

Sorbic alcohol hydrogenation

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Abstract

Hydrogenation of sorbic alcohol was carried out in homogeneous, two-phase and heterogeneous arrangements. The effects of the reaction conditions on the reaction rate and the selectivity were studied. The highest selectivity was reached using ethylene glycol as the solvent and in two-phase arrangement, in which ethylene glycol was used as the catalyst phase.

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1. Introduction

Many research works have been engaged in hydrogenation of sorbic acid or methyl-sorbate [1–3] in order to prepare the precursors of leaf alcohols—*trans*-hex-2-enoic acid and *cis*-hex-3-enoic acid or methyl *trans*-hex-2-enoate and *cis*-hex-3-enoate. These precursors could be further converted to the desired leaf alcohols by a chemical reduction. Few years ago, a very selective catalyst for the hydrogenation of sorbic acid to *cis*-hex-3-enoic acid was discovered [4–6]. This catalyst $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ (Cp^* = pentamethylcyclopentadienyl) was capable of catalyzing the hydrogenation of sorbic acid with a very high selectivity (up to 96%) under a relatively mild conditions (1 MPa, 60 °C). The same catalyst, although slightly modified, was used for the hydrogenation of sorbic alcohol. In our previous works [7,8], we have aspired to find optimal conditions for the hydrogenation of sorbic acid (hexa-2,4-dienoic acid) to *cis*-hex-3-enoic acid, which could be used as the starting substance for the preparation of one particular leaf alcohol (*cis*-hex-3-en-1-ol). The second step of the preparation of the above fragrance substance could be the chemical reduction of a monounsaturated acid. This step could, however, change the position or a configuration of the double bond of the unsaturated acid and decrease the yield of the leaf alcohol. In this

work, we have endeavored to carry out sorbic alcohol selective hydrogenation (hexa-2,4-dien-1-ol) directly to the desired *cis*-hex-3-en-1-ol.

2. Experimental

Catalyst precursor $[\text{Cp}^*\text{RuCl}_2]_n$, sorbic alcohol and silver triflate (AgOTf) were purchased from Aldrich. All solvents were before their use freshly distilled under nitrogen atmosphere.

2.1. $[\text{Cp}^*\text{Ru}(\text{sorbic alcohol})]\text{CF}_3\text{SO}_3$ preparation

The active ruthenium catalyst was prepared by the method described in the literature [4,9–11]. $[\text{Cp}^*\text{RuCl}_2]_n$ (0.013 g) was dissolved in ether (5 ml) with an excess of sorbic alcohol (0.15 g), zinc powder (0.15 g) and silver triflate (0.02–0.03 g) and stirred at laboratory temperature for 2.5 h. An orange solution of $[\text{Cp}^*\text{Ru}(\text{sorbic alcohol})]\text{CF}_3\text{SO}_3$ (0.08 mmol) was obtained.

2.2. $[\text{Cp}^*\text{Ru}(\text{sorbic alcohol})]\text{CF}_3\text{SO}_3/\text{SiO}_2$ preparation

The catalyst solution (20 mg in 5 ml of ether) was infused onto silica (200 m²/g, Aldrich). The suspension was stirred for at least 1 h (usually for 3 h). The solution, which was initially orange, was decolorized and silica took on the same color as the initial solution. The solvent was filtered off and the solid washed with ether. Leaching was determined by AAS and did not exceed 5% of the catalyst amount (1 mg).

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2.3. Kinetic experiments

Hydrogenations were carried out in a glass reactor equipped with a sampling probe and adapted for a pressure measurement up to 0.35 MPa or in a stainless steel autoclave equipped with a glass insertion piece. In both apparatuses, the stirring was arranged by a magnetic stirrer. The volume of the reaction mixture was in all the cases 12 ml. Twenty milligrams of the catalyst (ether was evaporated), prepared as mentioned above, was introduced to the hydrogenation reactor. In the case of heterogeneous hydrogenation, sorbic alcohol (typically 200 mg) was dissolved in 12 ml of MTBE, in the case of homogeneous hydrogenation, sorbic alcohol (typically 80 mg) was dissolved in 12 ml of MTBE and in the case of two-phase hydrogenation, sorbic alcohol was dissolved in the mixture of MTBE:ethyleneglycol 1:4. The reactor was heated and filled with hydrogen and the reaction was started. Reaction conditions changed in the range: temperature: 20–75 °C, pressure: 0.35–5 MPa, the catalyst amount was 3–10 wt.% of the amount of sorbic alcohol. Withdrawn samples were analyzed using GC or GC/MS in order to identify the products.

The obtained data were used for calculations of the selectivity and the reaction rate. For the homogeneous catalyst, the reaction rate was defined as $\text{TOF}_{90\%}$ (h^{-1}).

$$\text{selectivity} : S = \frac{n_{\text{desired product}}}{\sum_{\text{all products}} n} \text{ in } 100\% \text{ conversion.}$$

$$\text{TOF} : \text{TOF}_{90} = \frac{n_{\text{product}}}{n_{\text{catalyst}} \times t} \dots \text{time for } 90\% \text{ conversion.}$$

3. Results and discussion

For the hydrogenation of sorbic alcohol, the same catalyst was used as in the previous cases, except for sorbic alcohol having been used as the second ligand instead of sorbic acid: $[\text{Cp}^*\text{Ru}(\text{sorbic alcohol})]\text{Tf}$ (Cp^* = pentamethylcyclopentadienyl; Tf = trifluoromethanesulfonate). The hydrogenation was carried out in homogeneous, heterogeneous and in two-phase arrangements (the catalyst was dissolved in a polar solvent

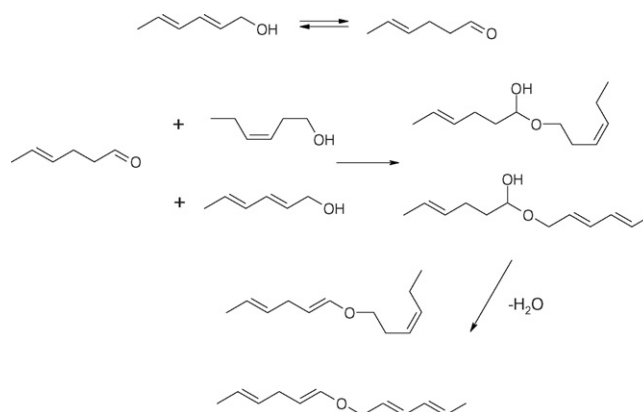


Fig. 1. Byproducts in sorbic alcohol hydrogenation.

and the products in a non-polar solvent, whereas both solvents were immiscible).

The hydrogenation of sorbic alcohol to *cis*-hex-3-en-1-ol proceeded with a relatively lower selectivity and a higher activity than the hydrogenations of sorbic acid. The selectivity was lower and the byproducts were markedly different from those in the case of sorbic acid. In this study, sorbic alcohol was isomerized to unsaturated aldehyde; moreover, some of hexenols could have isomerized to aldehydes. Therefore, the byproducts were hemiacetals produced from sorbic aldehyde and alcohols contained in the mixture (Fig. 1). These compounds were without difficulty separated from the desired alcohol by distillation and the leaf alcohol (purity 99.5%) was acquired.

Subsequently, hydrogenation conditions and changes in arrangements had been further examined in order to eliminate the isomerization of the initial sorbic alcohol to monounsaturated aldehyde as well as the consecutive formation of the undesired byproducts.

3.1. Homogeneous hydrogenation

In the first step, hydrogenations under homogeneous (the catalyst was dissolved in the same solvent as the substrate and the products) conditions were carried out. The influence of temperature, pressure and the catalyst amount on the activity and especially on the selectivity of the catalyst was studied.

Table 1

Influence of reaction conditions on selectivity and reaction rate in homogeneous arrangement (conversion of sorbic alcohol, 100%), solvent MTBE

| | Temperature (°C) | Pressure (MPa) | Catalyst amount (wt.%) | Selectivity | $\text{TOF}_{90\%}$ (h^{-1}) |
|------------------------|------------------|----------------|------------------------|-------------|---|
| Temperature (°C) | 30 | 1 | 3 | 0.16 | 112 |
| | 40 | | | 0.22 | 304 |
| | 50 | | | 0.55 | 320 |
| | 75 | | | 0.21 | 560 |
| Pressure (MPa) | 50 | 0.35 | 3 | 0.10 | 260 |
| | | 1 | | 0.54 | 300 |
| | | 2 | | 0.60 | 330 |
| | | 5 | | 0.82 | 450 |
| | | | 3 | 0.61 | 320 |
| Catalyst amount (wt.%) | 50 | 4 | 6 | 0.63 | 315 |
| | | | 10 | 0.40 | 321 |

Table 2
Separation coefficients of alcohols in sorbic alcohol hydrogenation

| Alcohol | Separation coefficient MTBE–ethylene glycol |
|--|--|
| Sorbic alcohol | 0.5 |
| Mixture <i>cis</i> -hex-3-en-1-ol and <i>trans</i> -hex-3-en-1-ol 1:1 | 0.9 |

The reaction selectivity increased (Table 1) with an increasing temperature up to 75 °C, when the selectivity started decreasing owing to the catalyst deactivation (indicated by a color change of reaction mixture). The selectivity increased also with an increasing pressure (range of 0.35–5 MPa). Using a higher temperature and pressure (50 °C and 5 MPa), it was possible to inhibit the byproducts formation and having used MTBE as the solvent and 6 wt.% of the catalyst, the hydrogenation selectivity to *cis*-hex-3-en-1-ol was raised to 82%. The apparent activation energy was calculated (46 kJ/mol). It was found that the catalyst amount had no effect on the selectivity, except when 10 wt.% and more of the catalyst to the substrate amount was used. The selectivity then apparently decreased as a result of a too high accessibility of the catalytic centre to the byproducts. The reaction rate increased in all of its parameters.

3.2. Two-phase hydrogenation

Two-phase hydrogenation was selected because of an expected possibility to recover the catalyst, which could be further reused. Ethylene glycol was utilized for the catalyst phase. The product phase was again MTBE. Using this arrangement, it was found that the reactant isomerization and the byproduct formation were distinctively inhibited.

Having found out that the catalyst permeated to the product phase, we have aspired to determine whether the substrate and the product were entirely contained only in the product phase as it was in the case of sorbic acid [7]. The separation coefficients (Table 2) were measured for such purpose in MTBE–ethylene glycol ratio, whose value throughout the reaction was 4:1 and was the same as in the case of separation coefficients measurement. Sorbic alcohol and the resulting hexenols were dissolved in this mixture and intensively stirred. Consecutively, the phases were separated and using an inner standard, the amount of alcohols was determined by GC.

Acquired separation coefficients showed that the two-phase hydrogenation was not for this case very suitable as the products were almost equally divided into both of the phases. As a result, after the phase separation, almost half of *cis*-hex-3-en-1-ol was lost to the catalyst phase and from the point of view of the catalyst stability, the alcohol could have in the same phase caused the catalyst deactivation. There was no influence of interfaces similar to e.g. the described example [12].

3.3. Hydrogenation in ethylene glycol

From the results mentioned above, we have found out that the chelation properties of ethylene glycol were optimal for

Table 3
Hydrogenation in glycols—5 MPa, 50 °C, 6 wt.% of catalyst

| Solvent | TOF _{90%} (h ⁻¹) | Selectivity |
|-------------------|---------------------------------------|-------------|
| Ethylene glycol | 80 | 0.99 |
| Glycerin | — | — |
| Diethylene glycol | 60 | 0.75 |

the hydrogenation of sorbic alcohol to the leaf alcohol *cis*-hex-3-en-1-ol. Using this solvent, the undesired isomerization to aldehydes and the formation of hemiacetals was distinctively inhibited. Nevertheless, similar boiling points of the final product and ethylene glycol brought about a negative factor for consecutive operations.

Therefore, we have tested the behavior of other glycols in the same hydrogenation arrangement (Table 3). For this purpose, two solvents: diethylene glycol and glycerine were used. In ethylene glycol, the reaction rate was lower than in other solvents (MTBE) used for the homogeneous hydrogenation probably due to their different viscosity. In diethylene glycol, the reaction rate was comparable to ethylene glycol. However, the selectivity decreased and hemiacetals were formed probably owing to the higher glycols having lost the specific properties of ethylene glycol. Glycerine viscosity was so high that the reaction mixture had been barely stirred and the reaction did not take place.

The separation of ethylene glycol and the product was enabled by an addition of water as hexenol is not soluble in water and forms another phase. Fig. 2 shows the minimal water amount for the separation of *cis*-hex-3-en-1-ol from the mixture of ethylene glycol–water.

Owing to the catalyst sensitivity, the amount of the alcohol contained in the mixture was regrettably very low and after the addition of water, only emulsion occurred.

On the other hand, the separation of the leaf alcohol from ethylene glycol by use of hexane turned out to be a successful procedure. Water and hexane were added to the reaction mixture

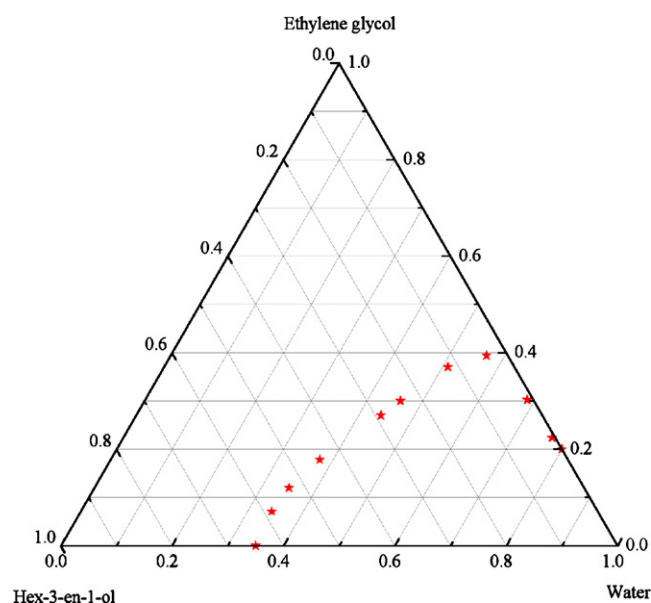


Fig. 2. Dissolution of hex-3-en-1-ol in mixture water–ethylene glycol.

Table 4
Influence of reaction conditions on selectivity and reaction rate in two-phase arrangement (sorbic alcohol conversion, 100%), solvents MTBE and ethylene glycol (1:4)

| | Temperature (°C) | Pressure (MPa) | Catalyst amount (wt.%) | Selectivity | TOF _{90%} (h ⁻¹) |
|------------------------|------------------|----------------|------------------------|-------------|---------------------------------------|
| Temperature (°C) | 20 | 2 | 6 | 0.75 | 110 |
| | 30 | | | 0.93 | 250 |
| | 50 | | | 0.96 | 300 |
| | 75 | | | 0.9 | 450 |
| Pressure (MPa) | 50 | 1 | 6 | 0.97 | 240 |
| | | 2 | | 0.96 | 300 |
| | | 4 | | 0.96 | 350 |
| Catalyst amount (wt.%) | 50 | 2 | 2 | 0.93 | 290 |
| | | | 4 | 0.95 | 300 |
| | | | 6 | 0.96 | 298 |
| Recycling (all steps) | 50 | 2 | 6 | 0.98 | 300 |
| | | | | 0.97 | 250 |
| | | | | 0.94 | 200 |

and two phases separated. Ninety-nine percent of alcohol was detected in the hexane phase.

In the next step, we have made efforts to recycle the glycol phase. This was realized by an addition of hexane to the reaction mixture (no water addition). When hexane was used for the treatment of the catalyst phase, the reaction rate was very low. It was apparently owing to the very high amount of the catalyst in the separated hexane phase. In hexane, the leaf alcohol has increased its polarity and the catalyst was separated from glycol as well. An addition of water would have produced a solution; however, it would have also deactivated the catalyst.

The optimal way to accomplish the hydrogenation of sorbic alcohol to *cis*-hex-3-en-1-ol (5 MPa, 50 °C, 6 wt.% of catalyst), with an inclusion of an effective recycling of the catalyst phase, was to carry out the hydrogenation in ethylene glycol with a little addition of MTBE or hexane (to increase the reaction rate) and then proceed, at first, with the separation of hexane phase to glycol resulting in all of the catalyst permeating to the glycol phase and almost all of the product remaining in the hexane phase. In the second step, proceeding with the separation of the glycol phase to hexane (pure) was useful in order to release

the remaining portion of the product from glycol. Using this approach, the separation of hexenol from the glycol phase was about 95%.

Changes in the reaction conditions did not exhibit any alteration of the selectivity (Table 4). Only at temperature above 65 °C, the selectivity decreased due to the catalyst decomposition. When lower temperature (20–30 °C) was used, the selectivity decreased to the same extent as in the case of homogeneous hydrogenation. Using the pressure of 5 MPa, the temperature of 50 °C and 6 wt.% of the catalyst related to the substrate amount, the selectivity of hydrogenation raised up to 98%. Reuse of the catalyst phase was possible using the approach mentioned above.

3.4. Heterogeneous hydrogenation

To complete the intended types of hydrogenation arrangements, heterogeneous hydrogenation was carried out. The immobilization was realized the same way as it was in the case of sorbic acid, i.e. by means of hydrogen bonds [8]. The objective was to find out whether the support (silica, silica gel or MCM-

Table 5
Influence of reaction conditions on selectivity and reaction rate in heterogeneous arrangement (sorbic alcohol conversion, 100%), solvent MTBE

| | Temperature (°C) | Pressure (MPa) | Catalyst amount (wt.%) | Selectivity | TOF _{90%} (h ⁻¹) |
|------------------------|------------------|----------------|------------------------|-------------|---------------------------------------|
| Temperature (°C) | 30 | 1 | 6 | 0.1 | 84 |
| | 40 | | | 0.5 | 220 |
| | 50 | | | 0.8 | 250 |
| | 70 | | | 0.3 | 400 |
| Pressure (MPa) | 50 | 0.35 | 6 | 0.6 | 147 |
| | | 1 | | 0.6 | 201 |
| | | 2 | | 0.7 | 254 |
| | | 5 | | 0.8 | 300 |
| Catalyst amount (wt.%) | 50 | 1 | 3 | 0.3 | 0.01 |
| | | | 6 | 0.7 | 100 |
| | | | 10 | 0.8 | 250 |
| Recycling (all steps) | 50 | 5 | 6 | 0.77 | 250 |
| | | | | 0.7 | 200 |
| | | | | 0.46 | 160 |

41) would be able to eliminate the production of byproducts as it was in the case of ethylene glycol. Using the immobilized catalyst, the selectivity was almost comparable to the selectivity in a homogeneous arrangement. The noteworthy difference in the heterogeneous arrangement was though the fact that the formation of hemiacetals was inhibited, however the synergic effect of the catalyst and the support caused *cis*-hex-3-en-1-ol to isomerize to *trans*-hex-3-en-1-ol (Table 5). This isomerization was very undesirable as the separation of *cis*- and *trans*-isomers was rather complicated.

3.5. Comparison of reaction systems

Three reaction systems were used for sorbic alcohol hydrogenation—homogeneous, “two-phase” and heterogeneous using the same reaction conditions. In the homogeneous arrangement, the reaction rate of hydrogenation was the highest—Ru catalyst was dissolved in the same phase as the reactant and the only limiting parameter was the transfer of hydrogen. The selectivity to the leaf alcohol was the lowest. In “two phase” arrangement with ethylene glycol as the solvent and with addition of MTBE, the catalyst was dissolved in the glycol phase and the reactant in both phases, the reaction rate was lower due to the transfer of hydrogen through MTBE phase to the catalyst phase (using only ethylene glycol was insufficient due to the high viscosity). The selectivity was the highest from all the applied systems due to the glycol properties. In the heterogeneous arrangement, the reaction rate was the lowest from all compared systems and the selectivity was higher than in the homogeneous arrangement, but significantly lower than in hydrogenation in ethylene glycol.

4. Conclusions

The hydrogenation of sorbic alcohol to *cis*-hex-3-en-1-ol was found feasible in the same arrangements as the hydrogenation

of sorbic acid to *cis*-hex-3-enoic acid. The optimal conditions for the highest selectivity (up to 98%) and the reaction rate were achieved in hydrogenation in ethylene glycol with the addition of MTBE or hexane to increase the reaction rate. Furthermore, it was demonstrated that ethylene glycol and the catalyst could be reused under the same conditions (50 °C, 5 MPa). Under heterogeneous conditions, a synergic effect of the catalyst and the support caused *cis*-hex-3-en-1-ol to isomerize to *trans*-isomer.

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