

Catalytic transfer-hydrogenations of olefins in glycerol

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Abstract: Glycerol has been successfully employed as a green solvent and hydrogen donor in the biphasic catalytic transfer-hydrogenation of olefins over Pd/C to yield the corresponding paraffins and dihydroxyacetone, respectively. The use of glycerol eased product separation and catalyst recycling and allowed for microwave-assisted reactions.

Keywords: Glycerol; catalysis; transfer-hydrogenation; green chemistry.

1. Introduction

Glycerol is a non-toxic, non-irritating, biodegradable, and recyclable liquid that comprises the main by-product from the conversion of oils and fats. As the production and use of fatty acid derivatives continues to rise in the food, cosmetics, and drugs industries and in biofuel synthesis, i.e., biodiesel, the supply of glycerol is growing, thus causing its price to decrease. The challenge, then, is to find economical ways to utilize the world's growing glycerol supply.

As recently reported, glycerol can also be successfully employed as a versatile and alternative green solvent in a variety of catalytic and non-catalytic organic reactions and synthesis methodologies, capable of yielding high product conversions and selectivities.¹⁻³ In this respect, it was found that the use of glycerol as a reaction medium facilitated the solubilities of reactants and catalysts, easy product separation, and transition metal complex recycling as well as microwave-promoted reactions. In addition, the crude glycerol byproduct of biodiesel production was also used, without any purification, as a reaction medium.⁴

Catalytic hydrogenation is a fundamental reaction in chemistry, and it is used in a large number of chemical processes.⁵ One of the routes to achieve such a transformation is by catalytic transfer-hydrogenation, in which an alcohol—especially a secondary alcohol and often 2-propanol—is used as hydrogen-donor in the presence of a transfer-hydrogenation catalyst.⁶ One of the advantages of this pathway is that it is performed in the absence of gaseous hydrogen, the inclusion of which

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necessitates extra precautionary measures and special equipment. We recently found that glycerol can be used as both solvent and hydrogen donor in the catalytic transfer-hydrogenation of various unsaturated organic molecules.^{7,8} During these reactions, glycerol was dehydrogenated to dihydroxyacetone, an important ingredient in sunless tanning compounds and a useful intermediate for organic synthesis. Glycerol oxidation and dehydrogenation were studied by applying different reaction conditions and different catalysts.^{9,10} Aerobic oxidation of glycerol over supported metal and bimetal catalysts resulted in a variety of products with a high selectivity for glyceric acid and glycolic acid. The use of microbial processes instead was found to be more active and to shift the selectivity toward dihydroxyacetone and glyceraldehyde.¹¹

In this study, glycerol was used as both solvent and hydrogen donor in the transfer-hydrogenation of different olefins and especially cyclohexene over Pd/C, during which it was dehydrogenated to dihydroxyacetone (Figure 1). The effects of reaction time, temperature, and substrate concentration on catalytic performance were tested. In addition, catalyst recycling tests and microwave-promoted reactions were also examined.



Scheme 1. Transfer-hydrogenation of olefins in glycerol.

2. Results and Discussion

The transfer-hydrogenation of olefin can be performed with different transition metal complexes and supported metal catalysts using a variety of hydrogen donors.⁶ As a representative olefin, the solubility of cyclohexene is relatively low (although higher than that of cyclohexane) in glycerol. Thus, the reaction was run under biphasic (glycerol-organic) mode. The investigation began by testing the effect of reaction temperature on the conversion of cyclohexene (Figure 2).

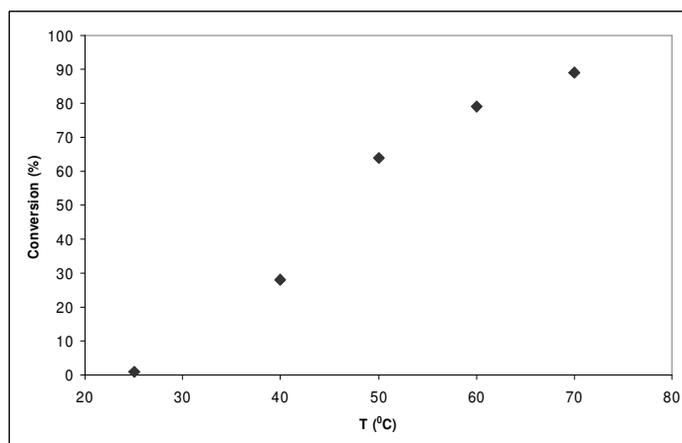


Figure 1. Effect of reaction temperature on the conversion of cyclohexene. Reaction conditions: 0.5 g cyclohexene, 0.03 g (5 wt.%) Pd/C, 5 glycerol, 5 h.

As can be seen from Fig. 2, increasing the reaction temperature increased the conversion from negligible at room temperature to almost full conversion at 70 °C. Several explanations can be offered for this observation: i) increasing the reaction temperature increased the reaction rate according to the Arrhenius equation or ii) increasing the reaction temperature increased the solubility of cyclohexane in glycerol or iii) the viscosity of glycerol decreased with increasing reaction temperature, thereby resulting in increased mass and heat transfer. Because the reactions were run in a closed glass vial, reaction temperature was not increased behind 70 °C since the vapor pressures of both cyclohexene and cyclohexane are relatively high under these conditions. In addition, the product can be easily separated at the end of the reaction by decantation, as cyclohexane is glycerol immiscible. But since the olefin and paraffin amounts are not too high, and part of the cyclohexene is miscible in glycerol, the product and the substrate residual were extracted or distilled to determine conversion.

Since the solubility of cyclohexane in glycerol is limited, we tested whether increasing the amount of cyclohexene would change the conversion and consequently the amount of cyclohexane produced (Fig. 3). The results in Fig. 3, which illustrates that the amount of cyclohexane produced was increased with the initial amount of cyclohexene, indicate that the reaction is relatively fast, and hence, it is limited by the concentration of cyclohexene in the glycerol phase. This observation can be explained by the fact that increasing the amount of cyclohexene in the organic phase led to relative increases in the amount in the glycerol phase and in the interface area during mixing of the phases, and therefore, the concentration of the substrate in the reaction mixture also increased.

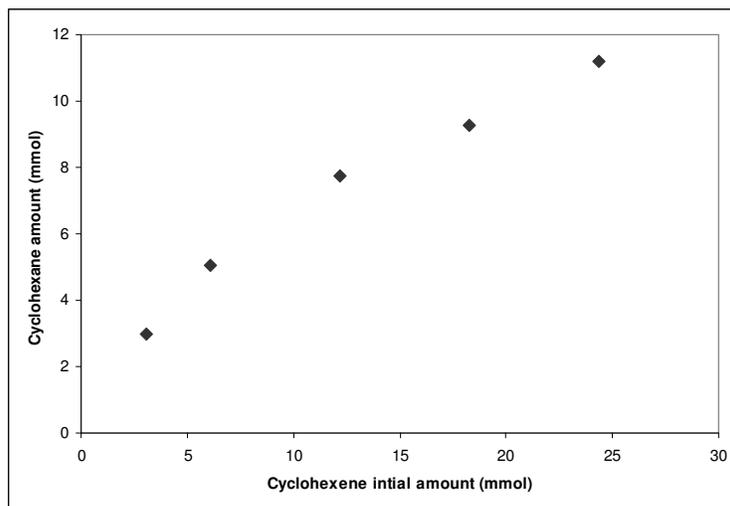


Figure 2. Effect of initial amount of cyclohexene on the amount of cyclohexane produced. Reaction conditions: 0.03 g (5 wt.%) Pd/C, 5 glycerol, 70°C, 5 h.

The reaction progress over time was also tested at 70 °C. The conversion increased rapidly to 95% in 7 h, but running the reaction beyond the initial 7 h did not change the conversion further (Fig. 4).

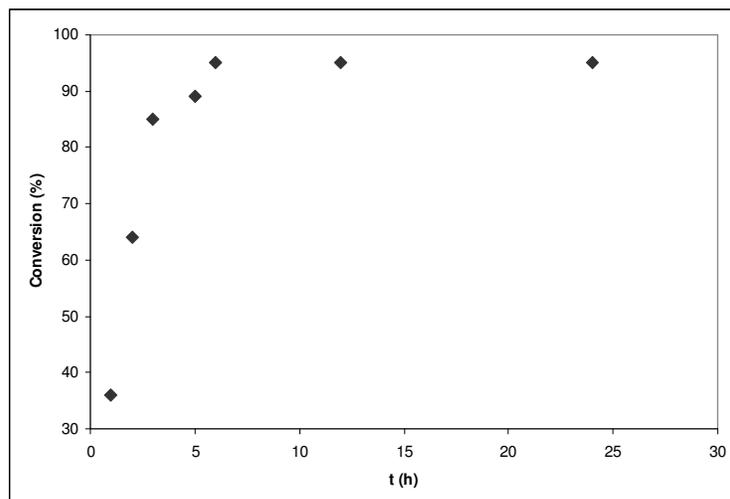


Figure 3. Effect of reaction time on cyclohexene conversion. Reaction conditions: 0.5 g cyclohexene, 0.03 g (5 wt.%) Pd/C, 5 glycerol, 70°C.

The effectivity of recycling Pd/C and glycerol, which also acts as hydrogen donor, was examined three times. The first reaction cycle was performed in a 100-mL Erlenmeyer with 2.5 g cyclohexene, 0.15 g (5 wt.%) Pd/C, and 25 g glycerol at 70 °C for 3 h. At the end of the reaction the product and the residual substrate were extracted with 10 mL of diethyl ether. For each sequential cycle, fresh cyclohexene was added, and the reaction was run again under similar conditions. The conversions of cyclohexene in the first, second, and third reaction cycles were 84%, 76% and 54%, respectively. The declining conversion rates may be attributable to partial deactivation of the catalyst and to the dehydrogenation of glycerol as hydrogen donor in each reaction cycle, thus decreasing the amount of available glycerol from one cycle to the next.

The transfer-hydrogenation of cyclohexene in glycerol was also examined under microwave irradiation instead of conventional heating. Based on the ability of the solvent to absorb microwave energy and convert it into heat, microwave heating is ideally suited to the high dielectric constants and high boiling points of polar solvents with hydroxyl substitution such as glycerol. The experiment was conducted in a domestic microwave oven at atmospheric pressure in a 10-mL vial covered with a watch glass. The reaction mixture was heated for 3 min from 26 °C to 72 °C. At the end of the reaction, the reaction mixture was cooled to room temperature and extracted with diethyl ether for GC analysis. The conversion was found to be 37 %, a level that is comparable to the conversion of cyclohexene after 1 h under conventional heating.

In order to gain more information about the structural effects of the reduced olefins, the reduction of several olefins was also tested in glycerol (Table 1). As can be seen from the data in Table 1, aromatic olefins are much more active toward reduction than aliphatic olefins, as expected. Besides electronic effect due to the aromatic ring, it should be taken into account that the solubility of linear olefins such as 1-hexene and 1-octene in glycerol is lower than that of aromatic and cyclic olefins. In addition, when more bulky aromatic olefins such as 1,1-diphenylethylene and cis-stilbene were employed (entry 4 and 5) the activity was decreased when compared with styrene (entry 3), probably due to steric effects.

Table 1. Transfer hydrogenation of olefins in glycerol^a

Entry	Substrate	Conversion [%]
1	Cyclohexene	89
2	4-Methyl-1-cyclohexene	81
3	Styrene	100
4	<i>cis</i> -Stilbene	35
5	1,1-Diphenylethylene	22
6	1-Hexene	9 (32) ^b
7	1-Octene	7

^a Reaction conditions: 0.61 mmol olefin, 0.03 g (5 wt.%) Pd/C, 5 g glycerol, 70°C, 5 h.^b After 24 h.

3. Conclusion

To conclude, olefins have been successfully produced in the biphasic catalytic transfer-hydrogenation of the corresponding paraffins in glycerol using Pd/C as the catalyst. Employed as a green solvent and hydrogen source, the glycerol dehydrogenated to dihydroxyacetone. The reaction conversion was affected by the reaction temperature and the concentration of cyclohexene, as representative olefin. Used as a solvent, glycerol also enabled easy product separation and catalyst recycling and allowed for the use of microwave-promoted reactions.

4. Experimental

In a typical procedure, 0.50 g of cyclohexene and 0.03 g of (5 wt.%) Pd/C were added to a vial with 5 g of glycerol (all purchased from Aldrich). The mixture was placed in a preheated oil bath and heated to 70 °C after which it was magnetically stirred for 5 h. At the end of the reaction, the reaction mixture was cooled and extracted with 2 mL of diethyl ether. Finally, the ether phase was analyzed by GC analysis using an HP-5 column (30 m × 0.25 mm, 0.25 μm thick) to determine the conversion.

Catalyst recycling experiments were done in a 100-mL Erlenmeyer. For the first reaction cycle, 2.50 g cyclohexene and 0.15 g of (5 wt.%) Pd/C were dissolved in 25 g of glycerol, and the reaction mixture was heated in an oil bath to 70°C for 3 h. At the end of the reaction the product and residual substrate were distilled and the catalyst was recycled by adding fresh cyclohexene and running the reactions under conditions similar to those of the first run.

The transfer hydrogenation of cyclohexene under microwave irradiation was carried out using the same reaction stoichiometry mentioned in the typical procedure described above. Experiments were conducted in a domestic microwave oven (Crystal WP900, 900 W) in a 10-mL glass vial, which was covered with a watch glass at atmospheric pressure. Reaction mixture temperature was increased for 3 min from 26 °C to 72 °C using microwave heating. After the vessel was cooled to room temperature, the reaction mixture was extracted with 2 mL of diethyl ether for GC analysis.

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