

Mechanochemical, solvent free, palladium-catalyzed hydrodechlorination of chloroaromatic hydrocarbons

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Abstract

Palladium-catalyzed, mechanochemical hydrodechlorination (HDC) of solid hexachlorobenzene (HCB) with various solid hydrogen donors was carried out at ambient temperature in a planetary ball-mill to give benzene and a mixture of partially chlorinated benzenes. The mechanochemical hydrogen transfer dechlorination is effected in the presence of Pd on carbon, or palladium(II) acetate, and in the absence of a solvent, while no such reaction took place in the absence of Pd. The presence of a base (NaOH) and mmol amounts of water (introduced in the form of sodium phosphate heptahydrate) were needed to improve HDC efficiency. Of the H-donors studied: sodium hypophosphite, sodium borohydride and calcium hydride, the last one was the most efficient, realizing complete loss of HCB over 20 h. The chemoselectivity of the HDC depends on the hydrogen donor, e.g., sodium hypophosphite (SHP) gives 1,2-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene as the major intermediates in the dechlorination process. A chemoselectivity similar to that determined in mechanochemical HDC was found in a liquid phase hydrogen transfer HDC using a Pd/C catalyst and SHP in aqueous acetonitrile.

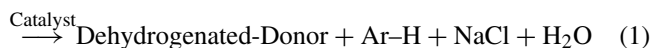
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1. Introduction

The catalyzed hydrodechlorination (HDC) of aryl chlorides has been studied extensively as a potential process for non-thermal removal of persistent organic pollutants (POPs). Such dehalogenation typically proceeds in solution or gas phase, via reactions with dihydrogen [1] or various hydrogen donors (hydrogen transfer reactions) [2–8], and requires activation by transition metal catalysts (mainly Pd or Pt) present as a solid phase component (Eq. (1)).

H-Donor + Ar-Cl + NaOH



Some recent publications have reported a solid phase, so-called mechanochemical reaction (MCR), in which an effective

dechlorination reaction occurs at ambient temperature when aryl chlorides are ball-milled in the absence of both solvent and a transition metal catalyst [9–14]. These MCRs are performed either under oxidative conditions in the presence of CaO and Ca(OH)₂ [9–11], or under reductive conditions in the presence of alkali earth metals [11], metal hydrides [12,13] or a combination of a metal and an organic H-donor [14]. A recent review presents a more general and comprehensive description of mechanochemistry [15].

Such an MCR process could be valuable, for example, in the decontamination of organochlorine contaminated soil and sludge; the reactions are attractive environmentally as they could be performed in closed vessels under controlled conditions, without the use of poisonous, inflammable or volatile solvents and diffusible hydrogen gas. Further, with selectivity toward organochlorine substrates, contaminated solids and non-chlorinated oils could be remediated without the need for a preceding separation of contaminants [11].

In contrast to the intensely studied gas and liquid phase, metal-promoted HDC (more than 1000 publications over the last 30 years) [1], no catalyzed MC hydrogen transfer hydrodechlorination has been reported. The goal of the present study was to find out if a catalyzed, mechanochemical hydrogen transfer

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HDC reaction was indeed feasible, and the findings reported here prove this concept. The work also looks at the reported, non-catalytic, solid phase, mechanochemical reductive dechlorination reaction [9–14], in comparison with the non-reactivity in solution unless a catalyst is present [1–8]. One suggestion is that some of these mechanochemical reactions [9–14] are actually catalyzed by some trace metallic contamination present in the ball-mill [16]. Further, according to a recent publication [17], solid–solid reactions (at least those performed with manual grinding) actually occur in a liquid melt phase, and thus it is possible that our MC hydrogen transfer HDC reactions occur in a melt phase [18]. In order to compare reactivity patterns of our mechanochemical reactions with those of a liquid phase hydrogen transfer HDC system, we studied also the latter system for HCB using sodium hypophosphite as H-donor in acetonitrile-containing media.

Use of powerful ball-milling for Ti-catalyzed transformation of compounds such as aluminum hydrides for hydrogen storage purposes is well known, and such MCRs for reversible hydrogen storage and release have been studied extensively [19]. The use of the later transition metals, so valuable in numerous applications of solution phase organic chemistry, has been little studied in MCR systems, but we note a FeCl_3 -catalyzed phenol coupling reaction [20] and Pd-catalyzed coupling reactions of bromo- and iodoaromatics reported recently [21].

2. Experimental

The mechanochemical HDC reactions were performed by continuous grinding of the solid reactants in a planetary ball-mill (Fritsch “pulverisette 6”) using an agate bowl (non-metallic) (80 mL) and 30 agate balls (10 mm diameter). Milling was performed at 450 rpm for 20 h at room temperature with 24 grinding cycles of 50 min each, and a 10 min cooling interruption between each cycle.

To a milling bowl was added: hexachlorobenzene (HCB, 284.8 mg, 1.0 mmol), an 8–12-fold molar excess of hydrogen donor (sodium hypophosphite (SHP), sodium borohydride (SBH), or calcium hydride) and a catalyst (10% Pd on C powder (Aldrich 52,088-8), 50 or 100 mg), or $\text{Pd}(\text{OAc})_2$ (16–23 mg, 0.07–0.1 mmol). Four other reagents were also added: decolourising carbon (Fisher Chemicals, 300–350 mg) in order to minimize the gumming of materials and to adsorb volatile products, NaOH pellets (400 mg, 10 mmol) for neutralization of the released HCl and for promotion of the dechlorination (Eq. (1)), sodium phosphate heptahydrate ($\text{SP}\cdot 7\text{H}_2\text{O}$, 275 mg, 1.0 mmol) in order to provide water that eliminates the pyrophoric nature of the solid product material, and 1,2,4,5-tetramethylbenzene (53 mg, 0.4 mmol) as an internal standard for the GC analyses.

After the milling procedure, the resulting black powder was washed with CH_2Cl_2 , and then triturated with water, the aqueous suspension then being centrifuged; the precipitate was washed again with CH_2Cl_2 and the aqueous phase was extracted with CH_2Cl_2 . The CH_2Cl_2 washings were combined and dried with anhydrous MgSO_4 . Samples of the filtrate from this solution were injected into a Hewlett Packard GC instrument 5890 fitted

with an FID detector and two capillary columns (an HP OV17 and a Supelco Simplicity 5) that successfully separated all the dechlorinated products, which were determined by comparison with data for the commercial aryl chlorides. All the reagents, organochlorides, H-donors, catalysts and solvents were used as purchased (Aldrich).

Note: In the uncatalyzed, mechanochemical CaH_2 decomposition of chloroaromatics [12], a controlled inert atmosphere was recommended; in the present reaction conditions, use of $\text{SP}\cdot 7\text{H}_2\text{O}$ eliminated any hazardous, spontaneous combustion problems.

A typical liquid phase HDC reaction mixture contained HCB (1 mmol), catalyst (10% Pd/C, 50 mg, 0.05 mg atom Pd), NaOH (~400 mg, ~10 mmol), 1,2,4,5-tetramethylbenzene (53 mg, 0.4 mmol) as the GC internal standard, and the hydrogen donor sodium hypophosphite (880 mg, 10 mmol). These reagents were introduced into a 100 mL reaction tube containing 10 mL acetonitrile, and the tube was then connected to a reflux condenser and the mixture was magnetically stirred for 5 min. Distilled water (1 mL) was added and the mixture was then refluxed for the desired reaction time. After being cooled to room temperature, the product mixture was worked-up by addition of CH_2Cl_2 (30–40 mL), decantation of solvents, followed by aqueous washings of the solid residue. The aqueous phase was extracted with CH_2Cl_2 , and the solid was washed again with CH_2Cl_2 . The CH_2Cl_2 fractions were combined, dried with anhydrous MgSO_4 , filtered, and brought to a known final volume by addition of further CH_2Cl_2 .

To ensure reproducibility, every reaction was duplicated, and every sample was injected at least three times into the two GC columns, where integration values varied by $\pm 5\%$.

3. Results and discussion

Data on the hydrogen transfer mechanochemical HDC of hexachlorobenzene are summarized in Table 1. Comparison of entries 1 and 2, entries 5 and 7, and entries 10 and 11, shows clearly that the hydrodechlorination using SHP, SBH or CaH_2 is promoted by the addition of the Pd/C catalyst; a useful way of quantifying this is the dechlorination efficiency (D.E.) as defined in footnote ‘c’ of the Table. Use of less catalyst results in a lower D.E. (Table 1, entries 5 and 6). $\text{Pd}(\text{AcO})_2$ also acts as a catalyst precursor (entries 3 and 4), but is less efficient than Pd/C; the brown acetate complex is reduced during the reaction to give a black powder (entry 3), presumably Pd metal, which has lower catalytic activity than that of well-dispersed Pd on carbon. However, the addition of carbon (entry 4 versus entry 3) improved significantly the catalytic efficiency, probably due to hydrogen spillover from the metal to carbon [22].

Of the H-donors tested in the absence of a catalyst, only CaH_2 showed any activity, pentachlorobenzene being the only product of this non-catalyzed reaction (entry 11). The reaction of CaH_2 in the presence of Pd/C (entry 10) gave a non-selective mixture of benzene (15%), chlorobenzene (6%), dichlorobenzenes (DCB) (26%), trichlorobenzenes (TCB) (33%), tetrachlorobenzenes (TetCB) (19%) and trace pentachlorobenzene (PntCB). A

Table 1
Product yields from MC hydrodechlorination of C₆Cl₆

	Reactants ^a catalyst (mg) H-donor (mmol)	Percentage distribution of products ^b (relative yields, mol%)						Total relative yield (mol%) ^b	D.E. ^c
		C ₆ H ₆	C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₃	C ₆ H ₂ Cl ₄	C ₆ HCl ₅	C ₆ Cl ₆		
1	Pd/C (100) SHP (8)	13	3 (1,2) ^d	3 (1,2,3)	4 (1,2,3,4)	10	54	87	23
2	No catalyst SHP (8)	0	0	0	0	0	85	85	0
3	Pd(AcO) ₂ (23) SHP (8) no carbon	0	0	0	2 (1,2,3,4)	28	60	90	6
4	Pd(AcO) ₂ (16) SHP (8)	13	1 (1,2)	1 (1,2,3)	1 (1,2,3,4)	2	71	89	17
5	Pd/C (100) SBH (10)	0	0	7 (1,2, 4)	78 (1,2,4,5); 10 (1,2,3,5)	Trace	Trace	95	35
6	Pd/C (50) SBH (10)	0	0	Trace	32 (1,2,4,5); 9 (1,2,3,5)	56	Trace	97	25
7	No catalyst SBH (10)	0	0	0	0	Trace	95	95	0
8	Pd/C (50) SBH (10) No SP·7H ₂ O	0	0	0	42 (1,2,4,5); 15 (1,2,3,5)	36	4	97	26
9	Pd/C (50) SBH + SHP (5 + 5)	0	0	0	13 (1,2,4,5); 3 (1,2,3,5)	65	17	98	17
10	Pd/C (100) CaH ₂ (12)	15	26 ^e (1,2)	16 (1,2,3); 17 (1,2,4)	6 (1,2,3,4); 13 (1,2,4,5)	Trace	0	99	61
11	No catalyst CaH ₂ (12)	0	0	0	0	37	62	99	6

^a A standard reaction mixture (see Section 2) contains: substrate (hexachlorobenzene, 1 mmol), hydrogen donor (SHP, SBH or CaH₂, 8–12 mmol), catalyst (e.g. 10% Pd/C, 50–100 mg, 0.05–0.1 mg atom Pd), NaOH (10 mmol), SP·7H₂O (1 mmol), GC internal standard (1,2,4,5-tetramethylbenzene, 0.4 mmol). This column lists just the catalyst, H-donor, and any differences from the standard reaction mixture.

^b The relative yield is based on the GC internal standard. Absolute yields were lower as a result of loss of material (approximately half of the initial amount of internal standard and presumably all other organics) during work-up, caused by irreversible adsorption on carbon and other fine powdered products.

^c Dechlorination efficiency (D.E.) is defined by $100 - [\sum 100nP_n/6 \sum P_n(n=0-6)]$ where P_n is percent yield of C₆Cl_nH_{6-n} ($n=0-6$). For quantitative dechlorination: D.E. = 100.

^d The numbers in parentheses refer to the Cl-substituent, e.g. (1,2) means 1,2-dichlorobenzene.

^e Chlorobenzene (6%) was also found.

different selectivity was found on using SBH as H-donor, HCB reacting almost quantitatively to give 1,2,3,5- and 1,2,4,5-TetCB (as well as PntCB, entries 5 and 8). The presence of the sodium phosphate hydrate (SP·7H₂O) enhanced this chemoselectivity to give basically just the TetCB products (entry 5), as well as preventing formation of the pyrophoric products mixture formed in the absence of the hydrate (entry 8).

The product mixtures from the Pd/C-SHP systems tended to stick to the walls and cover of the milling-bowl, while product mixtures from the corresponding SBH and CaH₂ systems were more powdery. This characteristic of the SHP system may account for its lower D.E. value (23, entry 1) compared to the values for the other two H-donor systems (35 and 61; entries 5 and 10, respectively). Consistent with this, the reaction utilizing a mixture of SHP (0.5 mmol) and SBH (0.5 mmol) (entry 9) was less efficient than that using solely 1.0 mmol SBH (entry 6).

Of note, in the case of Pd(AcO)₂ the main dechlorination pattern is via multiple-chlorine elimination to give benzene, as evidenced by the higher ratio of benzene to partially dechlorinated products (entry 4) when compared to data for the corresponding Pd/C catalyst (entry 1), where a consecutive mechanism (elimination of a single chlorine atom in each step) takes place.

The chemoselectivity of SHP dechlorination to give 1,2-, 1,2,3- and 1,2,3,4-chlorobenzene products (as well as benzene and PntCB) (entry 1) resembles one we have found in a Pd/C heterogeneously catalyzed, liquid phase HDC reaction of HCB using SHP in a 10:1 MeCN:H₂O medium. Conversions of some liquid phase HDC reaction are summarized in Table 2 [23].

Table 2 (entry i) shows that SHP is an effective H-donor in the presence of water as a co-solvent, while a less effective process takes place without added water (entry ii); however, SHP is a

Table 2
Product yields from liquid phase hydrodechlorination of C₆Cl₆

	Reactants ^a 10% Pd/C (mg) H-donor reaction time	Percentage distribution of HDCl products ^{b,c} (yields, mol%)						Notes ^d	
		C ₆ H ₆	C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₃	C ₆ H ₂ Cl ₄	C ₆ HCl ₅	C ₆ Cl ₆		(C ₆ H ₅) ₂
i	50 SHP 18 h	91	0	0	0	0	0	2	D.E. 100
ii	50 SHP 18 h	11	3 (1,2)	8 (1,2,3)	12 (1,2,3,4)	28	14	0	D.E. 34 no added H ₂ O solvent: MeCN (bp 81 °C)
iii	50 SHP 0.5 h	9	4 (1,2)	4 (1,2,3)	5 (1,2,3,4)	10	64	0	D.E. 18

^a A standard reaction mixture (see Section 2) contains: substrate (hexachlorobenzene, 1 mmol), hydrogen donor (SHP 10 mmol), catalyst (10% Pd/C, 50 mg, 0.1 mg atom Pd), NaOH (10 mmol), GC internal standard (1,2,4,5-tetramethylbenzene, 0.4 mmol) and solvent MeCN:H₂O (10:1) (bp 78 °C). This column lists the catalyst, H-donor, and reaction time.

^b Yield is based on the GC internal standard.

^c (1,2), (1,2,3), etc. represent various chlorobenzenes, e.g. (1,2,3) = 1,2,3-trichlorobenzene.

^d D.E. is defined in footnote 'c' of Table 1.

hydrated salt ($\text{Na}_2\text{H}_2\text{PO}_4 \cdot 0.8\text{H}_2\text{O}$), and thus a small quantity of water is being added via the solid SHP. Use of short reaction times allowed for detection of the intermediate chlorobenzene products (entry iii). The resemblance of the intermediates in the liquid phase and the mechanochemical reactions (entries ii and i, respectively) implies a link between the mechanisms of the two systems.

The data of Table 1 show unambiguously that the mechanochemical hydrodechlorination reaction is indeed catalytic when using SHP, SBH and CaH_2 as H-donors. The variation in chemoselectivity for these H-donor systems implies that the HDC reactions do not involve a gas–solid reaction, with H_2 being formed from decomposition of the H-donor, i.e. several different reductive species are involved.

As mentioned above, in the presence of CaH_2 , non-catalytic, mechanochemical HDC does occur to a limited extent (Table 1, entry 11), possibly via a thermal reaction occurring in local hot spots resulting from the impact of the grinding balls. Whether some of the previously reported [11–14], highly efficient HDC reactions in a steel milling bowl were indeed non-catalyzed remains an open question.

As the uncatalyzed, mechanochemical reactions of CaH_2 with chlorinated hydrocarbons, under inert atmosphere and high energy milling, have been reported to be highly exothermic [12], our Pd-catalyzed reactions, even though carried out under mild conditions at lower milling intensity and in the presence of air and humidity, may involve a melt phase, a key aspect that has been substantiated previously for several solid phase reactions [17].

In order to ascertain the absolute yields, a blank experiment was performed using a mixture containing benzene (43 mg), various chlorobenzenes (50–100 mg) and all the reaction components (NaOH and $\text{SP} \cdot 7\text{H}_2\text{O}$) except a catalyst and H-donor. This mixture was milled and worked-up as usual; GC relative yields (based on 50% loss of the internal standard) were 100% for the chlorobenzenes and ~50% for benzene. Presumably, partial vapourization of benzene occurs during the milling and work-up process, and the actual yields of benzene are likely higher than those given in Table 1 (entries 1 and 4). A quantitative, absolute yield of 1,2-DCB in the blank experiment indicates that the reaction temperature probably remains well below 180 °C (the bp of 1,2-DCB).

The data reported here are preliminary, and further studies on several aspects are needed to optimize the catalysis; for example, catalyst surface area, Pd dispersion, the effect of the nature of the carbon support, XRD, SEM/TEM pictures, catalyst re-use, etc. This type of solid phase, metal-catalyzed, mechanochemical reaction offers considerable potential; in addition to possible environmental applications, studies of the solid state chemistry could provide a better understanding of catalytic reactions where solvent and molecular solvation effects are absent.

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