

OXIDATION OF LIMONENE IN HIGH PRESSURE CO₂ REACTION MEDIA: THE INFLUENCE OF PHASE BEHAVIOUR.

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The influence of the phase behaviour on the oxidation of limonene in supercritical CO₂ as the reaction medium with molecular oxygen as the primary oxidant and isobutyraldehyde as the sacrificial co-oxidant was explored. Results on the kinetic of the reaction are presented at different carbon dioxide pressures, so that the reaction mixture would either be biphasic or at a single supercritical phase. The effect of the phase behaviour on the rate and selectivity of the reaction was investigated.

INTRODUCTION

The possibility of performing oxidation reactions in high pressure CO₂ media is a key goal in the area of green chemistry. Compressed CO₂ is a very attractive medium for oxidation reactions because it is non-flammable and cannot be further oxidized. Furthermore and from a process perspective, CO₂ is completely miscible with oxygen which eliminates the resistance to transport of oxygen presented by the liquid-vapour interface in a conventional substrate/solvent/oxygen mixture.[1]

Oxidation of olefins occurs effectively in supercritical CO₂ as the reaction medium with molecular oxygen as the primary oxidant and aldehydes as sacrificial co-oxidants. Leitner et al. [2] reported that the addition of a metal catalyst (Mukaiyama conditions) was not required to achieve high reaction rates and selectivities, experiments revealed that the presence of the stainless steel from the reactor wall promoted the epoxidation presumably by initiating radical reaction pathways.

A relevant advantage of performing reactions under high pressure CO₂ is the possibility of controlling chemical rates and selectivity through the fine tuning of the reactive system environment. There are a number of examples where a homogeneous single-phase is the more favourable condition for fast reaction rates and chemoselectivity. On the other hand, a heterogeneous state can in some circumstances dramatically increase the reaction rate or influence the outcome of a reaction. In previous publications from our laboratory Chouchi et al. [3] and Milewska et al. [4] obtained much higher yields for the hydrogenation of α -pinene in scCO₂, when the reaction mixture was under heterogeneous conditions than when the system became homogeneous at higher pressures. Thus, there is no universally favourable phase-state for reactions in scCO₂ and it is necessary to consider the effect of phase behaviour on reactivity for individual reactions.[5] Despite interesting results obtained by Loecker et al. in the oxidation of olefins in supercritical CO₂ as the reaction medium with molecular oxygen

as the primary oxidant and aldehydes as sacrificial co-oxidants, the role of the phase behaviour in this particular application is not well established and is clearly needed to allow for commercial development of this process.

A relevant oxidation reaction was selected for a detailed investigation in this research. Limonene is a naturally occurring terpene, which occurs in citrus oils, is available in bulk quantities and is particularly a very important precursor of valuable oxygenated products as limonene oxide, carveol and carvone. Oxygen containing terpenes often show valuable organoleptic properties and form the largest group of modern fragrance ingredients. Of particular interest carvone, is a spearmint flavour compound with a wide range of applications. Large amounts are consumed in cosmetics, toothpaste, chewing gum and pharmaceutical preparations. World production is substantially increasing due to growing demand of this compound. Presently, the production process utilizes nitrosylchloride which is environmentally demanding. A new, clean process is desired. [6,7]

In this work experiments on the oxidation of limonene in supercritical CO₂ as the reaction medium with molecular oxygen as the primary oxidant and isobutyraldehyde as sacrificial co-oxidants were performed. Different carbon dioxide pressures were studied, so that the reaction mixture would either be biphasic or at a single supercritical phase. The effect of the phase behaviour on the rate and selectivity of the reaction was investigated.

MATERIALS AND METHODS

Materials

Oxygen and carbon dioxide with a stated purity of 99.998 mol% were obtained from Air Liquide. (R)-(+)-Limonene, (+)-Limonene Oxide were obtained from Aldrich and hexane was obtained from Riedel-de-Haën.

Oxidation Experiments

Experiments on the oxidation of limonene in high pressure CO₂ reaction media were performed in the apparatus schematically presented in Figure 1. This apparatus is built around a stainless steel cylindrical cell with an internal volume of approximately 50 cm³ and two sapphire windows at the top that allowed a direct visual observation of the number of phases of the reaction mixture, as described in detailed by Milewska et al.[4] The pressure in the cell is measured with a pressure transducer 204 Setra calibrated between 0 and 34.3 MPa with a precision of ±0.1%. This cell is immersed in a thermostated water bath and has magnetic internal stirring for efficient mixing of the components. The temperature is measured with a mercury thermometer with a precision of ±0.1 °C. The temperature is assumed to be homogeneous inside the thermostated water-bath, heated by means of a controller that maintained temperature within ± 0.1°C. The bottom of the cell is connected, via a circulation pump, to a stainless steel tubular reactor with an inner diameter of 4.6 mm that enclosed the catalyst bed or simply pure silica (230-400 mesh) for the uncatalysed oxidation runs.

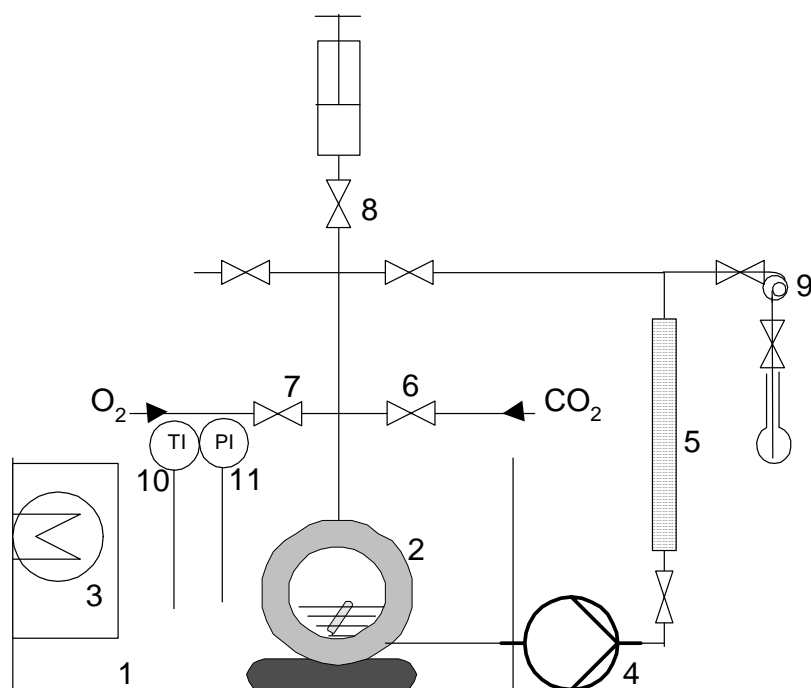


Figure 1: Schematic diagram of the apparatus: (1) thermostated water bath; (2) high pressure cell with sapphire windows; (3) temperature controller; (4) high pressure piston pump; (5), stainless steel tubular reactor; (6), CO₂ admission valve; (7), O₂ admission valve; (8), liquid admission valve; (9), sampling loop; (10), mercury thermometer; (11), pressure transducer.

Experiments were performed at 55°C using 6 mmol of limonene. Stoichiometry of the reaction was a fixed parameter in this study, limonene:isobutyraldehyde:molecular oxygen of 1:2:2.5. Carbon dioxide was added up to either 8,5MPa or 12MPa. In the first case, the reaction mixture was biphasic and in the second, a single supercritical phase. For the catalysed experiment (Mukaiyama conditions), 0,5g of Co(acac)₂trien@NaY catalyst was used diluted in pure silica and placed in a stainless steel tubular reactor, between two filters. The cell contents were vigorously stirred, in order to promote phase equilibrium, and continuously withdrawn from the bottom of the view cell, circulated through the catalyst bed, and sent back to the upper entrance of the cell. The flow-rates of circulation were very low. The main purpose was to keep the composition of the feed minimally disturbed by the reaction products entering the top of the cell. Samples were taken at regular intervals through a system of two valves with a sampling loop, at the top of the tubular reactor. The samples collected are diluted in hexane to a convenient volume and analyzed by gas chromatography with a FID detector, using nonane as internal standard.

RESULTS

The influence of the phase behaviour on limonene oxidation in supercritical CO₂ as the reaction medium with molecular oxygen as the primary oxidant and isobutyraldehyde as the sacrificial co-oxidant was studied.

Oxidation reactions were performed at 55°C, 6mmol of limonene and CO₂ total pressures of 8,5 MPa or 12 MPa. In the first case, the reaction mixture was biphasic and in the second, a single supercritical phase. An important fixed parameter in this study was the stoichiometry of

the reaction, limonene:isobutyraldehyde:molecular oxygen of 1:2:2.5. Therefore, it is possible to identify the influence of CO₂ pressure on the efficiency of the oxidation reaction.

In Figure 2 the consumption of limonene is plotted together with the formation of limonene oxide for the oxidation reactions performed at monophasic and biphasic conditions. After 7h, a higher conversion was observed for the reaction carried out at one single supercritical phase. In both cases a high selectivity, 96%, towards the epoxide formation was observed.

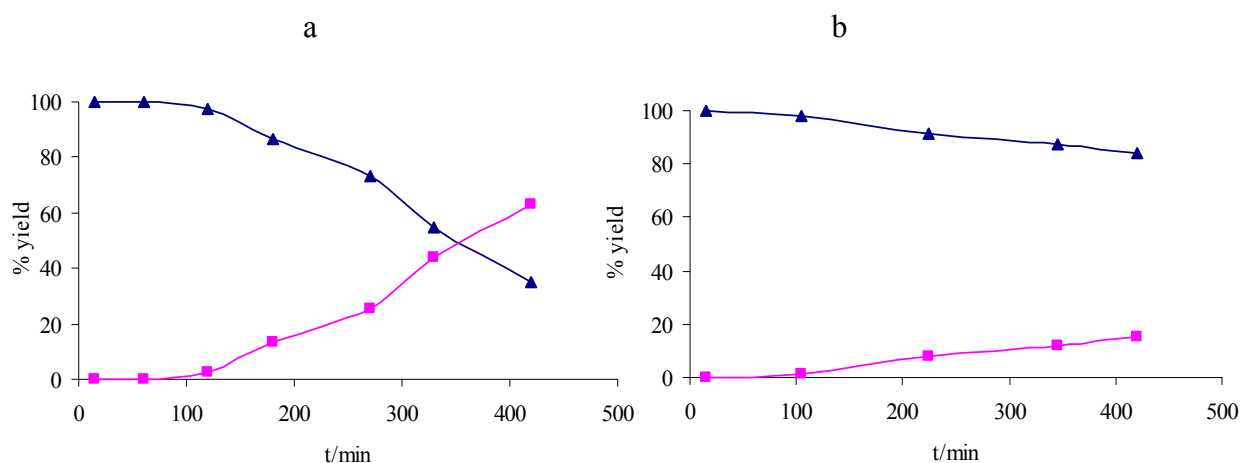


Figure 2: Mol percentages of limonene (▲) and limonene oxide (■), product of limonene oxidation in scCO₂ as the reaction medium in a) a single supercritical phase and b) at biphasic conditions.

The higher conversion obtained for the reaction in a single phase, is consequence of the complete miscibility at the conditions studied of the reactants, limonene, isobutyraldehyde and oxygen, thus implying the total elimination of phase barriers. For the biphasic reaction, the partition coefficient of the components between the liquid and the gas phase at the conditions tested did not favour limonene conversion in the liquid phase. Nevertheless to evaluate the potential role of supercritical CO₂ in this reaction, a detailed knowledge of the high pressure phase equilibrium involved is essential. In fact, small changes in pressure or temperature can produce large changes in the phase equilibrium behaviour, drastically altering for instance concentrations in the gas and liquid phases, densities, viscosities and diffusivities. A catalysed experiment (Mukaiyama conditions) was performed at 55°C and at biphasic conditions (8,5MPa) using 0,5g of Co(acac)₂trien@NaY catalyst diluted in pure silica and placed in a stainless steel tubular reactor. In a two-phase catalysed system the role of the CO₂ is to increase the solubility of oxygen in the substrate-rich phase, enhancing concentrations in contact with the catalyst. An increase in limonene conversion did not occur, which means that only the uncatalysed reaction is taking place. Other catalysts and operation conditions should be experimented in order to attain an optimum partition coefficient of the reaction components between the phases, favouring the oxidation to occur in the liquid phase, which would allow a lower pressure operation.

CONCLUSION

Experiments on the oxidation of limonene in supercritical CO₂ as the reaction medium with molecular oxygen as the primary oxidant and isobutyraldehyde as the sacrificial co-oxidant were performed. These preliminary results show that the phase behaviour significantly affected the conversion of the reaction with monophasic conditions presenting a much higher limonene conversion. The selectivity attained in both cases, was high towards the epoxide formation and was not affected by the phase behaviour. More conditions should be studied in order to gain a better understanding of the influence of CO₂ total pressure in this system.

The use of a metal complex catalyst in biphasic conditions had no effect on the total conversion obtained, which means that only the uncatalysed reaction is taking place. More experiments should be performed and a detailed knowledge of the high pressure phase equilibrium involved is essential to discuss the potential of scCO₂ in this particular application.

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