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Dalida Chouchi, Didier Gourgouillon, Mathilde Courel, Joaquim Vital, Manuel Nunes da Ponte. The Influence of Phase Behavior on Reactions at Supercritical Conditions: The Hydrogenation of  $\alpha$ -Pinene. Industrial and engineering chemistry research, 2001, 40, pp.2551 - 2554. 10.1021/ie000859p . hal-03904285

**HAL Id: hal-03904285**

**<https://hal.science/hal-03904285>**

Submitted on 16 Dec 2022

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# The Influence of Phase Behavior on Reactions at Supercritical Conditions: The Hydrogenation of $\alpha$ -Pinene

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In this paper, results on the hydrogenation of  $\alpha$ -pinene, a liquid reactant, in supercritical (SC) CO<sub>2</sub> are presented. Visual observation of phase equilibria under the conditions of the reaction experiments was also performed. Much faster reaction rates were obtained when a two-phase system was present in the reactor than when a homogeneous, one-phase situation occurred. This phenomenon is attributed to the fact that SC CO<sub>2</sub> can dissolve extensively in the liquid reactant, leading to the formation of an “expanded liquid”, which can dissolve large quantities of hydrogen. This seems to be the first time that this type of behavior is reported in the literature.

## 1. Introduction

Chemical reactions in supercritical fluid (SCF) media represent an expanding field.<sup>1,2</sup> One of the main advantages of using SCFs as solvents is their ability to dissolve large quantities of most gases. Carbon dioxide and hydrogen, for example, mix in all proportions<sup>3</sup> at temperatures above the critical temperature of CO<sub>2</sub> (304.1 K). If the other advantages over conventional liquid solvents, such as larger diffusion coefficients, lower viscosities, and nontoxicity, are added, SC CO<sub>2</sub> can be regarded as a potentially ideal solvent for carrying out hydrogenation reactions.

However, carbon dioxide has a serious drawback: it is a poor solvent for many substrates to be hydrogenated. Recently, Härröd and collaborators<sup>4</sup> discussed the heterogeneously catalyzed hydrogenation of sunflower oil in two supercritical solvents, carbon dioxide and propane. They based their discussion on the phase diagram for ternary mixtures of oil + hydrogen + supercritical solvent in terms of the number of phases in contact with the catalyst. Because of the poor solubility of the oil in carbon dioxide, there are always two phases, liquid and gas, when the process is carried out in CO<sub>2</sub>. As a result, the concentration of hydrogen near the catalyst is small, and the positive effect of the presence of CO<sub>2</sub> on the reaction rate is thought to be due to viscosity reduction by dissolution in the liquid. In contrast, propane and oil can be made totally miscible. Only one (gas) phase contacts the catalyst when propane is used as a solvent, and very large increases in the reaction rates are obtained.

Bertucco and collaborators<sup>5</sup> studied a different hydrogenation reaction in CO<sub>2</sub>, where the system in contact with the catalyst was clearly biphasic. They also observed large increases in the reaction rate, although not as high as those observed in the work of Härröd et al.

Polyakoff et al.<sup>6</sup> recently discussed these and similar results. They suggested that the liquid substrate dissolves a high quantity of CO<sub>2</sub>, becoming an “expanded liquid”. Hydrogen would be highly soluble in this liquid, thus significantly increasing its concentration in the vicinity of the solid catalyst. Consequently, they concluded that “further research is needed to determine whether single phase behavior is essential for high efficiency in catalytic reactions”.

Terpenes are a class of compounds with important industrial applications, especially in the fragrance and flavor industries.<sup>7</sup> Hydrogenation of these substances is commonly carried out for industrial purposes. On the other hand, most terpenes show a high affinity for CO<sub>2</sub>. There is, in fact, a large body of published research on phase equilibrium of terpenes + SC CO<sub>2</sub> (see, for example, Matos et al.,<sup>8</sup> Akgün et al.,<sup>9</sup> and Reverchon<sup>10</sup>). In general, supercritical CO<sub>2</sub> is highly soluble in most terpenes: at pressures close to the critical pressure, the liquid phase in a biphasic mixture can contain 80 mol % or more of CO<sub>2</sub>. Moreover, the critical pressures of these mixtures are reasonably low, often lower than 10 MPa.

It should therefore be easy to carry out experiments on hydrogenation reactions of terpenes in supercritical CO<sub>2</sub>, using either biphasic or single-phase mixtures, by small changes in the pressure. The results could represent a useful contribution to the discussion of the effect of phase behavior on catalytic efficiency.

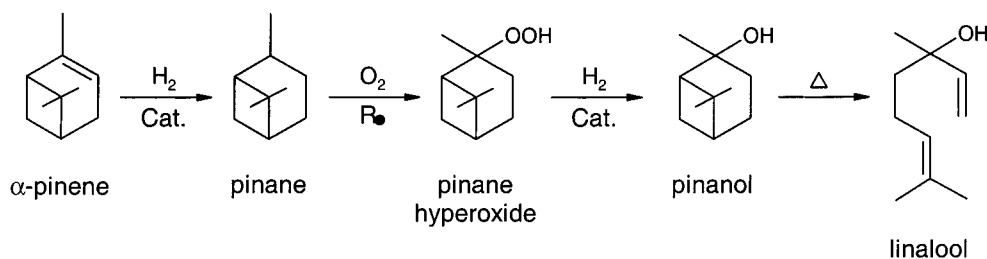
We used the hydrogenation of  $\alpha$ -pinene in SC CO<sub>2</sub> as a suitable model for that purpose. The hydrogenation of liquid  $\alpha$ -pinene is well-known, as it is the first step in a series of reactions that converts a cheap and versatile raw material into a variety of valuable products (aromas and vitamins).<sup>7</sup> Figure 1 gives an example of a reaction in which  $\alpha$ -pinene is used as a starting material for the synthesis of linalool.

Different metal-based catalysts can be used for the hydrogenation of  $\alpha$ -pinene, such as Adams catalyst (PtO<sub>2</sub>), Raney nickel, and carbon-supported metals (Pd/C, Pt/C), depending on the selectivities and yields being sought.<sup>11</sup> The mechanisms of these catalytic reactions are generally well-known, and it is possible to control the stereoselectivity by adjusting the operating condi-

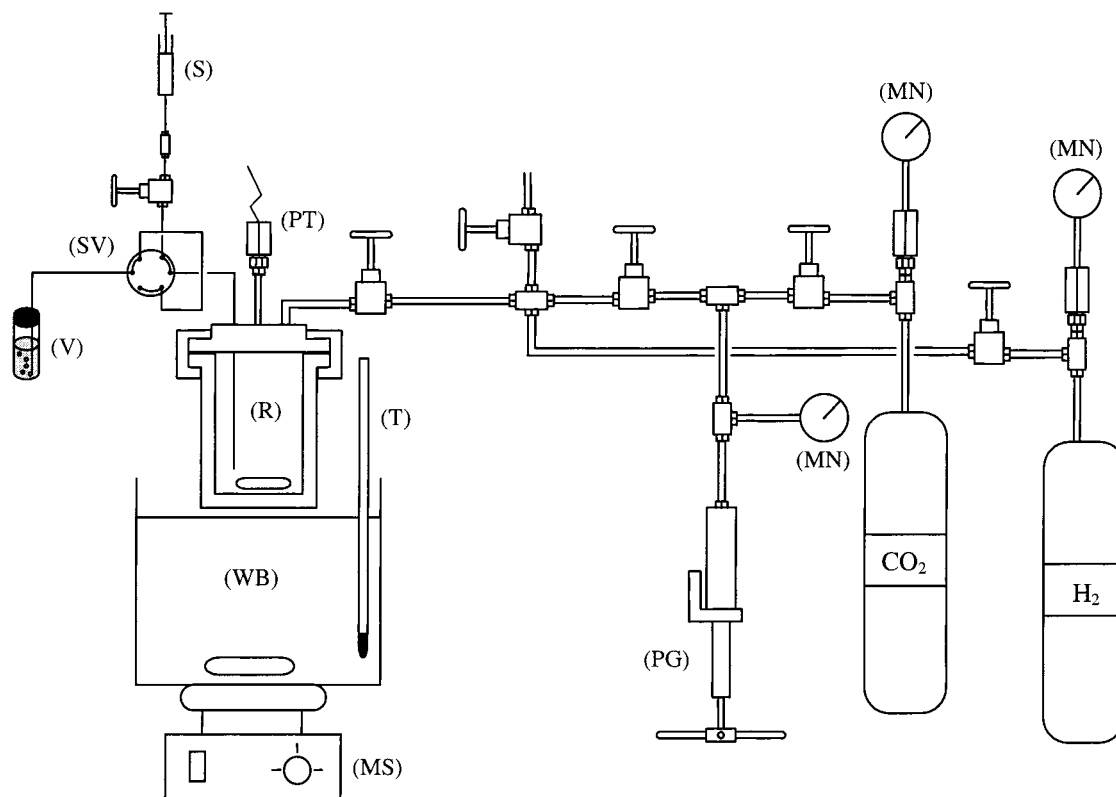
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**Figure 1.** Synthesis of linalool from  $\alpha$ -pinene through hydrogenation, oxidation, and pyrolytic ring cleavage.



**Figure 2.** Schematic representation of the apparatus for hydrogenation reactions at high pressure: (MN) manometer, (MS) magnetic stirrer, (PG) pressure generator, (PT) pressure transducer, (R) reactor, (S) syringe, (SV) switching valve, (V) vial, (T) glass thermometer.

tions. For example, Ilyna and Semikolenov recently proposed a mechanism for the hydrogenation of  $\alpha$ -pinene on Pd/C catalysts to *cis*- and *trans*-pinane.<sup>12</sup> They showed that the selectivity toward *cis*-pinane is determined by two parameters: the hydrogen pressure and the reaction temperature.

At the start, the objectives of this work were to check the feasibility of hydrogenating  $\alpha$ -pinene in SC CO<sub>2</sub> in the presence of a Pd/C catalyst and to examine the selectivity of the reaction under different pressures of CO<sub>2</sub> and H<sub>2</sub>. We chose CO<sub>2</sub> pressures corresponding to biphasic and monophasic conditions according to the data of Akgün et al.<sup>9</sup> To interpret the results obtained, a detailed study of the phase behavior under the conditions of the experiments (but without the presence of the catalyst) became necessary and was subsequently undertaken.

## 2. Experimental Section

**2.1. Materials.** Hydrogen and carbon dioxide with a stated purity of 99.998 mol % were obtained from Air Liquide.  $\alpha$ -Pinene (purity = 99%) and *cis*-pinane (purity > 99%) were obtained from Fluka. The catalyst was activated carbon-supported palladium (10 wt %) from Merck.

**2.2. Hydrogenation Experiments.** Figure 2 is a schematic representation of the apparatus used for the hydrogenation of  $\alpha$ -pinene with pressurized CO<sub>2</sub>. Reactions are carried out in a 316 SS reactor (R) with an approximately 40-cm<sup>3</sup> internal volume. Temperature control (323 K) is achieved through immersion in a thermostated water bath (stability better than 1 K, precision of  $\pm 0.1$  K). The stirring of the reaction mixture is achieved with a magnetic bar. The pressure inside the reactor is measured by a pressure transducer (PT) (Setra C204, precision of 0.1%).

The reactor is first flushed with low-pressure CO<sub>2</sub> and then loaded with 1 g of  $\alpha$ -pinene and 0.02 g of catalyst. After that, CO<sub>2</sub> is introduced up to the desired pressure by means of a pressure generator (PG) (HIP, 87-6-5). When the temperature and pressure of the system are stable, H<sub>2</sub> is introduced in the reactor up to a total pressure of 14 MPa. This time is chosen as the starting time of the reaction ( $t = 0$ ).

During the reaction, samples are withdrawn at regular intervals from the top of the reactor through a high-pressure switching valve (SV) (Rheodyne 7000) equipped with a 50- $\mu$ L loop and connected to the reactor outlet (see Figure 2). An important consequence of this arrangement is that, when the system inside the reactor

**Table 1.** Pd/C-Catalyzed Hydrogenation of  $\alpha$ -Pinene to Pinane: Reaction Yields as a Function of Time for Different CO<sub>2</sub> Pressures

$P_{\text{CO}_2} = 8 \text{ MPa}$		$P_{\text{CO}_2} = 9 \text{ MPa}$		$P_{\text{CO}_2} = 9.5 \text{ MPa}$		$P_{\text{CO}_2} = 10 \text{ MPa}$		$P_{\text{CO}_2} = 12 \text{ MPa}$	
time (min)	pinane yield (%)	time (min)	pinane yield (%)	time (min)	pinane yield (%)	time (min)	pinane yield (%)	time (min)	pinane yield (%)
5	6.3	5	17.2	7	16.5	11	4.2	5	5.9
10	29.5	10	22.2	15	16.1	15	5.8	10	1.8
15	54.6	15	43.7	30	28.4	20	5.9	15	2.9
20	66.7	20	64.2	45	48.8	25	9.7	20	2.2
25	74.3	26	76.7	60	72.8	30	11.3	25	3.8
30	83.9	30	86.4	75	85.2	50	14.7	30	4.7
40	85.1	40	92.7	90	88.8	80	24.5	45	6.8
50	93.6	50	97.9	105	97	100	25.4	60	13.5
62	100	60	100	110	98.5	105	35.5	80	17.6
								90	23.6
								92	28.4

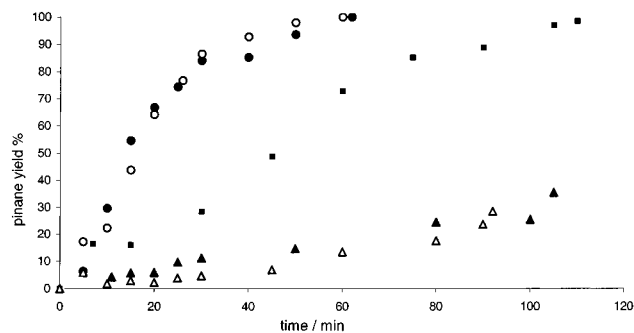
is biphasic, the samples are withdrawn from the gas phase. The additional volume of the loop induces a small pressure drop in the reactor, the extent of which depends on the working pressure. The content of the loop is then slowly depressurized at ambient temperature into a closed vial (V) filled with hexane in order to trap the  $\alpha$ -pinene and pinane. Finally, the switching valve loop is washed twice with approximately 2 mL of hexane and then flushed with N<sub>2</sub>. The hexane fractions are collected together and analyzed by gas chromatograph (Varian 3800 GC) with a FID detector, equipped with a dimethylpolysiloxane column (CP-Sil 8 CB, 30 m long, 0.32 mm i.d., film thickness of 0.25 mm), working between 373 and 473 K with a heating rate of 15 K min<sup>-1</sup>. The concentrations of  $\alpha$ -pinene and pinane in the collected samples are determined using dodecane as the internal standard (response factor for  $\alpha$ -pinene = 0.90, response factor for pinane = 0.81, precision of the method is better than 10%). The relative amounts of  $\alpha$ -pinene and pinane in each sample taken from the reactor can then easily be calculated.

**2.3. Phase Equilibrium Experiments.** To monitor the influence of pressure on the phase behavior of the system consisting of CO<sub>2</sub>, H<sub>2</sub>,  $\alpha$ -pinene, and pinane during the reaction, we used a sapphire-windowed reactor (New Ways of Analytics) with an internal volume of approximately 50 cm<sup>3</sup>. This reactor is provided with a magnetically driven stirrer and anchor for efficient mixing of the components (max speed = 2500 rpm), as well as a large sapphire window (diameter = 36 mm, thickness = 16 mm). Temperature control is achieved by means of a PID controller (Eurotherm 2216e) connected to a Pt-100 probe located in the reactor and two 100-W resistors inserted in the reactor walls. The pressure inside the reactor is measured with the same pressure transducer as used for hydrogenation experiments (Setra C204).

### 3. Results

All reaction experiments were performed at 50 °C, using 1 g of  $\alpha$ -pinene and 0.02 g of catalyst. Five different experiments were carried out at CO<sub>2</sub> pressures of 8.0, 9.0, 9.5, 10.0, and 12.0 MPa. The total pressure of the system was 14 MPa in all cases and was reached by further introduction of H<sub>2</sub>.

Under these conditions, the initial concentration of  $\alpha$ -pinene in the reactor varies from 4 to 11% of the CO<sub>2</sub> mass. The quantity of hydrogen cannot be calculated precisely, because of the lack of information on the densities of CO<sub>2</sub> + H<sub>2</sub> mixtures at high pressures. However, a rough calculation indicates that H<sub>2</sub> is in

**Figure 3.** Pd/C-catalyzed hydrogenation of  $\alpha$ -pinene to pinane. Reaction yields as a function of time for different CO<sub>2</sub> pressures: (●)  $P_{\text{CO}_2} = 8.0 \text{ MPa}$ ; (○)  $P_{\text{CO}_2} = 9.0 \text{ MPa}$ ; (■)  $P_{\text{CO}_2} = 9.5 \text{ MPa}$ ; (▲)  $P_{\text{CO}_2} = 10.0 \text{ MPa}$ , (△)  $P_{\text{CO}_2} = 12.0 \text{ MPa}$ .

molar excess by 4–12 times in relation to the quantity required for the complete hydrogenation of 1 g of  $\alpha$ -pinene. The results obtained in terms of mass percentages of pinane relative to  $\alpha$ -pinene + pinane as a function of the reaction time are given in Table 1 and are plotted in Figure 3.

As the reactor used in these reaction experiments was a closed, no observation of the number of phases present was possible. Phase equilibrium experiments were separately performed in the previously described sapphire-windowed view cell. The main objective of these experiments was to determine the transition pressure from a two-phase (liquid–gas) system to a one-phase (fluid) system, under conditions of concentration that were similar to those in the reaction experiments. For this purpose, two separate experimental runs were carried out. In the first, 1 g of  $\alpha$ -pinene was introduced into the cell, and CO<sub>2</sub> pressure was applied until all of the liquid disappeared and the system became monophasic. Subsequently, H<sub>2</sub> was added up to a pressure of 14 MPa. In the second run, instead of pure  $\alpha$ -pinene, a 50/50 w/w liquid mixture of  $\alpha$ -pinene + *cis*-pinane was used. Apart from this, the experiment was carried out as described for pure  $\alpha$ -pinene. The purpose of the two different experiments was to mimic reaction conditions in the beginning (pure  $\alpha$ -pinene) and at the midpoint (50/50 w/w mixture) of the reaction. However, no catalyst was added, to avoid any change of composition during the experiments. The transition pressures observed were 9.32 MPa for pure  $\alpha$ -pinene and 9.37 MPa for the  $\alpha$ -pinene + pinane mixture. In both cases, addition of H<sub>2</sub> did not induce any phase separation. The first result is in excellent agreement with the data presented by Akgün et al.<sup>9</sup> using static and dynamic methods.



#### 4. Discussion

The results graphically represented in Figure 3 can be grouped in three different categories: the reactions at 8.0 and 9.0 MPa of CO<sub>2</sub> proceed at essentially indistinguishable, fast rates; the reactions at 10.0 and 12.0 MPa of CO<sub>2</sub> proceed at similar rates, but they are very slow; the reaction at 9.5 MPa of CO<sub>2</sub> is an intermediate case, where the reaction rate is low during the first 30 min and then increases significantly. It must also be remarked that, in the first two cases, the hydrogen pressure does not affect the reaction rates.

The phase equilibrium results obtained in this work determined that the first group (8.0–9.0 MPa) corresponds to biphasic conditions, whereas for the second group (10.0–12.0 MPa), the reaction proceeds in a single gas phase. For the intermediate case, the CO<sub>2</sub> pressure is very close to the transition pressure. It is possible, in fact, that the reaction initiates in a single phase and continues, after approximately 30 min, in two phases. There are three possible explanations for this phenomenon. (1) The sampling method induces a small pressure drop in the system, typically between 0.03 and 0.04 MPa. (2) The appearance of the reaction product pinane modifies the phase behavior. Indeed, pinane is slightly less soluble in CO<sub>2</sub> than  $\alpha$ -pinene, and consequently, in our system, the one phase–two phase transition pressure increases as the reaction proceeds, as explained above. (3) The catalyst acts as a nucleus of condensation due to capillary forces and electrostatic interactions and leads to phase separation at surface or in the pores.

The hydrogenation of  $\alpha$ -pinene in this work, therefore, was much faster under two-phase conditions than when a single phase contacted the catalyst. The reaction rate in each group did not depend on the quantity of H<sub>2</sub>, which in every case was present in large excess.

A possible explanation for this surprising result is that, under the conditions of this work, the limiting step for the catalysis might be the access of  $\alpha$ -pinene, and not hydrogen, to the catalyst. Liquid mixtures of  $\alpha$ -pinene and carbon dioxide at 8.0 and 9.0 MPa and 323 K have concentrations of  $\alpha$ -pinene on the order of 10 mol. %. If the liquid surrounds the catalyst,  $\alpha$ -pinene will have ready access to the metal. On the other hand, these liquid mixtures have a very high content of CO<sub>2</sub> and are a good model of the above-mentioned expanded liquids. Large amounts of gaseous hydrogen should be soluble in these liquids, maintaining a relatively high concentration of this substance close to the solid catalyst.

When single-phase conditions are obtained at higher CO<sub>2</sub> pressures, the concentration of  $\alpha$ -pinene in the medium surrounding the catalyst is about 1 order of magnitude lower, on the order of 1 mol %.

A well-founded discussion of the factors involved would require adsorption data of  $\alpha$ -pinene on Pd/C catalysts, so that quantitative considerations about the effect of the concentration differences of  $\alpha$ -pinene in the vicinity of the metal might be produced. One might, however, speculate that this difference is the leading factor in this case.

#### 5. Conclusions

The present case seems to be the first in which two-phase conditions lead to better rates of hydrogenation than single-phase conditions. These findings call attention to important factors, such as the composition of liquid mixtures in the vicinity of the critical region and adsorption isotherms of the substrates on the catalyst.

#### Acknowledgment

D. Chouchi thanks the European Commission for a Marie Curie postdoctoral fellowship (TMR ERBFMBICT 972062). M. Courel also thanks the European Commission for a postdoctoral fellowship, granted through the Network Super-Clean Chemistry (TMR ERBFMRX-CT97-0104). All authors thank Fundação para a Ciência e a Tecnologia (Lisbon, Portugal) for additional support through Project PRAXIS/P/QUI/10075/1998.

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Received for review October 2, 2000

Revised manuscript received February 22, 2001

Accepted February 22, 2001

IE000859P