Hydrogenation and Hydrogenolysis with Pd/C in Poly(Ethylene Glycol) (PEG): A Practical and Recyclable Medium

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Abstract: Pd/C in PEG (400) has been found to be an efficient reusable reaction medium for hydrogenation and hydrogenolysis. Both the catalyst and PEG were recycled efficiently over four runs without appreciable loss of activity.

Key words: hydrogenation, hydrogenolysis, Pd/C, poly (ethylene glycol), recycling

Catalytic hydrogenation and hydrogenolysis occupy an important status in organic synthesis¹ especially as these transformations are high yielding and more chemoselective. Palladium is arguably the most versatile and widely applied metal catalyst. Many Pd catalysed reactions give reliable results and are easy to perform in ordinary equipments. The major drawback of this catalyst is its flammability and danger of ignition while adding the catalyst to solvent or during filtration of the catalyst irrespective of the volume and scale of the reaction. The reaction conditions for hydrogenation and hydrogenolysis are identical even though some modifications in the catalyst such as poisoning may help to moderate or activate one over the other. The most common hydrogenation reactions involve reduction of alkynes and olefins to saturation.^{2,3} The hydrogenolysis reactions involve cleavage of O-benzyl ethers and N-benzyl compounds.⁴

En route to the recently liquid polymers or low melting polymers have been used as solvents.⁵ We have developed poly(ethylene glycol) (PEG) as an efficient recyclable reaction medium for the Heck reaction⁶ and Sharpless asymmetric dihydroxylation.⁷ Herein we disclose PEG (400 Dalton) as the most efficient solvent system for complete hydrogenation and hydrogenolysis of various functionalities virtually at ambient temperature and atmospheric pressure. The solvent (PEG) and catalyst (Pd/C) were recycled with retention of efficiency and activity over four runs.

We initially examined the deprotection of benzyl ether (Scheme 1, entry **1a** in Table 1; 500 mg, 2 mmol), 2 g of PEG (400) and 10% Pd/C (20 mg, 0.02 mmol) were stirred under hydrogen balloon for 6 hours. Anhydrous diethyl ether (5 mL) was added, the mixture stirred for five minutes and the reaction was allowed to settle for 5 minutes. Cooling of the contents in an acetone–dry ice bath

led to precipitation of solid PEG and catalyst. This technique allowed us to decant the ether layer without loss of PEG and catalyst. The method was repeated twice with 5 mL portions of diethyl ether to extract the product, which was concentrated and purified by column chromatography to give the required product **1b** in 95% yield. Encouraged by this observation we verified the recyclability of both catalyst and solvent. The residual PEG–catalyst mixture obtained from the first run was brought to room temperature and for the benzyl ether **1a** added under the hydrogen atmosphere. Work-up followed as described above.

R = alkyl, aryl

Scheme 1

$$R' \xrightarrow{R''} \frac{Pd-C (1 \text{ mol}\%)}{H_2 (1 \text{ atm}), \text{PEG } (400)} R' \xrightarrow{R''} R''$$

R', R" = alkyl, aryl

Scheme 2

This protocol was continued for third and fourth runs, which resulted in 93% and 90% yields respectively. Sugar derivative **2a** underwent hydrogenation resulting the desired product **2b** in 90% yield. Keto derivatives **3a** and **4a** debenzylated chemoselectively to give products in 92% and 90% yield respectively.

In addition, hydrogenation of alkenes, alkynes was achieved with Pd/C in PEG (Scheme 2). Simple alkynes **5a** and **6a**, alkene **7a**, were reduced under the same conditions yielding **5b**, **6b** and **7b** in 97%, 93% and 92% yield respectively. Unsaturated esters and lactol ethers were also efficiently hydrogenated without any difficulty resulting to in 85% and 86% yield respectively.

In conclusion, this communication describes hydrogenation and hydrogenolysis in PEG as a recyclable solvent medium. The Pd/C catalyst was found to be recycled efficiently for 4 runs.

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Table 1	Hydrogenation ar	d Hydrogenolysis in	PEG Using Pd/C
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Compd	Substrate a	Product b	Time (h) ^a	Yield (%) ^b
1	BnO	HO	6	95
2			10	90
	BnO "O			
3			8	92
4	BnO ''O' \		8	90
	OBn	ОН		
5	PhPh	Ph Ph	4	97
6		ОН	5	93
7	- СОН	е СОН	4	92
8	C ₁₂ H ₂₅ OH	С ₁₂ Н ₂₅ ОН	4	95
9	CO_Et	CO.Et	8	85
10			7	86

^a Time in hours.

^b All the products were characterised by ¹H NMR and mass spectra.

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