

Pd-CATALYSED HYDROGENATION OF LIMONENE

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INTRODUCTION

Terpene feedstocks are natural products built up from isoprene units. Many sources of terpenes are thus balsams, natural resins and essential oils, but they are also by-products of lemon and orange juice production, as well as of pulp and paper industries. Some of them, such as (-)- α -pinene and (+)-limonene are among the more readily available optically active products and therefore used for the synthesis of other optically active products and as reagents for cleaving racemates. Terpenes are very cheap precursors of fragrances, flavors, drugs and agrochemicals. [1] Within the fine chemical industry, they are an important source of intermediates and ingredients for flavours and fragrances. In the perfumery industry, the synthesis of compounds closely related to these natural identical materials led to the discovery of ingredients that are similar in odour, but which are much easier and cheaper to make than their natural counterparts.[2] One of the example is that of jasmine[3]: jasmine absolute (natural) costs \$4500-7000/kg; the natural identical materials-jasmone and methyl jasmine-cost \$450-700/kg; and the simpler cyclopentanone derivatives, \$15-70/kg. According to Swift [4], the flavour and fragrance industries consume approximately 30000 tons per year of pinene, which are used to produce a diverse range of products. Limonene production is around 30000 tons per year, making it a valuable and renewable feedstock.

Limonene is one of the most commonly occurring natural compound of essential oils in plants. Limonene and p-cymene are monocyclic terpenes, α -pinene is a bridged bi-cycle terpene and geraniol is a monoterpene alcohol. For all the above compounds, antifungal and antibacterial activities have been demonstrated [5]; in particular the antimicrobial activity has been attributed to their interaction with cellular membranes.[6] Limonene displayed the strongest acaricidal activity against *Otodectes cynotis* (Psoroptidae)[7] , commonly named ear mite, a frequent nonburrowing mite causing ear infections (otocariasis) in dogs, cats, ferrets, foxes and other wild carnivores.[8]

The high reactivity of terpenes molecules often makes it difficult to achieve a selective transformation. However, the target is worth pursuing as almost all products can be useful.[9]

There are many literature reports concerning reactions of a variety of different terpenes: catalytic hydrogenation/hydrogenolysis, dehydrogenation, rearrangement/ isomerisation/aromatisation, reactions with carbon monoxide, epoxidation, and the addition of alcohols and acids.[4] The existence of many terpene isomers and otherwise similar compounds makes selectivity an important issue in these reactions, as different catalysts and reaction conditions lead to different products.

Hydrogenation is of particular importance in the chemical modification of naturally occurring terpenes. Very early work in the area of terpene hydrogenation under high-pressure conditions was published by Ipat'ev.[10] One of its main problems is the mass transfer limitation imposed

by the low solubility of hydrogen in the liquid terpenes. This limitation can be overcome by the use of high-pressure carbon dioxide, either as a supercritical solvent or as a “liquid expander”. In fact, most terpenes dissolve high-pressure carbon dioxide in large quantities, and critical pressures of CO₂ + terpene binary mixtures are often lower than 100 bar, at temperatures around 50 °C, as confirmed by extensive collections of data on high pressure phase equilibrium for this type of mixtures that have been published (see, for instance, Reverchon[11], Matos et al.[12], Fonseca et al.[13]).

This means that mixtures of terpenes, carbon dioxide and hydrogen can be brought to a single, supercritical phase at moderate pressures. Alternatively, they can remain biphasic mixtures, but with a much enhanced solubility of hydrogen in the liquid, due to the high quantities of dissolved carbon dioxide.[14] The high quantity of CO₂ in the liquid makes it an “expanded fluid”, as pointed out by Wei et al.[15], avoiding the need to generate a single phase of CO₂, reactants and products. In that situation, the solubility of gaseous reactants in the liquid phase increases, and transport limitations towards the catalyst are, at least, greatly minimised.

Chouchi et al.[16] carried out the hydrogenation of α -pinene in CO₂-containing mixtures. These mixtures can be easily turned either biphasic (liquid + gas) or single-phase (supercritical), by small changes in pressure, at moderate pressures-around 100 bar. Using a Pd catalyst, the hydrogenation of α -pinene was surprisingly faster in a two-phase system than when a single-phase contacts the catalyst. This was possibly the first study where a comparison was made using the same reactants and catalyst, but with different phase behaviour, with only small changes in the process parameters. More recently, Milewska et al.[17] carried out the same type of study, using carbon-supported platinum catalysts.

Limonene (1-methyl-4-isopropenyl-1-cyclohexene) has two C-C double bonds that can be hydrogenated (figure 1). Grau et al.[18] published results of the biphasic (limonene + hydrogen) hydrogenation of limonene, using Pd catalysts with carbon or alumina supports. They examined the products of hydrogenation, isomerisation and dehydrogenation under different reaction conditions. They listed ten possible reaction products, including the two isomers of p-menthane, which result of straightforward hydrogenation of the two double bonds. They followed the reaction, at different temperatures, during more than 5 hours, and identified six of them, in variable quantities during the process. One important conclusion was that p-cymene, a three double bond compound resulting from de-hydrogenation, appeared in quantities up to 15 % in mass. The amount of the total hydrogenation product, p-menthane, was lower than 40 % in mass after more than 5 hours of reaction time.

These authors have also called attention to the different mechanisms of hydrogenation on palladium vs. platinum catalysts. This makes it attractive to compare reaction rates and yields with different catalysts.

Moutet et al.[19] examined the electrocatalytic hydrogenation of limonene using zerovalent palladium, platinum and rhodium catalysts dispersed in thin poly(pyrrole-alkylammonium) films coated on carbon electrodes. The main products obtained from these reactions are p-menthene and p-menthane.

The influence that the presence of high pressure CO₂ can have on the limonene hydrogenation yield has never been studied before. Herein we report studies of the catalytic hydrogenation of limonene in mixtures with high-pressure CO₂ and hydrogen, using a carbon-supported palladium catalyst. The carbon dioxide pressure was regulated so that the mixtures studied would either be

biphasic (at lower pressure) or in supercritical single phase (at higher pressure). The results were compared with previously reported studies [20], conducted with platinum catalysts.

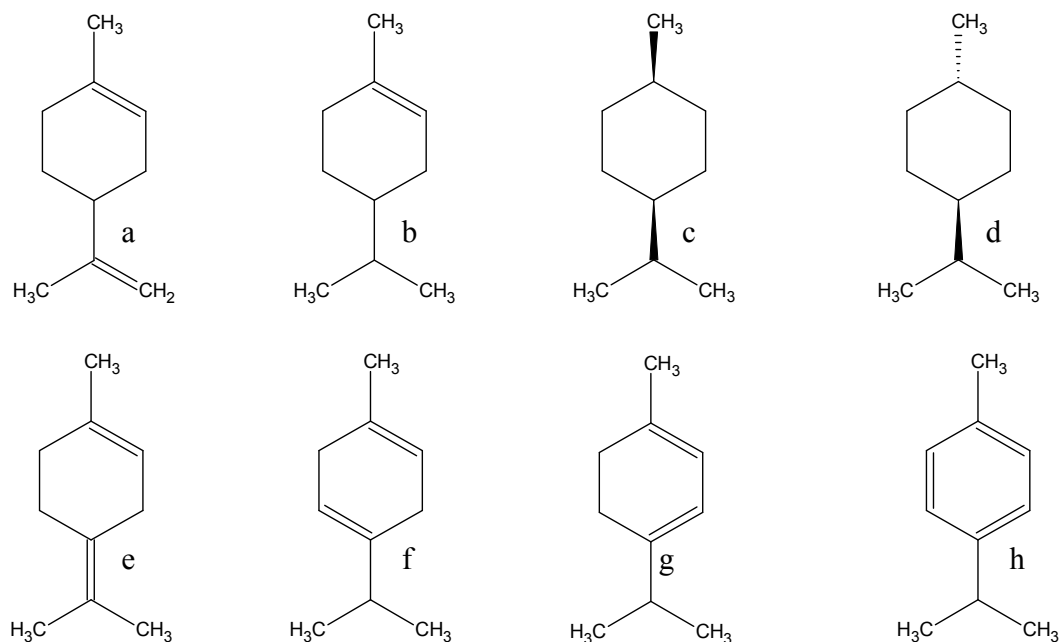


Figure 1

Limonene and possible Pd-catalysed reaction products [18]: a) 1-methyl-4-isopropenyl-1-cyclohexene or limonene, b) 1-methyl-4-isopropyl-1-cyclohexene or *p*-menthene, c) *cis*-1-methyl-4-isopropyl-cyclohexane or *cis-p*-menthane, d) *trans*-1-methyl-4-isopropyl-cyclohexane or *trans-p*-menthane, e) 1-methyl-4-isopropylidene-1-cyclohexene or terpinolene, f) 1-methyl-1-methyl-4-isopropyl-1,4-cyclohexadiene or γ -terpinene, g) 1-methyl-4-isopropyl-1,3-cyclohexadiene or α -terpinene, h) 1-methyl-4-isopropyl-1,3,5-cyclohexatriene or *p*-cymene.

METHODS

Reaction experiments were performed at 50 °C, using 2 ml of limonene and about 0.4 g of catalyst. The hydrogenations were performed with an apparatus consisting of one sapphire-windowed cell connected by a pump to a tubular reactor – short tube that encloses a catalyst bed. This apparatus is a modification of the one described by Milewska et al. [17]

The reactants were continuously withdrawn from the bottom of the view cell, circulated through the catalyst bed, and sent back to the upper entrance of the cell. Samples have been taken at regular intervals through a system of two valves with a sampling loop. CO₂ in the loop was carefully vented to the atmosphere. Before taking the sample the loop was filled by the fresh reaction mixture, which was collected in a separate vial, and in next step fresh mixture was collected and analysed by gas chromatography.

Analyses were performed using GC with a HRGC-3000C gas chromatograph. Column: 30 m x 0.32 mm i.d. fused silica capillary column coated with a 0.25 μm thickness film of 5 % phenyl groups in the dimethylpolysiloxane (CP-Sil 8 CB) from Varian Inc.. Oven temperature program: 87-91°C ramp at 0.5°Cmin⁻¹, and 91-240°C ramp 20°Cmin⁻¹. Injector and detector temperature: 250 °C.

Pure terpenes have been used to prepare samples to identify compounds from the reactions. Nonane in hexane (1.5 mM) was used as external standard for GC analysis.

RESULTS

Experiments were carried out at 4 MPa hydrogen pressure plus either 8.5 or 12 MPa carbon dioxide pressures, corresponding to total pressures in the cell of 12.5 MPa (and a two-phase system) or 16 MPa (and a single phase regime), respectively. The change in carbon dioxide pressure ($\Delta p=3.5$ MPa) determines the number of phases.

Contrarily to what was observed with platinum as catalyst [20], the influence of phase behaviour in the case of palladium is very small. In both biphasic and monophasic conditions, limonene is hydrogenated in less than 40 minutes after the reaction starts, leading to total hydrogenation of the two double bonds. The p-menthane isomers are produced in the ratio 2/3 trans to 1/3 cis, in marked contrast with the reaction catalysed by platinum, where the proportion was approximately 1:1.

The reaction in biphasic conditions had a long period of induction of about 50 minutes after the circulation of the mixture through the catalyst bed was started, where no reaction products were detected. The reaction at higher pressure, in single phase, showed practically no induction period. Comparison of the limonene concentration profiles show that the consumption of the reagent is faster in single phase, but proceeds through the formation of the intermediate p-menthene (Fig. 2b), while this intermediate is scarcely detected at all during the biphasic reaction.

CONCLUSIONS

The main product of hydrogenation of limonene with a palladium catalyst in both single and biphasic conditions was trans-p-menthane. The concentration of trans-p-menthane is twice higher than the second isomer (cis-p-menthane). Therefore, the conditions of the reactions do not change the selectivity of final products, contrarily to what happened when a platinum catalyst was used. Reaction time depends on the phase behaviour of investigated systems.

REFERENCES:

- [1] Bauer, K., Garbe, D., Surburg, H., Common Fragrance and Flavours Materials (Wiley-VCH, New York, **1997**)
- [2] Mata, V. G., Gomes, P. B., Rodrigues, A. E., Bioengineering, Food, and Natural Products, Vol. 51, **2005**, p. 2834
- [3] Behan, J. M., Perring, K. D., Int. J. Cosmet. Sci., Vol. 9, **1987**, p. 261
- [4] Swift, K. A. D., Topics in Catalysis, Vol. 27, **2004**, p. 143
- [5] Hammer, K. A., Carson, C. F., Riley, T. V., J. Appl. Microbiol., Vol. 95, **2003**, p. 853

- [6] Sikkema, J., de Bont, J. A., Poolman, B., *Microbiol. Rev.*, Vol. 59, **1995**, p. 201
- [7] Traina, O., Cafarchia, C., Capelli, G., Iacobellis, N. S., Otranto, D., *Experimental and Applied Acarology*, Vol. 37, **2005**, p. 141
- [8] Sweatman, G. K., *Can. J. Zool.*, Vol. 36, **1958**, p. 849
- [9] Ravasio, N., Zaccheria, F., Guidotti, M., Psaro, R., *Topics in Catalysis*, Vol. 27, **2004**, p. 157
- [10] Ipat'ev, V., Balachinskii, G. J., *Russ. Phys. Chem. Soc.* Vol. 43, **1912**, p. 1754
- [11] Reverchon, E., *J. Supercrit. Fluids*, Vol. 10, **1997**, p. 1
- [12] Matos, H. A., Gomes de Azevedo, E. J. S., Simões, P. C., Carrondo, M. T., Nunes da Ponte, M., *Fluid Phase Equilib.*, Vol. 52, **1989**, p. 357
- [13] Fonseca, J., Simoes, P., Nunes da Ponte M., *J. Supercrit. Fluids*, Vol. 25, **2003**, p. 7
- [14] Solinas, M., Pfaltz, A., Cozzi, P.G., Leitner, W., *J. Am. Chem. Soc.*, Vol. 126, **2004**, p. 16142
- [15] Wei, M., Musie, G. T., Busch, D. H., Subramanian, B., *J. Am. Chem. Soc.*, Vol. 124, **2002**, p. 2513
- [16] Chouchi, D., Gourgouillon, D., Courel, M., Vital, J., Nunes da Ponte, M., *Ind. Eng. Chem. Res.*, Vol. 40, **2001**, p. 2551
- [17] Milewska, A., Banet Osuna, A., Fonseca, I. M., Nunes da Ponte, M., *Green Chem.*, Vol. 7, **2005**, p. 726
- [18] Grau, R. J., Zgolic, P. D., Gutierrez, C., Taher, H. A., *J. Mol. Catal. A: Chem.*, Vol. 148, **1999**, p. 203
- [19] Moutet, J. C., Ouenoughi, Y., Ourari, A., Hamar-Thibault, S. *Electrochim. Acta*, Vol. 40, **1995**, p. 1827
- [20] Bogel-Lukasik, E., Fonseca, I.M., Nunes da Ponte, M., *Conference on Knowledge-based Materials and Technologies for Sustainable Chemistry*, Estonia, **2005**.

ACKNOWLEDGMENT

This work has been supported by the European Commission in framework of the Marie Curie Research Training Network „Green Chemistry in Supercritical Fluids: Phase Behaviour, Kinetics and Scale-up” (EC Contract No:MRTN-CT-2004-504005).