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A new advanced method for heterogeneous catalysed dechlorination of polychlorinated biphenyls (PCBs) in hydrocarbon solvent

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Abstract—The dechlorination of PCBs with solid hydrazine hydrochloride catalysed by palladium, in an organic solvent, yields biphenyl in short reaction times. The catalyst system can be efficiently reused for several cycles. Ultrasonication of the heterogeneous catalysed reaction increases the dechlorination rate remarkably. The reactivity of the C–Cl bond on the PCB ring are in the order *meta*>*para*≫*ortho*. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Polychlorinated biphenyls (PCBs) have been classified (EPA), as priority pollutants due to their widespread presence and persistence. The PCBs have been applied in a wide variety of industrial uses including heat transfer, flame retardation, and dielectric fluids,[1] but have actually received attention as endocrine disruptors, human carcinogenes,[2] and environmental estrogens.[3]

The most widely accepted method for the destruction of the PCBs consists of incineration,[4] although this is expensive and may produce undesirable byproducts such as polychlorinated dibenzofurans and polychlorinated dibenzodioxins.[4b] Catalytic dehydrochlorination has proved to be an efficient method for the detoxification of hazardous chlorinated wastes,[5] but the practical application of catalysts to the dechlorination of organic halides was always accompanied by the problem of the deactivation of the catalyst.[6]

We have found a new heterogeneous catalytic method for the complete dechlorination of the PCBs, in an organic solvent under mild conditions of temperature or using an ultrasound source.

2. Results and discussion

Samples of 2,4,5-trichlorobiphenyl (PCB-29) or 2,5-dichlorobiphenyl (PCB-9) with well-known concentrations in hexane, were prepared for the dechlorination reaction. Thus, PCB-29 (12.5 mg, 0.05 mmol) or PCB-9 (11.0 mg, 0.05 mmol) were dissolved in hexane (40 g) and were treated with a mixture of hydrazine hydrochloride (moderately toxic reagent[7]) (250 mg, 3.65 mmol) and sodium carbonate (390 mg, 3.65 mmol) and palladium on carbon (100 mg, Pd/C 10%). A multifrequency generator and ultrasonic reactors have been designed (with frequencies centred at 250, 475, 650 and 800 kHz) to improve the heterogeneous catalytic dechlorination.

The reaction was run in a bath with stirring at variable temperature or in a reactor with ultrasonication at room temperature, finally yielding biphenyl as the sole aromatic product (HPLC). The dechlorination at 60°C (external bath) shows the highest rate. The rate of the reaction increases remarkably at room temperature with ultrasound radiation at all of the frequencies experimented, but proceeds to completion for the shortest times at 487 kHz versus 250 and 650 kHz. The analysis of all the reaction products was carried out by HPLC with a UV–vis detector, with an error of <0.1%. Hexane solutions of the required dechlorinated compounds such as dichlorobiphenyl, monochlorobiphenyl and biphenyl were used as reference.

Keywords: dechlorination; polychlorinated biphenyl; PCBs; palladium; hydrazine; sonochemistry.

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2.1. Dechlorination of 2,4,5-trichlorobiphenyl (PCB-29)

The dechlorination of PCBs was analysed taking 2,4,5-trichlorobiphenyl (PCB-29) as a reactive reference model, which shows three different C–Cl positions on the biphenyl ring: (a) *ortho*, *meta* and *para* biphenyl positions of the chlorine atoms; (b) 1,2-, 1,3- and 1,4-dichloro relative positions, Scheme 1.

The dechlorination of PCB-29 was carried out with the heterogeneous hydrazine hydrochloride/palladium (HZ/Pd) catalyst system above referred at different temperatures (rt, 40 or 60°C), at 60°C it reaches the optimal kinetic results, which are summarised in Table 1 and Scheme 1.

From Table 1, some aspects of the reaction must be considered: (a) At 60°C, from the dechlorinated compounds, the more inactive C–Cl bond was that on the *ortho* position (PCB-1, PCB-7 and PCB-9); (b) PCB-29 was transformed into PCB-9 and PCB-7, both having an *ortho* chlorine atom. Moreover, the *ortho* elimination product PCB-12 was not detected; (c) the 1,3-dichlorinated product PCB-9 (or PCB-7) shows the highest rate for the *para* (or *meta*) versus *ortho* C–Cl bond dechlorinations, PCB-1 was detected while PCB-2 was never detected. Hence, the *meta-rule* fails for PCB-29,[8] meaning that the C–Cl bonds with more neighbouring chlorine atoms in the *meta* position are removed preferentially.

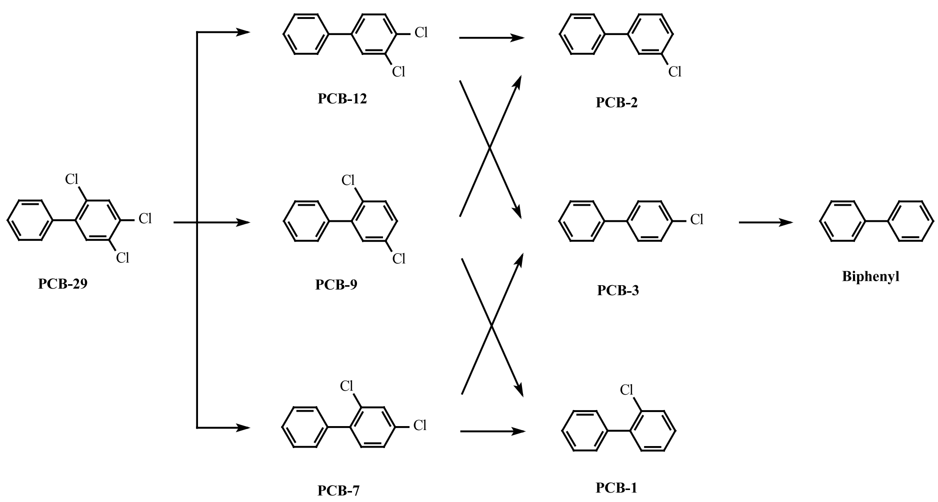
The dechlorination of PCB-29 by ultrasonication at 487 kHz, at room temperature, in general, shows a remarkably high efficiency, which is improved in the second and third catalytic cycles (Table 2).

2.2. Dechlorination of 2,5-dichlorobiphenyl (PCB-9)

In order to observe the reactivity of the dichlorinated derivatives, we carried out the dehydrochlorination of PCB-9. The results of the dechlorination under the above conditions are summarised in Table 2.

After the first catalytic cycle, the palladium catalyst was recovered by filtration on sodium carbonate and completed with the necessary hydrazine hydrochloride and was then reused in the dechlorination of a new sample. Analysis of Table 2 shows that the dechlorination happened in shorter times than for PCB-29 and small differences were observed: (a) At 60°C, the more inactive chlorine atom was also that on the *ortho* position, and the PCB-1 was observed; the *ortho* dechlorinated PCB-2 was detected in low concentration; (b) the highest rate for the C–Cl bond dechlorination was for that in the *meta* position; (c) although the recovered catalyst system exhibits a low efficiency at 60°C, the kinetic of dechlorination shows the same activity order observed in the first catalytic cycle.

The dechlorination of PCB-9 in the second and third catalytic cycles shows a remarkably high efficiency by ultrasonication of the reaction at 487 kHz, at room temperature.



Scheme 1.

Table 1. Dechlorination of the PCB-29

t (min)[a]	PCB-29	PCB-9	PCB-7	PCB-3	PCB-1	Biphenyl
15	25	20	7	5	13	30
30	2	8	0	0	6	84
45	0	0	0	0	0	100
15[b]	0	0	0	0	0	100

[a] At 60°C.

[b] Ultrasonic radiation (487 kHz).

Table 2. Dechlorination of the PCB-9

Catalytic cycle	*t* (min)[a]	PCB-9	PCB-2	PCB-1	Biphenyl
1	15	0	0	0	100
	5[b]	0	0	0	100
2	15	64	2	3	31
	90	0	0	0	100
	5[b]	38	0	8	54
	15[b]	0	0	0	100
3	15	85	2	4	9
	180	52	0	10	38
	5[b]	63	3	6	28
	45[b]	0	0	0	100

[a] At 60°C.

[b] Ultrasonic radiation (487 kHz).

Dechlorination of an industrial PCBs sample (2768 ppm) in a mineral dielectric oil (100 g) was satisfactorily carried out with the HZ/Pd system. By GC analysis, after 15 min, the mineral oil shows <25 ppm of PCBs. The same experiments, but with sonication, increases the reaction rate and leads to the practically complete destruction of the PCBs (after 5 min <4 ppm, by GC).

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