

Selective Hydrogenolysis of Glycerol with Raney Nickel[†]

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Glycerol, a cheap renewable feedstock, was converted selectively to 1,2-propanediol by heating under low hydrogen pressure (10 bar), in the presence of Raney nickel. No solvents or additives were required, and the product could be distilled out of the reaction mixture. Addition of a phosphonium salt, a liquid at the reaction temperature, improved the selectivity and rate to a small extent but did not facilitate the separation of the final reaction mixture.

Introduction

Propylene glycols are important chemicals. 1,3-Propanediol (1,3-PD) is a high-value specialty chemical used primarily in polyester fibers, films, and coatings. 1,2-Propanediol (1,2-PD) is a medium-value commodity chemical used for polyester resins, liquid detergents, pharmaceuticals, cosmetics, antifreeze, etc. Both are produced industrially starting from petrochemical resources.

One of the goals of Green chemistry is to use renewable resources as feedstocks for the chemical industry, in place of fossil-derived starting materials, especially if they are byproducts of other production processes.¹

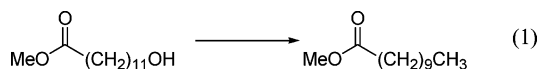
Glycerol can be regarded as an example of such a feedstock because it is formed in large quantities as the byproduct in the saponification of triglycerides in the production of free fatty acids for detergents and of fatty esters for biofuels. In fact, glycerol is becoming a cheap, large-volume market product, and the ability to use it as a source of organic carbon, and as a starting material for chemical transformations, is very appealing.

Much work is being done toward the oxidation of glycerol to more valuable products, while less is performed on its hydrogenolysis, and most of this by microbial reduction, toward the production of 1,3-PD.^{2,3}

Only recently, has a paper addressed the hydrogenolysis of glycerol using heterogeneous Cu, Pd, and Rh catalysts supported on ZnO, C, and alumina and in the presence of tungstic acid as a modifier to improve the selectivity toward 1,3-PD (highest selectivity 1,3-PD/1,2-PD = 2). A solvent (water, sulfolane, or dioxane) was used, under 80 bar of hydrogen and at 180 °C.⁴

In addition, the patent literature describes the hydrogenolysis of glycerol to propylene glycols.^{5–7} In all cases, either selectivity was low or high pressure, high temperature, or complex catalytic systems were required.

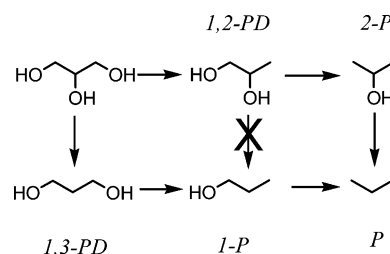
Krafft et al. have shown that alcohols can be deoxygenated with Raney Ni. In particular, primary alcohols refluxed in toluene with Raney Ni gave rise to deoxygenated compounds with one carbon less (e.g., eq 1).⁸



[†] In honor of David C. Sherrington on his 60th birthday.

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Scheme 1. Pathways for Hydrogenolysis of Glycerol



Other goals of Green chemistry are the use of catalysts in place of stoichiometric reagents and the replacement, or elimination, of dangerous solvents.

This paper describes some preliminary results on the hydrogenolysis of glycerol with hydrogen, using Raney Ni as the catalyst. The reaction was carried out without added solvents (using only glycerol + catalyst + H₂) and in the presence of a liquid phosphonium salt. Recently, it has been recognized that onium salts, and in particular liquid ones dubbed "ionic liquids" (ILs), can offer advantages in some catalytic reactions as far as yields, rates, selectivity, and product separation are concerned. In particular, we have shown that Raney Ni is strongly active for hydrodehalogenation reactions of haloaromatics when a lipophilic ammonium salt such as Aliquat 336 is present in a multiphase reaction system.^{9,10} Under these conditions, the Ni catalyst becomes immobilized in the liquid Aliquat 336 phase, thus facilitating product–catalyst separation.

Results and Discussion

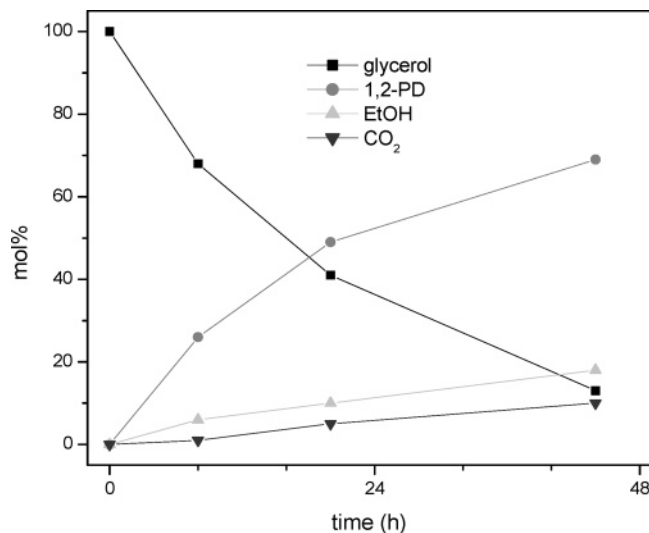
The hydrogenolysis of glycerol can proceed by different pathways (Scheme 1), depending on whether the primary or secondary hydroxyl is more easily reduced. Catalytic –OH cleavage with noble metals under reductive conditions usually favors reduction of primary hydroxyl groups over secondary. Tertiary hydroxyls are cleaved faster than secondary but likely because of different mechanisms (e.g., S_N1). In the first case, the hydrogenolysis of the two primary hydroxyls yields 1,2-PD, then 2-propanol (2-P), and eventually propane (top pathway). In the second case, 1,3-PD is formed first, and then consecutive removal of the remaining OH's yields 1-propanol (1-P) and propane (bottom pathway). The alternating primary–secondary–primary hydroxyl reduction pathway is obviously unlikely.

At first, an appropriate reaction temperature was sought. When glycerol and Raney Ni were heated at 150

Table 1. Hydrogenolysis of Glycerol with Raney Ni^a

conditions	<i>T</i> (°C)	time (h)	conv (%)	selectivity (%)		
				1,2-PD	EtOH	CO ₂
1 neat	150	20	12	93	1	6
2	190	8	32	79	18	3
3		20	63	77	15	8
4		44	97	71	19	10
5	210	20	91	48	40	12
6 Bu ₄ PBr ^b	190	20	49	68	26	6
7 (C ₆ H ₁₃) ₃ C ₁₄ H ₂₉ PCl ^b	190	20	47	81	13	6

^a *p*(H₂) = 10 atm, 8.0 g (87 mmol) of glycerol, 2.0 g (34 mmol) of Raney Ni. ^b 2.0 g of phosphonium salt.

**Figure 1.** Hydrogenolysis of glycerol with Raney Ni at 190 °C.

°C for 20 h in a steel autoclave with 10 atm of hydrogen, conversion reached 12%, with 93% selectivity toward 1,2-PD, plus small amounts of ethanol and CO₂ (Table 1, entry 1). At 190 °C, the reaction proceeded faster, with selectivity toward 1,2-PD in the range of 70–80% and ethanol and CO₂ as the sole byproducts (Table 1, entries 2–4). At 210 °C, the reaction was still faster, but selectivity toward 1,2-PD dropped to 48% (Table 1, entry 5). No 1,3-PD was observed.

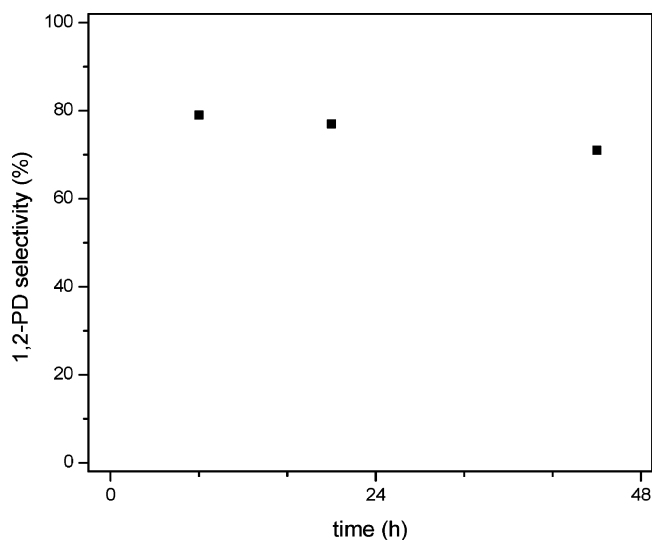
The reaction profile at 190 °C (Figure 1) indicates that good yields of the diol can be obtained and that hydrogenolysis proceeds with good selectivity (Figure 2) toward 1,2-PD.

The temperature is critical: at 150 °C, the reaction is selective toward the formation of 1,2-PD but too slow to be practical. At 210 °C, the reaction is fast and good conversion is achieved rapidly, but selectivity toward the desired diol drops. The optimal tradeoff between the rate and selectivity is at 190 °C. At this temperature, selectivity is in the range of 70–80%, even after prolonged reaction, and the yield of 1,2-PD is good.

The diol is recovered from the mixture by simple distillation, thus making the reaction, in principle, suited for continuous-flow operation.

No further –OH hydrogenolysis of 1,2-PD is observed, e.g., to give propan-2-ol. This can be accounted for mainly by poorer reactivity of the second primary hydroxyl and, in part, also by the fact that 1,2-PD may be in the gas phase and less in contact with the catalyst.

The absence of 1,3-PD indicates that the secondary OH is unreactive under our conditions, unlike other systems where competitive formation of the two diols was observed.⁴

**Figure 2.** Selectivity toward 1,2-PD at 190 °C.

Lower hydrogen pressures were not sufficient to achieve significant conversion, while higher H₂ pressures were not investigated in this study.

Ethanol and CO₂ are the only observed byproducts, along with traces of hydrocarbons (C1–C6). Ethanol derives from reductive cleavage of a C–C bond to give ethylene glycol, followed by hydrogenolysis. Formation of CO₂ is somewhat unexpected in such a reductive environment but is unavoidable even by removal of oxygen from each experiment by purging with H₂, prior to heating.

We then investigated two phosphonium salts, liquid at the reaction temperature, to see if the Raney Ni catalyst improved its performance over the neat reaction. Phosphonium salts were preferred in view of their better thermal stability with respect to nitrogen-based analogues. Both of the investigated salts provided two-phase mixtures at the reaction temperature.

The hydrogenolysis of glycerol, conducted by adding tetrabutylphosphonium bromide (C₄H₉)₄PBr (mp = 100 °C) as the modifier, proceeded with lower conversion and selectivity with respect to those of the neat system (Table 1, entry 6).

With (C₆H₁₃)₃C₁₄H₂₉PCl (liquid at room temperature), the reaction reached 47% conversion, with a 81% selectivity toward 1,2-PD, after 20 h at 190 °C. The final reaction mixture presented a second liquid phase of IL (provided the temperature was kept over 100 °C) at the end of the reaction (Table 1, entry 7).

In comparison to the neat system, tetrabutylphosphonium bromide gave poorer yields and selectivity; in addition, its boiling point of 100 °C did not allow recovery of a biphasic system at room temperature. The more lipophilic phosphonium chloride instead showed lower conversion but a slightly higher selectivity for the formation of 1,2-PD (81%). While the desired yield and selectivity improvement was not as good as expected even though 1,2-PD was well soluble in the phosphonium salt, it was hoped that the two-phase mixture at the end of the reaction would provide an advantage for the separation of products from the catalyst–reagent mixture. This, however, was not the case, and 1,2-PD was recovered only from the glycerol–catalyst phase, not from the phosphonium salt.

An attempt to use a different catalyst, i.e., charcoal-supported palladium, demonstrated that, under these conditions, it is not as active as Raney Ni.

The quantification and characterization of the liquid products were done by ^1H NMR analyses of the crude reaction mixtures. The gaseous portion of the reaction was instead analyzed directly by gas chromatography–mass spectrometry (GC–MS). A good estimate of the amount of gaseous products was derived from the total weight difference of the condensed phases before and after the reaction.

In conclusion, Raney Ni is an active catalyst for the hydrogenolysis of glycerol even at 10 atm of hydrogen. Selectivity toward 1,2-PD is high, with the only byproducts being ethanol and CO_2 . The reaction is straightforward, does not require solvents, promoters, or harsh conditions, and can conceivably be run continuously. The product can be separated easily by distillation from the heterogeneous catalyst.

Experimental Section

Glycerol, Bu_4PBr , and $(\text{C}_6\text{H}_{13})_3\text{C}_{14}\text{H}_{29}\text{PCl}$ were purchased from Sigma-Aldrich and used as received, Raney Ni (Actimet M) was a gift by Engelhard, and hydrogen was of reagent grade from SIAD.

Representative Experimental Procedure. The alkaline Raney Ni slurry in water (2.5 g) was weighed in a centrifuge tube; it was neutralized by six washing–stirring–centrifuging cycles using 10-mL aliquots of distilled water, discarding the supernatant water after each cycle. The remaining wet catalyst (approximately 2.0 g) was transferred to a 100-mL glass reactor using 8.0 g of glycerol. After weighing, the reactor was inserted in a 180-mL steel autoclave. When the phosphonium salt was present, 2.0 g were added to the catalyst–glycerol mixture. The reactor was sealed, charged, and purged repeatedly with hydrogen to eliminate air, pressurized to 10 atm with H_2 , stirred (700 rpm), and heated to the desired temperature. After the appropriate time, the reactor was cooled to room temperature, and the gaseous contents was vented to a previously evacuated balloon and analyzed by GC–MS. After the glass reactor was weighed in order to quantify the loss of gaseous components, the liquid phase containing the catalyst was collected, centrifuged, filtered through a cotton plug to eliminate Ni particles, and analyzed by NMR.

Yields and selectivities were calculated by repeating the experiments at least twice. CO_2 was identified by

GC–MS and quantified based on the weight loss that occurred during the reaction. Traces of C1–C6 hydrocarbons were not considered as they remained <1% (GC). 1,2-PD and ethanol were identified by ^1H and ^{13}C NMR, by comparison with authentic samples, using CD_3OD as the solvent. They were quantified by integrating selected peaks versus those of residual glycerol.

Acknowledgment

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Literature Cited

- (1) Tundo, P.; Anastas, P.; Black, D. St. C.; Breen, J.; Collins, T.; Memoli, S.; Miyamoto, J.; Polyakoff, M.; Tumas, W. Synthetic pathways and processes in green chemistry. Introductory overview. *Pure Appl. Chem.* **2000**, *72*, 1207–1228.
- (2) Papanikolaou, S.; Ruiz-Sanchez, P.; Pariset, B.; Blanchard, F.; Fick, M. High production of 1,3-propanediol from industrial glycerol by a newly isolated *Clostridium butyricum* strain. *J. Biotechnol.* **2000**, *77*, 191–208.
- (3) Zhu, M. M.; Lawman, P. D.; Cameron, D. C. Improving 1,3-Propanediol Production from Glycerol in a Metabolically Engineered *Escherichia coli* by Reducing Accumulation of *sn*-Glycerol-3-phosphate. *Biotechnol. Prog.* **2002**, *18*, 694–699.
- (4) Chaminand, J.; Djakovitch, L.; Gallezot, P.; Marion, P.; Pinel, C.; Rosier, C. Glycerol hydrogenolysis on heterogeneous catalysts. *Green Chem.* **2004**, *6*, 359–361.
- (5) Che, T. M. (Celanese Co.). Production of propanediols. U.S. Patent 4,642,394, 1987.
- (6) Fleckenstein, T.; Gobel, G.; Carduck, F.-J. (Henkel KGaA). Preparation of propylene glycol from re-generable fossil fuel sources. DE Patent 4302464A1, 1994.
- (7) Drent, E.; Jager, W. W. (Shell Oil Co.). Hydrogenolysis of glycerol. U.S. Patent 6,080,898, 2000.
- (8) Krafft, M. E.; Crooks, W. J., III; Zorc, B.; Milczanowski, S. E. Reaction of Raney nickel with alcohols. *J. Org. Chem.* **1988**, *53*, 3158–3163.
- (9) Zinovyev, S. S.; Perosa, A.; Yufit, S.; Tundo, P. Hydrodechlorination and Hydrogenation over Raney-Ni under Multiphase Conditions. Role of Multiphase Environment in Reaction Kinetics and Selectivity. *J. Catal.* **2002**, *211*, 347–354.
- (10) Tundo, P.; Perosa, A.; Zinovyev, S. Modifier effects on Pt/C, Pd/C, and Raney-Ni catalysts in multiphase catalytic hydrogenation systems. *J. Mol. Catal. A* **2003**, *204–205*, 747–754.

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