Palladium-nanoparticles catalyzed hydrodehalogenation of aryl chlorides in ionic liquids

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Abstract

Pd-nanoparticles, in molten tetrabutylammonium bromide as the solvent and tetrabutylammonium acetate as the base, catalyze the hydrodehalogenation of various aryl chlorides under hydrogen at atmospheric pressure. Recycling experiments show a decreasing activity of this catalyst due to a small leaching of palladium from the ionic liquid phase during the extraction of the reaction products with cyclohexane. On the contrary, leaching is avoided when vacuum distillation is used to separate the dehalogenated products form the reaction mixture, thus allowing an extensive recycling of the Pd-catalyst.

1. Introduction

Chlorinated organic compounds, especially polychlorinated biphenyls (PCBs), are high risk pollutants widely distributed in the environment. Therefore, their destruction or conversion to harmless compounds has attracted growing interest. Detoxification of halogenated aromatic wastes by catalytic hydrodehalogenation has been preferred, as an environmentally benign and cost saving alternative [1] to incineration, because the latter process produces highly toxic dibenzofurans and dibenzo-*p*-dioxins [2,3]. Besides the Pd-catalyzed hydrodehalogenation with phosphanes as ligands under homogenous conditions [1,4], recently, palladium supported on carbon [5–7], mesoporous silicate [8], alumina [9], organic polymers [10], zirconium phosphate [11], and hydroxyapatite [12] have been utilized as catalysts together with hydrogen [7,9,13], alcohols, hydrides and hydrazine [6] as reducing agents. The hydrodehalogenation of aryl chlorides were also performed by Pd–carbene [14] or Ni–carbene complexes [15] under homogeneous conditions.

Although hydrogen-transfer reactions proceed, in general, under milder conditions, more acceptable and economical for industry is the use of molecular hydrogen [12]. In addition, for an industrial application of this reaction, both an extensive recycling and an easy recovery of the spent Pd-catalysts are mandatory. Despite the importance of these aspects, there are few examples in the literature that report recycling experiments [8,10b,11]. With the advent of accessible methods for the preparation and handling of nanometal particles, catalytic organic transformations with these catalysts have been gaining in popularity [16]. However, unsupported monometallic palladium catalysts have been scarcely utilized for hydrodehalogenation reactions; in fact, to the best of our knowledge, only a few examples have been reported in the recent literature [17,18].

Following Reetz's discovery [19] on the easy preparation of Pd-nanoparticles (Pd-NPs) by reaction of Pd salts with

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tetraalkylammonium alkanoates, we recently published several papers concerning the Heck [20–22], Suzuki and Stille [23] reactions in ionic liquids (ILs) showing the strong influence exerted by these solvents on both the Pd-NPs life and efficiency. The advantages of using ILs would be manifold: in addition to an ease recovery of both the catalysts and reaction products, they exhibit high thermal, air stability and negligible vapour pressure.

However, in spite of the increasing use of ILs as recyclable solvents in a plethora of reactions [24], few papers have been published concerning the transfer hydrogenation in these solvents [25].

This paper reports the hydrodehalogenation of aryl chlorides catalyzed by Pd-NPs in tetrabutylammonium bromide (TBAB) as the solvent and tetrabutylammonium acetate (TBAA) as the base, under hydrogen at atmospheric pressure.

To the best of our knowledge, this is the first example reported in the literature on the use of stable and highly recyclable Pd-nanoparticles dissolved in IL useful for a hydrodechlorination process.

2. Experimental

Materials: Tetrabutylammonium bromide (TBAB), tetrabutylammonium acetate (TBAA), aryl chlorides and Pd acetate were purchased from Fluka and utilized as received. The structures of the aromatic dehalogenated compounds were determined by comparison with authentic samples.

General procedure for hydrodechlorination of aryl chlorides catalyzed by Pd-nanoparticles in IL.

A pyrex reaction flask charged with a mixture of TBAB (2 g, 6.2 mmol), TBAA (0.36 g, 1.2 mmol) and Pd acetate (0.03 mmol) is heated at 90 °C, under air and under stirring, until a dark suspension of Pd-nanoparticles is obtained (10 min ca.). Next, the reaction vessel is evacuated and refilled with hydrogen several times; then the aryl chloride (1 mmol) and the standard (decane) were added by a syringe and a balloon containing hydrogen at atmospheric pressure, was connected to the reaction vessel. The reaction mixture was heated under stirring at 90 °C (100 °C in the case of Arochlors) for the reaction times.

After completion of the reaction, the dehalogenated products and acetic acid were distilled under vacuum, leaving a mixture of TBAB and tetrabutylammonium chloride containing the catalyst that was repeatedly recycled upon addition of fresh TBAA and aryl halide. Because of the catalytic system proved to be air-stable, no care was taken to exclude oxygen during operations to distill products and add additional aliquots of starting materials.

On the contrary, an inadequate recycling was observed when the reaction products were extracted with cyclohexane. This was due to the extraction, beside the reaction products, of small quantities of the TBAB containing trace of catalyst. We observed, after the seventh cycle, that the content of the Pd in the IL, as determined by ETAAS spectroscopy, decreased to 0.025 mmol.

3. Results and discussion

While searching for a phosphane-free Pd-catalyzed regio- and stereo-selective Heck arylation of cinnamates [20] and methacrylates [21] in ILs, we found that by dissolving palladium acetate in molten TBAB and using TBAA as the base, the immediately formed dark suspension of PdNPs efficiently catalyzed the reaction of aryl bromides and chlorides. Reaction occurred at the surface of the monodisperse nanoparticles whose structure, defined core-shell, was composed of a metallic core (∼3.3 nm in size) surrounded by a stabilizing shell containing tetrabutylammonium cations, Br^- and $[PdBr_4]^{2-}$.

Although the effectiveness of nanosized catalysts has been widely demonstrated in the C–C bond forming reactions, the use of ILs as reaction media jointly with a PdNPs-catalyzed hydrodehalogenation of aryl halides is a relatively unexplored area.

Therefore, we decided to test the performance of this catalyst in the hydrodehalogenation of aryl chlorides in TBAB containing TBAA as the base.

The addition of Pd acetate to the mixture of the two ILs, afforded Pd-NPs that catalyzed, at 90 °C and under an atmospheric pressure of hydrogen, the hydrodehalogenation of chlorobenzene, 4-chloroanisole and 4-chloroacetophenone, affording quantitatively the corresponding aromatic compound (Table 1).

The reaction products were extracted with cyclohexane, leaving the catalyst and TBAB that were recycled. However, some leaching of palladium was observed in the extracted phases after each cycle, due to the extraction by cyclohexane of small quantities of TBAB containing traces of palladium. This precluded an extensive reutilization of the catalyst system as revealed by the increasing reaction times required, after each cycle, to achieve a complete conversion of the chloroarene (Table 1, entries 3–6).

Table 1
PdNPs catalyzed hydrodechlorination of aryl chlorides followed by extraction of the reaction products with cyclohexane[a]

Entry	R	Time (h)	Convn. (%)[b]	Yields (%)[b]
1	H	14	>99	95
2	OMe	21	>99	92
3	COMe	2.5	>99	96
4[c]	COMe	3	>99	90
5[c]	COMe	4	>99	88
6[c]	COMe	10	>99	82

[a] All reactions were carried out in 2 g of molten TBAB containing 3 mol% of Pd, 1 mmol of aryl chlorides and 1.2 mmol of TBAA and hydrogen at atmospheric pressure at 90 °C.
[b] Evaluated by GLC using decane as internal standard.
[c] Reused catalyst of the previous entry.

Table 2
Recycling of Pd-nanoparticles

R—⟨benzene ring⟩—Cl $\xrightarrow[\text{H}_2,\ \text{TBAB, TBAA}]{\text{Pd-NPs}}$ R—⟨benzene ring⟩—H

Run	R = OCH$_3$[a]	R = COCH$_3$[a]
Initial use	95	96
1st reuse	94	90
10th reuse	95	90
19th reuse		95

[a] Isolated yields (%) by vacuum distillation.

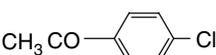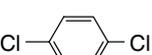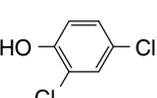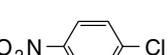As the work-up by extraction with cyclohexane did decrease the concentration of the catalyst in the IL, we decided to distill the products under vacuum. By using this procedure aryl chlorides were efficiently dehalogenated, with an extensive catalyst recycling. For example, in the case of 4-chloroacetophenone and 4-chloroanisole, the catalyst was recycled, with an almost constant reaction rate after each cycle, more than nineteen and ten times, respectively (Table 2).

Moreover, this experimental procedure allows to leave the IL and the catalyst for further reactions avoiding the use of toxic and volatile (VOCs) extractants.

Next, we extended this method to a variety of aryl chlorides (Table 3). Electron rich (Table 3, entries 2, 5) as well as electron poor substrates (Table 3, entries 3, 4, 6) were efficiently dehalogenated, affording the corresponding aromatic compounds with tolerance for functional groups such as ketone, amine and phenolic hydroxyl. Two types of polychlorinated biphenyls (Table 3, entries 7, 8) were also completely dechlorinated. The slow reaction rates observed for the latter two compounds probably depend on steric hindrance, since the Aroclors are a complex mixture of *ortho*- and *para*-polychlorinated compounds. In addition, the slow dehalogenation of 2,4-dichlorophenol (entry 5), a widespread pollutant, can be justified since the TBAA, by deprotonating the phenol, decreases the rate of the oxidative addition step.

We tested also the use of ammonium formate as the reducing agent in place of hydrogen and TBAA. Under these conditions, a slower dehalogenation was observed but, after two recycles, the increasing concentration of

Table 3
Hydrodechlorination of aryl chlorides in IL by Pd-nanoparticles[a]

Ar—Cl $\xrightarrow[\text{H}_2,\ \text{TBAB, TBAA}]{\text{Pd-NPs (3\%)}}$ Ar—H
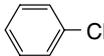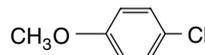
Entry	Ar–Cl	Time (h)	Convn. (%)[b]	Yields (%)[b]
1	⟨C$_6$H$_5$—Cl⟩	14	>99	89
2	CH$_3$O—⟨C$_6$H$_4$⟩—Cl	21	>99	95
3	CH$_3$CO—⟨C$_6$H$_4$⟩—Cl	2.5	>99	96
4	Cl—⟨C$_6$H$_4$⟩—Cl	19	>99	85
5	HO—⟨C$_6$H$_3$(Cl)⟩—Cl	44	>99	76
6	O$_2$N—⟨C$_6$H$_4$⟩—Cl	6.30	>99	80[c]
7	Aroclor 1254	36	>99	71[d]
8	Aroclor 1248	42	>99	75[d]

[a] All reactions were carried out in TBAB (2 g), TBAA (1.2 mmol), aryl chlorides (1 mmol) and 3% of Pd acetate at 90–100 °C.
[b] Evaluated by GLC using decane as internal standard. Yields average of two runs.
[c] Aniline was the product.
[d] Isolated yields of biphenyl extracted with cyclohexane.

ammonium chloride, insoluble in TBAB, afforded an intractable medium inadequate for further recycling purposes.

Indeed, one of the most observed limitation in recycling the Pd-catalyzed reactions in molecular solvents, as well as in imidazolium or pyridinium ILs, is represented by the gradual catalyst deactivation due to an increase of inorganic salts or ammonium halides deriving from H–Pd–Cl neutralization by inorganic or organic bases such as tertiary amines. On the contrary, the reaction of TBAA with H–Pd–Cl affords, besides the restoration of the Pd(0) catalyst, acetic acid and tetrabutylammonium chloride miscible with TBAB. When necessary, tetrabutylammonium chloride may be reconverted into TBAA by simple methatesis with sodium acetate in acetone. The effectiveness of TBAA in neutralizing the PdH is due to the higher basicity of the acetate in TBAA than in water. In this IL, for steric reasons, the acetate is distant from the bulky tetraalkylammonium and therefore less solvated than in water [26].

Results reported above point out the fundamental role of TBAB as an IL in governing the catalyst life and activity by means of the stabilization of the Pd-nanoparticles. However, despite the observed beneficial effects exerted by quaternary ammonium salts on the Heck reaction [27], the exact nature of this influence cannot be ascribed to a single effect such as the high polarity or phase-transfer ability, but rather to a superposition of several factors. For example, Reetz and Maase [19] found that Pd-nanoparticles were stabilized by large ammonium cations. Furthermore, Amatore and Jutand [28], demonstrated that Pd(0)(PPh$_3$)$_2$, the proposed catalyst in the C–C coupling reactions, was unstable in the absence of halide or acetate ions which transform this complex into a more stable and catalytically active 16-electron anionic complex as [Pd(PPh$_3$)$_2$X]$^{(-)}$. Following these conclusions and to elucidate the ionic liquid effects, we propose some considerations that would assist in explaining our results. In TBAB the collapse of the Pd-nanoparticles into inactive "Pd-black" is inhibited by the capping of the catalyst due to the large tetraalkylammonium cations [23]. In this situation the Coulombic repulsion amongst the nanoparticles impedes their aggregation [19,20].

4. Conclusions

Palladium-nanoparticles, stabilized by tetrabutylammonium bromide as the solvent and in the presence of tetrabutylammonium acetate as the base, do allow the hydrodehalogenation of aryl chlorides under hydrogen at atmospheric pressure. In this solvent the nanoparticles are so stable to permit an extensive recycling of both the catalyst and the ionic liquid. In addition, as the catalyst is air-stable, the experimental procedure does not require special cares during both work-up and recycling operations, such as for example the use of the inert atmosphere, thus increasing the value of this methodology.

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