biphenyls (PCBs) were commercially produced as complex mixtures beginning in 1929 through the mid 1970s and they are a class of nonpolar chlorinated hydrocarbons with a biphenyl nucleus on which one to ten of the hydrogens have been replaced by chlorine. Commercial PCBs were manufactured and sold as complex mixtures containing multiple isomers at different degrees of chlorination. PCBs are widespread, persistent, bioaccumulate and pose a risk of causing adverse effects to human health and the global ecosystem,<sup>1</sup> while some part of the world production (ca. 1.5 million tons) has been destroyed, the major part still remains in use or awaits destruction, whilst a substantial proportion has been released to the environment. Because of the high thermodynamic, chemical and biological stability of PCBs, all degradation methods are extremely difficult.<sup>1c,d</sup> Furthermore, as is clear from the recent report commissioned by the Environment Programme of the United Nations, many countries still do not have suitable PCB disposal or treatment facilities.<sup>1d</sup> Therefore, an effective remediation methodology for PCBs is a critical factor for future protection from improper disposal or an accidental leak (e.g. fire, earthquake, war and so on) of stored PCBs. Currently they are principally being destroyed by high-temperature incineration, but public concerns about discharges from incinerators are strongly forcing a move to chemical methods.<sup>1c,d,2</sup> Chemical remediation techniques currently under development include substitution of chlorides,<sup>3</sup> hydride reduction,<sup>4</sup> hydrodechlorination,<sup>5</sup>

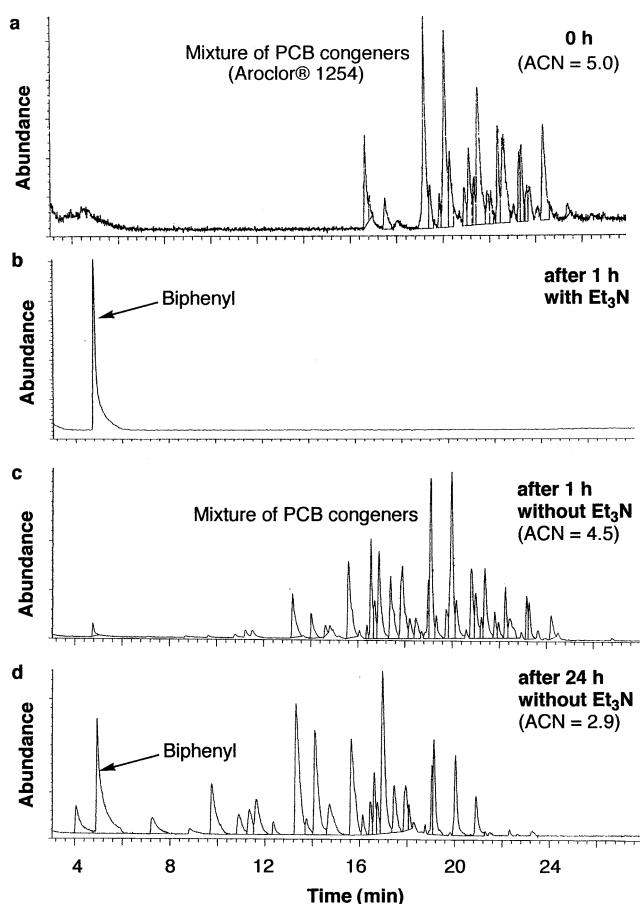
dechlorination using metals,<sup>6</sup> photolysis,<sup>7</sup>  $\gamma$ -radiolysis,<sup>8</sup> oxidation,<sup>9</sup> electrolysis,<sup>10</sup> supercritical degradation<sup>11</sup> and so on.<sup>1c,2a,12</sup> Some of them are used commercially to treat mainly liquid PCBs, and PCB-contaminated oils (4), however, the low reactivity and/or selectivity of most reagents is manifested by the low applicability to dechlorination of especially multichlorinated aromatic compounds, and most processes require high heat, high pressure, radiation, stoichiometric reagents, vast amounts of catalyst and/or strongly-basic conditions and many of them are very frequently incomplete.<sup>13</sup>

In our preceding paper on chemoselective hydrogenation using the Pd/C–Et<sub>3</sub>N system, we reported that the catalytic activity of Pd/C toward the hydrodechlorination of only aromatic chlorides was outstandingly and selectively **activated** by the addition of Et<sub>3</sub>N.<sup>14</sup> To explore the application of our dechlorination method, the hydrodechlorination of some PCBs which are complex mixtures of multichlorinated biphenyls was investigated.<sup>15</sup> Triethylamine was used in 1.2 equiv. versus the average chlorination number (ACN)<sup>4c</sup> of the PCBs and 10% Pd/C was employed in 10% of the weight of the substrate in the case of PCBs degradation for safety reasons, although 3% of the weight of the substrate was used for the hydrodechlorination of mono-chlorinated aromatic substrates.<sup>13</sup> Degradation of a 10% PCBs (Aroclor<sup>®</sup> 1254, Monsanto Chemical Co., ACN=5.0) solution in methanol using 10% Pd/C and triethylamine under ambient temperature and hydrogen pressure is shown in Fig. 1. As expected, GC peaks of the PCB congeners of Aroclor<sup>®</sup> 1254 disappeared completely after 15 min, while a small amount of intermediates,

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2-chlorobiphenyl, 2,6-dichlorobiphenyl and a trichlorobiphenyl, was also detected. However, the generated intermediates were entirely dechlorinated within 1 h suggesting the complete degradation of Aroclor® 1254, and accumulation of biphenyl **1** was observed as the sole product. In contrast, the degradation of Aroclor® 1254 without triethylamine was quite slow. Very little dechlorination was observed after 1 h (ACN=4.5), and approximately 60% of the chlorine of Aroclor® 1254 still remained even after 24 h hydrodechlorination (ACN=2.9) (Fig. 1).

It is well known<sup>1c,d</sup> that a preponderance of the PCBs was used as electrical insulating oil in capacitors and transformers. Our fundamental concept to develop a safe and reliable degradation method of PCBs should be applicable to spent PCBs that have been used in

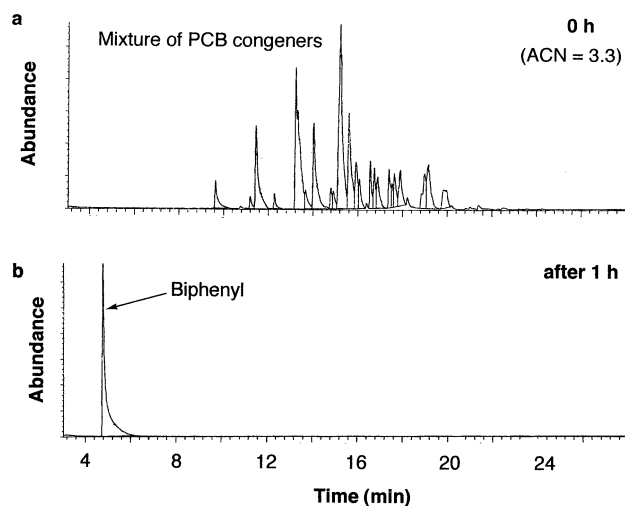


**Figure 1.** Formation of biphenyl from a commercial mixture of PCB congeners, Aroclor® 1254. GC/MS observation of the hydrodechlorination process in the presence of Et<sub>3</sub>N: (a) GC/MS of Aroclor® 1254. (b) GC/MS after 1 h hydrodechlorination (balloon) of Aroclor® 1254 (100 mg, 0.31 mmol) at ambient temperature (ca. 20°C) using 10% Pd/C (10 mg) in methanol (10 ml) in the presence of Et<sub>3</sub>N (37 mg, 0.37 mmol). Degradation of Aroclor® 1254 is completed (ACN=0.0). GC/MS observation of the hydrodechlorination process without triethylamine; (c) GC/MS after 1 h at ambient temperature (ACN=4.5). (d) After 24 h. Degradation of Aroclor® 1254 is quite slow and a large amount of PCB congeners still remains even after 24 h (ACN=2.9).

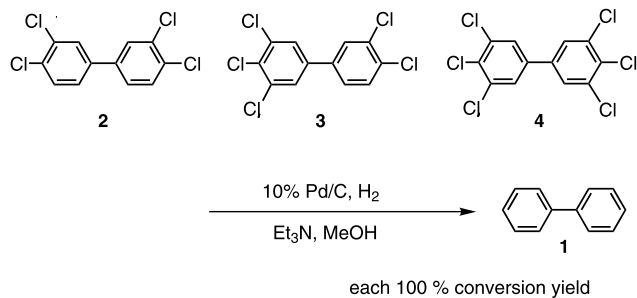
devices. In order to investigate this possibility, we chose PCBs practically used as high-tension capacitor oil for over a quarter-century for the substrate of the hydrodechlorination. The PCBs, amber and viscid oil, possess 3.3 chlorine per molecule on average (ACN=3.3). The results from the hydrodechlorination of the PCB congeners in the presence of triethylamine are identical to those of Aroclor® 1254. After 1 h, biphenyl is the sole product from the hydrodechlorination of the PCB congeners and the degradation is completed (Fig. 2).

A major reason for the concern about the regulation of PCBs in the environment is their effects on biological systems. Co-planar PCB congeners that possess no chlorine in the 2,2',6 and 6' (*ortho*-) positions of a biphenyl nucleus can assume a planar dioxin-like conformation because they lack the steric hindrance of *ortho*-chlorines and elicit serious dioxin-like toxicity and carcinogenicity.<sup>1c</sup> For the reason that a certain amount of co-planar PCB congeners was contained in almost all PCB products during the production process, the degradation of commercially available (AccuStandard Inc.) pure co-planar PCB congeners such as 3,3',4,4'-tetrachlorobiphenyl **2**, 3,3',4,4',5-pentachlorobiphenyl **3** and 3,3',4,4',5,5'-hexachlorobiphenyl **4** has been studied in detail. Under our hydrodechlorination conditions, each co-planar PCB congener was smoothly converted to biphenyl **1** within 1 h and a mixture consisting only of **1** (100%) was obtained (Scheme 1).

In summary, these examples illustrate major improvements in reliability, time, simplicity, safety and cost as compared with previously proposed chemical remediation



**Figure 2.** GC/MS observation of the hydrodechlorination process of PCB congeners used as a high-tension capacitor oil (standardized voltage=6.6 KV) in practice for over a quarter-century (manufactured by Shizuki Seisakusho Co. in 1965). (a) GC/MS of the capacitor oil (PCB congeners, ACN=3.3). (b) After 1 h hydrodechlorination (balloon) of the PCBs oil (500 mg) at ambient temperature (ca. 20°C) using 10% Pd/C (50 mg) in methanol (5 ml) in the presence of triethylamine (726 ml, 7.2 mmol). Degradation is completed (ACN=0.00).



**Scheme 1.** Hydrodechlorination of co-planar PCB congeners. *Reaction conditions:* 0.01–0.08 mmol of a co-planar PCB; 10% Pd/C (10% of the weight of the co-planar PCB); Et<sub>3</sub>N (1.2 equiv. for each mol of chlorine in the co-planar PCB); H<sub>2</sub> (balloon); methanol (3–5 ml); at ambient temperature within 1 h.

tion processes of PCBs.<sup>1,2,13</sup> All reagents and solvents used are reusable, and the reaction mixture only contains biphenyl **1** and triethylammonium chloride (triethylamine is regenerated by neutralization using NaOH). Nevertheless, this study clearly sets the framework for a practical and truly catalytic degradation method of PCBs and, by implication, of structurally related chlorinated aromatic environmental pollutants, such as chlorinated *p*-dioxins, dibenzofurans and benzenes and DDTs. The results are easily applicable to industrial degradation processes of PCBs for future protection of the environment from additional dispersion of PCBs.

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- For examples: (a) Spatola et al. reported<sup>5a,b</sup> an effective dechlorination method using catalytic transfer hydrogenation (CTH) with Pd/C–HCO<sub>2</sub>NH<sub>4</sub> combination. However, the degradation of 0.44 g of Aloclor 1254 required 0.44 g of 10% Pd/C and 3 g of HCO<sub>2</sub>NH<sub>4</sub>; (b) Tundo et al. also reported<sup>5c</sup> an applicable dechlorination method using catalytic hydrogenation with a Pd/C–H<sub>2</sub> system. However, the degradation of Aroclor 1254 required a 50% KOH aqueous solution and bubbling H<sub>2</sub> gas (1 mL/min).
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- After two vacuum/H<sub>2</sub> cycles to remove air from a round-bottom flask or a high-pressure glass cylinder (Hyper Glass Cylinder, Taiatsu Techno Co.), a vigorously stirred mixture of the PCBs (50 mg–50 g), 10% Pd/C (10% of the weight of the PCBs) and triethylamine (1.2 equiv. for each mol of chlorine in the PCBs) in methanol (up to 40% solution of PCBs) was hydrogenated (H<sub>2</sub> balloon for a round-bottom flask and 1 atm of H<sub>2</sub> for a high-pressure glass cylinder) at ambient temperature (ca. 20°C) for 1–6 h. The reaction mixture was filtered using a membrane

filter (Advantec Dismic-13HP, 0.45 mm) or Celite<sup>®</sup> cake and the filtrate was evaporated to dryness. The residue was partitioned between hexanes and water, and the organic layer was dried over anhydrous magnesium sulfate. After filtration, the organic solvents were evaporated to afford biphenyl quantitatively. The products

of the hydrodechlorination were analyzed by GC/MS (Hewlett Packard, Model 5972A, measurable limit = approx. 0.5 ppm) and <sup>1</sup>H NMR (JEOL, EX-400). Further, the aqueous layer was evaporated to dryness to afford triethylammonium chloride also quantitatively.