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Detoxification of aryl-organochlorine compounds by catalytic reduction in supercritical carbon dioxide

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Pentachlorophenol, octachloronaphthalene and decachlorobiphenyl were smoothly converted to cyclohexanol, decalin and dicyclohexyl, respectively, by reaction, during 0.5–2 h, with excess hydrogen over alumina-supported palladium (5% w/w) in the presence/absence of supercritical carbon dioxide (50–90 °C). With these conditions, dechlorinations and dearomatization to their cyclic analogs were complete but no carbon–carbon bond scission was observed and only traces of partial deoxygenation/dimerization of the pentachlorophenol substrate (to form 1,1'-oxybis(cyclohexane)) was seen. The scCO₂ medium functioned as an inert support for the reactions; differences in rates of reaction between chlorinated compounds and their aromatic hydrocarbon homologs were not observed. These results suggest that environmentally recalcitrant chlorinated aromatic compounds can be detoxified facily by catalytic reduction with H₂ under mild conditions.

Introduction

scCO₂ Reaction media

The use of mixtures of molecular hydrogen with supercritical carbon dioxide (scCO₂) as a medium to perform reductive dechlorinations has remained less extensively explored, yet this phase possesses several attractive properties. The use of scCO₂ has often been considered to be an ideal phase because of its mild critical properties ($T_C = 31\text{ °C}$, $P_C = 7.4\text{ MPa}$), non-toxicity, non-flammability, modest cost and a lack of restrictive regulations. Molecular hydrogen is completely miscible in near-critical CO₂,¹ and can result in a very high initial rate of reaction—up to 1400 mol of formic acid have been produced from CO₂ per mol of catalyst per h²). The same reaction under identical conditions but in liquid organic solvents is much slower principally the result of decreased diffusion rates and the limited solubility of H₂ in most organic solvents. Solvent polarity of the reaction medium can be fine tuned with ease in the near-critical region (generally $1.05\text{--}1.2T_C$)³ by simply changing the pressure. To achieve suitable substrate solubility, the reaction medium can be modified by adding an inert co-solvent. As an example, ethanol can be volume expanded several fold with dense-phase CO₂ in which this solvent becomes totally miscible. Moreover, the reactants/products can be separated readily from the reaction medium by pressure reduction. Because aromatic hydrogenations are highly exothermic,⁴ reaction is favoured and selectivities can be increased by operation at lower temperatures yet for hydrogenations on a larger scale some means of heat dissipation can become necessary. The heat capacities of scCO₂ can also be pressure-tuned to be more liquid-like⁵ and to minimize product hold up. For porous solid catalysts, product selectivity can also be optimized to mitigate pore-diffusion limitations and the accumulation of coke-forming precursors that can inactivate catalytic sites. Clark and Subramaniam⁶ have reported that in scCO₂, 1-butene/isobutane alkylation resulted in virtually

steady alkylate (trimethylpentanes and dimethylhexanes) production during two days. The ability of the carbon dioxide based supercritical reaction mixtures to mitigate coking and thereby to maintain better pore accessibilities was evident from the narrow product spectrum (confined to C₈ products), the lighter color of the spent catalyst samples, and relatively low surface-area and pore-volume losses (<25%) in the spent catalysts. For identical 1-butene space-velocity and feed isobutane/olefin ratios in the absence of CO₂, alkylate formation declined continuously with time. At the high temperatures (>135 °C) required for supercritical operation without carbon dioxide, cracking and coking reactions were dominant.

Catalytic inactivation has been reported during hydrogenations over Pt⁰/Al₂O₃ in near-critical CO₂⁷ that might have resulted from the possible formation of one or more surface species including formates, carbonates and/or CO in the presence of CO₂ + H₂. A variety of fats and oils have been reduced successfully in near-critical CO₂ over Ni,⁸ Pd or Pt.⁹ As well, as the reduction of double bonds of unsaturated ketones over Pd/Al₂O₃ has been reported.¹⁰ Several insightful reviews,^{11–13} have been published recently.

Green Context

The destruction of problematic pollutants such as polychlorinated aromatics is an urgent task, which falls at the fringes of green chemistry. When the destruction is replaced by a method which detoxifies and simultaneously converts the pollutant into useful molecules this represents a distinctly green process. Here, the catalytic reduction of some chloroarenes is demonstrated which leads to the efficient production of *e.g.* cyclohexanol, a useful industrial intermediate. The process proceeds smoothly in supercritical CO₂ under relatively mild conditions

DJM

Hydrodechlorinations

The gas phase hydrodechlorination of chlorophenols [dichlorophenols (DCPs), trichlorophenols (TCPs) and pentachlorophenol (PCP)] in H_2 over Ni (1.5%, w/w and 15.2%) loaded silica and Ni (2.2%, w/w) exchanged Y zeolite catalysts were evaluated over the temperature range 200–300 °C. In every instance, the Ni catalysts were 100% selective in cleaving the Cl component from the ring, leaving the aromatic nucleus and OH substituent intact.¹⁴ Similarly, the gas phase hydrodechlorination of methanolic and mixed methanol–water solutions of 2-chlorophenol, 2,6-dichlorophenol, 2,4,5-trichlorophenol and pentachlorophenol has been studied at 300 °C over Ni/SiO₂ catalysts of varying (1.5–20.3 wt% Ni) nickel loading.¹⁵ Each catalyst was again 100% selective in promoting hydrodechlorination.

Hydrogen temperature programmed desorption (TPD) revealed the existence of three forms of surface hydrogen: (i) hydrogen bound to the surface nickel; (ii) hydrogen at the nickel/silica interface; (iii) spillover hydrogen on the silica support.¹⁶ The spillover hydrogen appeared to be hydrogenolytic in nature and was responsible for promoting hydrodechlorination while the hydrogen that was chemisorbed on, and remained associated with, the surface nickel metal participates in aromatic hydrogenation. Hydrodechlorination proceeded *via* an electrophilic mechanism, possibly involving spillover hydronium ions. The gas-phase hydrogenation/hydrogenolysis of alcoholic solutions of phenol was studied at 150–300 °C using a Y zeolite-supported Ni catalyst and a Ni/SiO₂ catalyst.¹⁷ Phenol hydrogenation proceeded in a stepwise fashion giving cyclohexanone as a reactive intermediate while a combination of hydrogenolysis and hydrogenation yielded cyclohexane. Hydrogenolysis to benzene was favored by high Ni loadings and elevated temperatures. The gas-phase hydrogenation of PhOH at 150–300 °C has also been studied over Pd⁰/Mg⁰ (1% w/w). Hydrogenation proceeded in a stepwise fashion with cyclohexanone as the partially hydrogenated product and cyclohexanol as the fully hydrogenated product.¹⁸ The catalyst provided 96% selectivity with respect to cyclohexanone at 150 °C, but the cyclohexanone yield decreases at higher temperatures as conversion declined and cyclohexanol was increasingly preferred. Conversion and selectivity were both stable with prolonged catalyst use (*i.e.*, time on stream > 55 h). The catalytic hydrodechlorination of chlorobenzene in ethanol over Ni⁰/C, Pd⁰/C and Ni⁰/Pd⁰ was studied at 50 °C, 1 atm H_2 . All three catalysts had mediated efficient dechlorination after 3 h.¹⁹

Dechlorinations in scCO₂ of polychlorinated biphenyl (PCB) compounds or pentachlorophenol (PCP) have been performed in a flow-through reactor filled with zero-valent metal (Fe⁰ or Mg⁰) or bimetallic mixture (Ag⁰/Fe⁰, Pd⁰/Fe⁰ or Pd⁰/Mg⁰). Substrate (20–30 mg min⁻¹) was dechlorinated very efficiently (but not quantitatively) within a 25 × 1 cm reactor column operated at ~450 °C. The only appreciable products were biphenyl (or phenol) and chloride ion that remained on the ZV metal surface.^{20–22} Aqueous slurries of four surfactant formulations were evaluated for the mobilisation of PCB compounds from contaminated soil²³ and coupled with *on line* dechlorination.²⁴ The objectives of the current study were to evaluate mixtures of H_2 with scCO₂ for their ability to mediate the catalytic dechlorination of aromatic organochlorine compounds.

Experimental

Reactor

The dechlorination assembly consisted of source of pressurized scCO₂, [a K-type cylinder of compressed CO₂ that was further

pressurized with an diaphragm compressor (Newport Scientific, Jessop, MD)], and a reactor unit. The supercritical fluid reactor consisted of a 50 ml high-pressure cylindrical vessel with a demountable top that had been modified with the addition of two 1/16" stainless steel (ss) tubes that served as gas inlet and outlet. The tubes were each terminated with a high pressure needle valve. In operation, the vessel was equilibrated in a water bath to the desired operating temperature of the experiment then charged with substrate (1 or 10 mg) in 0.2 ml hexane, test catalyst (25 mg), and a Teflon-coated stirring bar. The mixture was then pressurized to 345 or 690 kPa with H_2 gas. For certain runs, the reaction medium was overpressured with CO₂ (to 0.69–30.34 MPa). Post reaction for 0.5–2 h, the pressure was vented gradually by release through a capillary restrictor (5 µm × 20 cm) into ethanolic trapping solvent (10 ml). All trials were performed in triplicate [each entry in the Tables represent the mean recovery (mol%) ± 1 relative standard deviation]. The course each trial was monitored by gas chromatography–mass spectrometry (GC–MS).

Chemicals

Biphenyl, cyclohexanol, cyclohexanone, *o*-chlorophenol, *p*-chlorophenol, decachlorobiphenyl, 2,3-dichlorophenol, methanol, naphthalene, octachloronaphthalene, phenol, 2,3,4,5-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, 2,3,5-trichlorophenol and 2,3,6-trichlorophenol were purchased from Aldrich Chemical Co., Oakville, ON, Canada. Chemicals were ACS Reagent Grade or better and were used as received. Catalysts, Ni⁰/SiO₂–Al₂O₃ (66 ± 3% w/w, catalog #31276), Pd⁰/γ-Al₂O₃, reduced (5% w/w, catalog #11713) and Pt⁰/γ-Al₂O₃ reduced (1% w/w, catalog #11797) were purchased from Alfa Aesar, Ward Hill, MA, USA whereas Fe⁰/γ-Al₂O₃ (0.3% w/w) and Ag⁰/Fe⁰/γ-Al₂O₃ (0.3%/1.7% w/w) were synthesized by A. Majid.

Gas chromatography–mass spectrometry

GC–MS was performed on a Varian model 3900 gas chromatograph fitted with a model 8400 autosampler and a model 2100T ion trap detector. The DB-5 capillary column (30 m × 0.25 mm i.d.) was eluted with helium at 1.0 ml min⁻¹. After an initial hold for 1 min at 50 °C, the column was ramped, at 10 °C min⁻¹, to 300 °C and held for a further 3 min prior to cool down. The temperature of the injector and detector were maintained at 250 and 150 °C, respectively. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the National Institute of Standards and Technology (NIST) or the Saturn spectral libraries and corroborated by co-chromatography and spectral matching with authentic standards.

Results and discussion

It was envisaged that the overall process of decontamination of natural media (soils/sediments) would become more appealing if supercritical carbon dioxide (scCO₂) extractions of organochlorine (OC) contaminants from polluted media were to be coupled with an *on line* detoxification sequence. Generally, OC compounds have been considered to be environmentally recalcitrant due principally to their relatively non-polar nature (that decrease aqueous solubility and hinder physical dispersal processes) and the general lack of functional groups (that can facilitate metabolic transformations). Toxicities of both alkyl and aryl OC compounds, that generally increase with increasing chlorine content,²⁵ can be reduced appreciably by reductive dechlorination to form relatively innocuous hydrocarbon and chloride ion. It was further anticipated that once mobilized into

supercritical carbon dioxide (scCO₂), dechlorination might be accelerated further by contact of the solution with molecular hydrogen in the presence of a catalyst.

It was also anticipated that operation above the boiling point of hexane would assure a single supercritical phase for the solution. In initial experiments, the capacities of five alumina supported catalysts to accelerate the dechlorination of pentachlorophenol (PCP) in the presence of a large excess of hydrogen were evaluated (Table 1). With 0.5 h of reaction at 80 °C, the bare alumina support material mediated only partial dechlorination to tetrachlorophenol species (~5 mol% conversion) that was only marginally more efficient than trials in the absence of either catalyst or hydrogen for which no reaction was observed. The zero-valent iron (Fe⁰) loaded support was not more efficient at mediating dechlorination than was the bare alumina. Product distributions for reactions in the presence of Ag⁰/Fe⁰ supported bimetallic mixture contained only totally dechlorinated product that had also been ring reduced to cyclohexanol (~11 mol%) in addition to unreacted substrate (~67 mol%). The Pt⁰ and the Ni⁰ supported catalysts did not produce more cyclohexanol (~12 and 14 mol%, respectively) than the bimetallic catalyst but less substrate remained after reaction (~47 and 37 mol%, respectively) and smaller quantities of tetrachlorophenols (~7 and 18 mol%) and 1,1'-oxybiscyclohexane (~3 and ~5 mol%, respectively) were formed. The Pd⁰/Al₂O₃ formulation was appreciably more efficient again. Chlorinated materials were absent, cyclohexanol was the one appreciable product (~71 mol%) and small quantities of cyclohexanone (~2 mol%) and 1,1'-oxybiscyclohexane (~2 mol%) were also detected. Thus, for this catalyst, dechlorination and de-aromatization were complete and only ~1 mol% of the substrate had lost an oxygen substituent.

In subsequent studies (Table 2(a)), the pressure was maintained at 22 MPa while the temperature of the reaction of PCP with H₂ over Pd⁰/Al₂O₃ was varied between 50 and 90 °C without any appreciable change in the product distribution after

2 h of reaction. Both the cyclohexanone and the 1,1'-oxybiscyclohexane were present in the product mixture only at trace quantities so that quantitation was somewhat less repeatable for these products. The reaction mixture was also over-pressured with CO₂ (to 0.69–30.34 MPa) while the temperature was maintained at 60 °C (Table 2(b)). Again, there was no perceptible effect on the product distribution. With these conditions, the scCO₂ functioned as an inert medium for the reaction and apparently did not influence the course of the reaction. Table 3(a) summarizes efforts to detect time–pressure interactions. The product distributions remained unchanged by increasing the total pressure from 8.3 to 13.8 MPa and the duration of reaction from 1 to 2 h. In subsequent trials in H₂ alone (Table 3(b)), the quantity of PCP was increased 10-fold [3.75 μmol PCP or aqueous phenolate (NaOC₆Cl₅)] while the solvent was maintained at 0.2 ml. Hydrodechlorination and ring reduction were complete for PCP, however, the quantity of 1,1'-oxybiscyclohexane was elevated (~20 mol%) relative to the mean of Table 3(a) (6.6 mol%). By contrast, the reaction was incomplete for the phenolate (~33 mol% as cyclohexene/cyclohexanol) but the remainder (~40 mol%) was unreacted substrate. Apparently, conversion to phenolate influenced the rate of reaction but the course of the reaction was essentially unchanged. It had been anticipated that introducing anionic character to the substrate might have accelerated electrophilic hydrodechlorination but it is also probable that the H₂ was only sparingly soluble in this medium so that the rates of substrate reduction were compromised.

The variations among replicate trials, performed under the same operating conditions, was superior to the variations among trials at different operating conditions. A possible explanation for the variations in recoveries resides in the differences in the total pressure at which the various trials were performed. In general, the recoveries of products were greater for release from relatively lower pressure (0.69 MPa) than from higher operating pressures (8.27–30.34 MPa). The products were considered to

Table 1 Variations in product yield (mol% ± 1 relative standard deviation) with catalyst identity for the reaction of 0.375 μmol PCP in the presence of 25 mg catalyst and ~1% H₂ (0.69 MPa, ~570 μmol) in scCO₂ (22.1 MPa) at 80 °C

Product	Ag ⁰ /Fe ⁰ /Al ₂ O ₃	Pd ⁰ /γ-Al ₂ O ₃	Fe ⁰ /Al ₂ O ₃	Pt ⁰ /γ-Al ₂ O ₃	Ni ⁰ /SiO ₂ -Al ₂ O ₃	Al ₂ O ₃	No catalyst	no H ₂
Cyclohexanone	N.D. ^a	2.0 ± 7.6	N.D.	2.5 ± 60.7	1.0 ± 20.8	N.D.	N.D.	N.D.
Cyclohexanol	11.4 ± 1.6	71.1 ± 2.6	N.D.	12.2 ± 15.8	14.5 ± 4.3	N.D.	N.D.	N.D.
1,1'-Oxybiscyclohexane	N.D.	2.0 ± 1.5	N.D.	3.4 ± 0.6	4.8 ± 13.2	N.D.	N.D.	N.D.
Tetrachlorophenols	N.D.	N.D.	3.8 ± 5.9	6.6 ± 17.6	17.5 ± 11.4	4.9 ± 21.3	N.D.	N.D.
PCP	66.9 ± 5.2	N.D.	76.4 ± 2.4	46.9 ± 11.7	37.4 ± 0.9	71.7 ± 8.8	75.5 ± 2.2	76.2 ± 16.3
Mass balance	0.773 ± 0.043	0.751 ± 0.027	0.802 ± 0.024	0.716 ± 0.052	0.752 ± 0.036	0.766 ± 0.094	0.755 ± 0.022	0.762 ± 0.163

^a N.D., none detected (<0.05 mol%).

Table 2 Variations of product recoveries (mol% ± 1 relative standard deviation) with (a) temperature (50–90 °C) at 22 MPa or (b) pressure (0.69–30.3 MPa) at 60 °C for 2 h of reaction of PCP (0.375 μmol) with H₂ (0.69 MPa) in scCO₂ in the presence of 25 mg of 5% (w/w) Pd⁰/γ-Al₂O₃.

(a)		Temperature/°C						
Product		50	60	70	80	90		
Cyclohexanone		1.0 ± 8.4	2.9 ± 7.0	3.6 ± 29.3	3.7 ± 10.1	7.8 ± 10.1		
Cyclohexanol		66.8 ± 0.4	70.1 ± 3.3	66.8 ± 6.1	78.4 ± 0.8	75.1 ± 0.2		
1,1'-Oxybiscyclohexane		5.9 ± 6.7	4.7 ± 1.4	6.4 ± 9.4	7.0 ± 0.6	6.8 ± 1.2		
Mass balance		0.736 ± 0.044	0.777 ± 0.033	0.768 ± 0.048	0.891 ± 0.004	0.898 ± 0.009		
(b)		Pressure/MPa						
Product		0.69	8.27	13.79	18.62	22.06	26.20	30.34
Cyclohexanone		24.4 ± 0.5	7.0 ± 69.8	5.9 ± 52.9	1.5 ± 0.4	0.8 ± 4.3	7.4 ± 3.6	4.4 ± 81.6
Cyclohexanol		64.7 ± 0.2	59.5 ± 5.7	59.4 ± 2.3	62.9 ± 3.6	71.0 ± 8.0	58.4 ± 1.1	55.7 ± 10.1
1,1'-Oxybiscyclohexane		6.5 ± 0.1	7.2 ± 5.9	6.4 ± 4.5	6.3 ± 0.1	7.2 ± 1.0	5.3 ± 0.4	5.3 ± 6.0
Mass balance		0.966 ± 0.002	0.732 ± 0.081	0.717 ± 0.035	0.708 ± 0.034	0.790 ± 0.053	0.711 ± 0.021	0.654 ± 0.046

be somewhat volatile so that trapping of products from the CO₂ was more efficient when released from lower operating pressures than release from higher operating pressures. A more efficient trapping procedure might have solved this problem.

Other highly chlorinated aromatic compounds were also subjected to reaction under similar conditions. Octachloronaphthalene (~70% chlorine by weight) was reacted with H₂ (0.69 MPa) in the presence/absence of 25 mg Pd/Al₂O₃ for 0.5 or 2 h. Only decalin (C₁₀H₁₈) was observed in the crude product mixture (Table 4). Interestingly, the ratio of *trans*- to *cis*-product that was approximately 3:1 after 0.5 h had been decreased to 2.3:1 after 2 h of reaction and might have become nearly equal after extended equilibration. In companion trials, reaction to decalin, in the presence of sufficient hexane (5 ml) to cover the catalyst surface completely, was also virtually complete at 80 or at 60 °C but at 50 °C, tetralin was the major product (~75 mol%). The other products were decalin (ratio *trans* to *cis*, 3.2:1) and traces of substrate. A possible explanation is a two-phase system (at 50 °C but perhaps not at 60 °C) that hindered H₂ access to the catalyst surface. A doubling of reaction rate for a 10 degree increase in reaction temperature would seem to be insufficient to account for the

observed differences between 50 and 60 °C. Naphthalene also served as substrate for reaction during 0.5 h. In this case, the ratio of *trans*- to *cis*-decalin was different again (~0.8:1). There was no tendency for dehydrogenation with these reaction conditions. Neither *trans*- nor *cis*-decalin, when pressurised to 690 kPa with nitrogen in the presence of Pd⁰/Al₂O₃ and reacted at 70 °C for 0.5–1 h, provided evidence for dehydrogenation to tetralin or naphthalene or for configurational isomerization.

In a final series of trials, decachlorobiphenyl (~71% Cl by weight) served as substrate (Table 5). Post 0.5 h reaction at 70 °C/0.69 MPa, only dicyclohexyl was observed in the crude product mixture. The reaction was complete; chlorine was removed from the substrate and the product had been de-aromatized but no carbon–carbon bond scission had occurred.

In summary, highly chlorinated aromatic compounds were dechlorinated quantitatively when exposed to alumina supported palladium in hydrogen atmospheres under mild conditions. With these conditions, perchlorinated phenol, naphthalene or biphenyl substrates as well as their hydrocarbon homologs were also smoothly dearomatized to their cyclic analogs but no carbon–carbon bond rupture was observed and in the case of PCP only small quantities of partial deoxygenation

Table 3 Variations in the distribution of products (mol% ± 1 relative standard deviation) for (a) the reduction of PCP (0.375 μmol) with H₂ (575 μmol) in scCO₂ (8.3 or 13.8 MPa) or (b) with substrate (3.75 μmol)/solvent combination for reactions at 60 °C for 1 or 2 h

(a)	Reaction time/h (scCO ₂ pressure/MPa)			
	1 (8.3)	1 (13.8)	2 (8.3)	2 (13.8)
Product				
Cyclohexanone	9.9 ± 1.7	8.6 ± 3.7	7.0 ± 69.8	5.9 ± 52.9
Cyclohexanol	53.2 ± 0.05	54.1 ± 4.8	59.1 ± 5.7	59.4 ± 2.3
1,1'-Oxybiscyclohexane	6.3 ± 1.7	6.3 ± 3.3	7.2 ± 5.9	6.4 ± 4.5
Tetrachlorophenols	N.D. ^a	N.D.	N.D.	N.D.
PCP	N.D.	N.D.	N.D.	N.D.
Mass balance	0.694 ± 0.050	0.690 ± 0.039	0.732 ± 0.081	0.717 ± 0.035
(b)				
	PCP (3.75 μmol) in 0.2 ml hexane		Na-PCP (3.75 μmol) in 0.2 ml water	
Cyclohexanone	2.7 ± 12.4		23.1 ± 2.6	
Cyclohexanol	67.8 ± 1.9		9.6 ± 0.8	
1,1'-Oxybiscyclohexane	20.1 ± 1.9		N.D.	
Tetrachlorophenols	N.D.		N.D.	
PCP	N.D.		39.6 ± 12.1	
Mass balance	0.906 ± 0.015		0.723 ± 0.074	

^a N.D. = none detected (<0.05 mol%).

Table 4 Variations in decalin recoveries (mol% ± 1 relative standard deviation) after 0.5 or 2 h of hydrogenation (70 °C/0.69 MPa) of 1 mg octachloronaphthalene or naphthalene in the presence/absence of 25 mg of 5% (w/w) Pd⁰/γ-Al₂O₃

Products	C ₁₀ Cl ₈			C ₁₀ H ₈	
	2 h, no cat.	0.5 h	2 h	2 h, no cat.	0.5 h
C ₁₀ Cl ₈	95.2 ± 5.1	N.D. ^a	N.D.		
C ₁₀ H ₈	N.D.	N.D.	N.D.	93.1 ± 5.5	N.D.
<i>cis</i> -C ₁₀ H ₁₈	N.D.	23.3 ± 4.8	29.8 ± 6.6	N.D.	54.6 ± 6.4
<i>trans</i> -C ₁₀ H ₁₈	N.D.	71.7 ± 3.5	67.7 ± 3.4	N.D.	44.5 ± 3.4
Mass balance	0.952 ± 0.051	0.950 ± 0.020	0.975 ± 0.042	0.931 ± 0.055	0.991 ± 0.051

^a N.D. = none detected (<0.05 mol%).

Table 5 Variations in dicyclohexyl recoveries (mol% ± 1 relative standard deviation) after 0.5 h of hydrogenation (70 °C/0.69 MPa) of 1 mg decachlorobiphenyl or biphenyl in the presence/absence of 25 mg of 5% (w/w) Pd⁰/γ-Al₂O₃

Product	C ₁₂ Cl ₁₀		C ₁₂ H ₁₀	
	0.5 h, no cat.	0.5 h	0.5 h, no cat.	0.5 h
C ₁₂ Cl ₁₀	102.7 ± 5.8	N.D. ^a		
C ₁₂ H ₁₀	N.D.	N.D.	93.1 ± 3.4	N.D.
Dicyclohexyl		101.6 ± 1.4		96.9 ± 9.6
Mass balance	1.027 ± 0.058	1.016 ± 0.014	0.931 ± 0.034	0.969 ± 0.096

^a N.D. = none detected (less than 0.05 mol%).

was observed. These observations, under mild reaction conditions, suggest that they might be applied to other aromatic compounds including environmentally recalcitrant poly-aromatic hydrocarbons (PAHs).

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