

An Ionic Liquid as Catalyst Medium for Stereoselective Hydrogenations of Sorbic Acid with Ruthenium Complexes

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Dedicated to Professor Dr. Othmar Stelzer on the Occasion of his 60th Birthday

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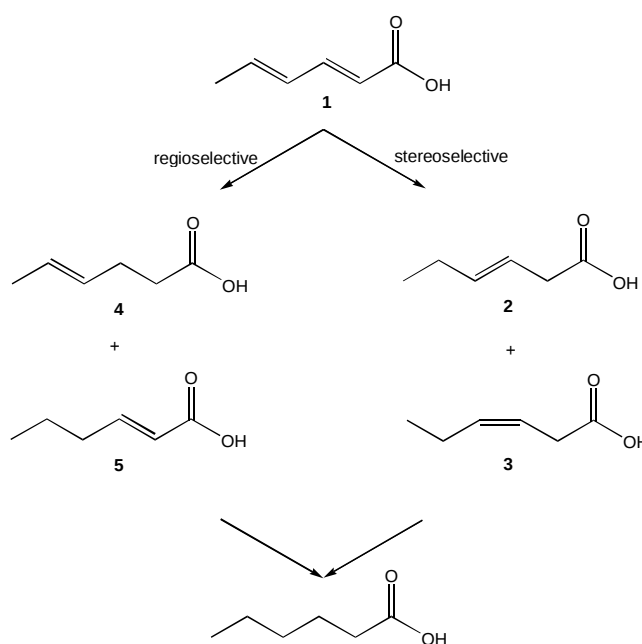
Abstract. The ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (bmim PF₆) (**6**) has been studied as catalyst medium for biphasic homogeneous hydrogenations of sorbic acid (**1**). As catalyst we used the Cp*-ruthenium-complex [Cp*Ru(η^4 -CH₃-CH=CH-CH=CH-COOH)(CF₃SO₃)] which efficiently enables the stereoselective hydrogenation of sorbic acid leading to the formation of *cis*-3-hexenoic acid

(**3**) in selectivities of up to 90% with turnover frequencies of up to 1100 h⁻¹. Compared to other biphasic systems the hydrogenation in bmim PF₆ proceeds with enhanced activity. The kinetics can be described with a Michaelis–Menten-equation, and the activation energy for the whole process was determined to be $E_A = 78 \pm 5$ kJ/mol.

Transition metal complex catalyzed reactions in two immiscible liquid phases can be industrially important alternatives to homogeneously catalyzed one-phase-reactions. The synthesis of butyric aldehyde by the Ruhrchemie/Rhône-Poulenc-process [1] serves as one example as well as the production of α -olefins in the SHOP-Process [2]. After the catalytic reaction one phase solves the products and the other phase contains the catalyst. After simply separating the two phases, the catalyst phase can be recycled without any further treatment. Another innovative effect of two-phase catalysis is the possibility to extract primary products during the catalytic reaction into the organic phase. This often results in novel possibilities of controlling the product selectivity [3]. A very suitable solvent for the catalyst phase is water, since it is very cheap and immiscible with many organic solvents, which may serve as solvents for the products [4]. However, ionic liquids (room temperature molten salts) have also proved to be particularly useful for two-phase catalytic reactions [5]. In most cases the transition metal complexes are soluble in ionic liquids whereas organic compounds are often immiscible.

We are interested in selective transformations of multifunctional substrates using two-phase-catalysis. The hydrogenation of the industrially available sorbic acid **1** can lead to many different products, some of them being shown in scheme 1.

Generally, hexenoic acids like **2**–**5**, bearing one C=C-bond, are interesting starting materials for the production of fine chemicals. We could show that it is possible to hydrogenate **1** stereoselectively by means of homogeneous ruthenium catalysis [6]. Esters of sorbic acid and sorbic alcohol were hydrogenated using catalytic

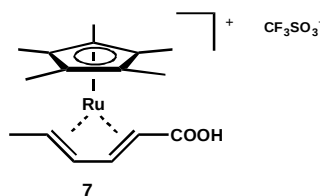


Scheme 1 Possible products in the hydrogenation of sorbic acid **1**

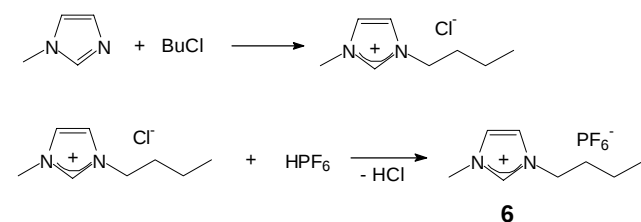
one-phase-techniques [7]. Among others chromium catalysts were used for this reaction [7f, 7g]. The aim of our study was to find out if the hydrogenation of **1** can selectively produce *cis*-3-hexenoic acid **3**. In this paper we present stereoselective hydrogenations of sorbic acid **1** using 1-*n*-butyl-3-methylimidazolium hexafluorophosphate salt (bmim PF₆) **6**/MTBE as biphasic reaction system and a ruthenium catalyst, which was immobilized in the ionic liquid phase.

Results and Discussion

We used complex **7** as catalyst for the hydrogenation of sorbic acid **1**. It is a naked Cp*Ruthenium complex with sorbic acid bonded cisoid to the ruthenium centre. The catalyst was specially synthesized for this reaction [8].



The substrate was dissolved in MTBE and bmim PF₆ contained the catalyst **7**. By variation of the anion of the ionic liquid, the coordination properties can be tuned. Previous hydrogenation results obtained with **7** using other solvents prompted us to use **6** with a non-coordinating hexafluorophosphate anion. In analogy to a procedure published by Fuller *et al.* [9], **6** can be synthesized easily in kilogram amounts according to scheme 2.



Scheme 2 Synthesis of bmim PF₆ **6**

In our special case, butyl chloride was used in excess (1.5 equivalents) to transform methyl imidazole quantitatively. The second step was done in an aqueous solution at 0 °C and bmim PF₆ **6** separates as a second liquid layer from this solution. The ionic liquid layer was washed several times with water. Finally, the content of chloride ions was checked with a silver nitrate solution. We also synthesized bmim Tf after a similar procedure to check the coordination properties of the

anion in ionic liquids and to compare its influence on the catalyst activity.

During hydrogenation, the two phases were mixed thoroughly in the presence of hydrogen. First results are shown in Table 1 and 2.

Compared to the hydrogenation in ethylene glycol the hydrogenation activities in bmim PF₆ are higher at temperatures above 40 °C. The TOF increases from 89 h⁻¹ (glycol) to 212 h⁻¹ (bmim PF₆) at 40 °C and from 300 h⁻¹ (glycol) to over 1000 h⁻¹ (bmim PF₆) at 60 °C. The TOF in both solvents is comparable at room temperature. We assume that the high viscosity of the ionic liquid at room temperature leads to mass transport problems and to the relatively low activity at this temperature. The selectivities to *cis*-3-hexenoic acid **3** are lower in ionic liquids (70%, table 1, no. 5) than those in ethylene glycol (90%) under identical conditions. By reducing the hydrogen pressure to 10 bar H₂ the selectivities increase to 90% (Table 2, No. 8). Remarkably, no *trans*-2-hexenoic acid is formed as side product in the ionic catalyst solution.

Bmim Tf was also used as catalyst medium for the hydrogenation of sorbic acid with **7**, and no reaction occurred. The excess of triflate ions may block the coordination sites at the ruthenium centre and inhibit the hydrogenation.

Since the catalyst **7** reached the best activities in the biphasic system ionic liquid **6**/MTBE, we tested the catalyst recycling in this system. In order to have a less polar extraction phase and to circumvent leaching dibutyl ether was added to the MTBE phase. The recycling experiments were run at room temperature because the time between two hydrogenations has to be minimized. Table 3 shows the results.

The activities are nearly the same for the first and the second run (No. 9A and 9B). After the second run the autoclave containing the catalyst phase had to stand overnight. Nevertheless, the decrease in activity is not very significant (run 9B and 9C, TOF: 43,0 → 33,8 h⁻¹). In this context, it is noteworthy that the catalyst slowly decomposes when standing in a hydrogen atmosphere without substrate.

We investigated the kinetics of this reaction in order to optimize and understand the hydrogenation and the rate of product formation. We looked for a mathematic

Table 1 Hydrogenation of sorbic acid **1** with catalyst **7** in bmim PF₆ **6**/MTBE at 60 bar H₂

No.	<i>T</i> (°C)	<i>n</i> _{catalyst} (mmol)	<i>t</i> (h)	Conversion (%)	TOF (h ⁻¹)	<i>S</i> (<i>cis</i> -3) 3 (%)	<i>S</i> (<i>trans</i> -3) 2 (%)
1	21	0.0565	3.0	31.6	40.5	74	25
2	40	0.0545	2.0	99.7	191	61	37
3	40	0.0561	1.30	70.0	212	69	30
4	60	0.0583	0.34	99.7	1126	38	55
5	60	0.0283	0.58	39.9	539	71	27

Conditions: 25 mL bmim PF₆, 44 mL MTBE, 21–22 mmol sorbic acid.

Table 2 Hydrogenation of sorbic acid **1** with catalyst **7** in bmim PF₆/MTBE at 10 bar H₂

No.	<i>T</i> (°C)	<i>n</i> _{catalyst} (mmol)	<i>t</i> (h)	Conversion (%)	TOF (h ⁻¹)	<i>S</i> (<i>cis</i> -3) 3 (%)	<i>S</i> (<i>trans</i> -3) 2 (%)
6	21	0.0263	15.3	70.5	37.7	92	8
7	40	0.0561	1.42	52.3	141	93	7
8	60	0.0553	0.42	44.8	416	90	10

Conditions: 25 mL bmim PF₆, 44 mL MTBE, 21–22 mmol sorbic acid.

Table 3 Catalyst recycling with **7** in bmim PF₆/(MTBE/Bu₂O)

No.	<i>t</i> (h)	Conversion (%)	TOF (h ⁻¹)	<i>S</i> <i>cis</i> -3-hexenoic acid 3 (%)	<i>S</i> 3-hexenoic acid (%)
9A	3.78	74.0	44.5	66	98
9B	3.83	77.4	43.0	53	97
9C	3.73	59.6	33.8	59	90
9D	3.75	35.8	20.2	67	97

Conditions: 25 mL bmim PF₆; 23 mL MTBE/23 mL Bu₂O; 0.0583 mmol **7**; 12.4 mmol sorbic acid; 19 °C; 50 bar H₂; after run 9B the catalyst phase has to stand overnight in the autoclave.

equation that allows a description of the sorbic acid consumption versus time and the determination of the reaction rates. From these data the activation energy for the whole process can be calculated.

The kinetic data might contain small deviations from ideal state since we had to meet some experimental needs:

- The regulation of temperature may vary in the range of ± 0.5 °C.
- The GC analysis may contain faults between ± 1 –2%.
- The reaction may be probably blocked during the time needed to take the sample.

Figure 1 shows a typical concentration profile of the hydrogenation of sorbic acid.

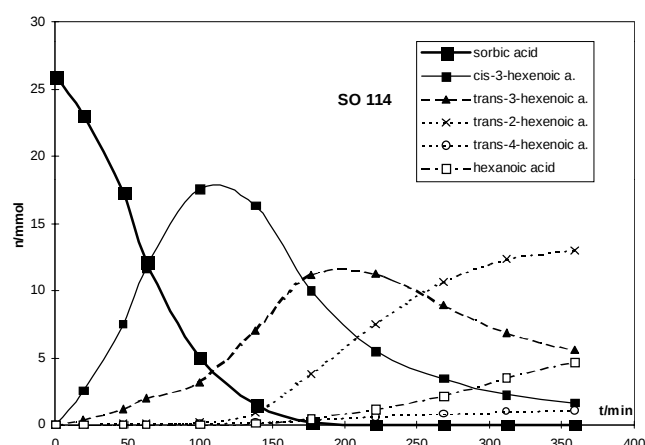
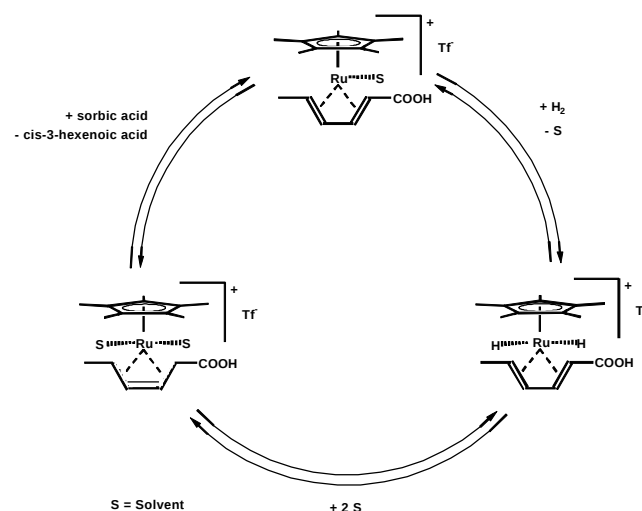


Fig. 1 Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL MTBE, 30 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂, 34 °C, 0.0824 mmol cat.

The profile of the sorbic acid concentration in the beginning of the reaction indicates the existence of a small activation period since the reaction rate is increas-

ing in the first forty minutes. Probably, it took some time to saturate the catalyst phase (bmim PF₆) with hydrogen. In liquid/liquid biphasic systems the phase with the smaller volume is normally dispersed in the phase with the higher volume so that in our case the ionic liquid phase may be the dispersed one. Hydrogen molecules have to pass two phase boundaries from the gas phase to the continuous organic phase and from there to the ionic liquid phase in order to reach the catalyst. After the activation period the decrease of sorbic acid concentration is linear up to a reaction time of 100 minutes. Then, a significant decrease of the reaction rate is observed indicating that the rate determining step of the reaction is changing. This behaviour is in good agreement with our postulated mechanism for this reaction (Scheme 3).



Scheme 3 Postulated mechanism for the hydrogenation of sorbic acid **1** with **7**

The hydrogen addition to the catalyst-substrate-complex is rate determining in the beginning. Consequently, the reaction rate is nearly independent from the sorbic acid concentration. At constant hydrogen pressure a linear decrease of sorbic acid concentration is resulting. At the end of the reaction (from 80% conversion) the formation of the sorbic-acid/catalyst-complex becomes rate determining. At high sorbic acid conversion, the reaction rate is found to be a function of the sorbic acid concentration.

The concentration of *cis*-3-hexenoic acid reaches a maximum at a conversion of 85%. From this point, the consecutive isomerization of the product to *trans*-3-hexenoic acid becomes a major side reaction. The maximum of the concentration of *trans*-3-hexenoic acid is reached when all sorbic acid is consumed. The generation of *trans*-2-hexenoic acid – which should be the most stable compound of all hexenoic acids thermodynamically (possible mesomeric with the acid function) – starts in the region of very low sorbic acid concentrations. At the same time hydrogenation of the second C=C double bond takes place. The amount of *trans*-4-hexenoic acid rests very low. Figure 2 shows the product selectivities versus reaction time and Figure 3 clarifies the dependence of product selectivities from the conversion grade. The selectivities keep constant up to conversions of 80%. Again, at higher conversion the isomerization reaction takes place.

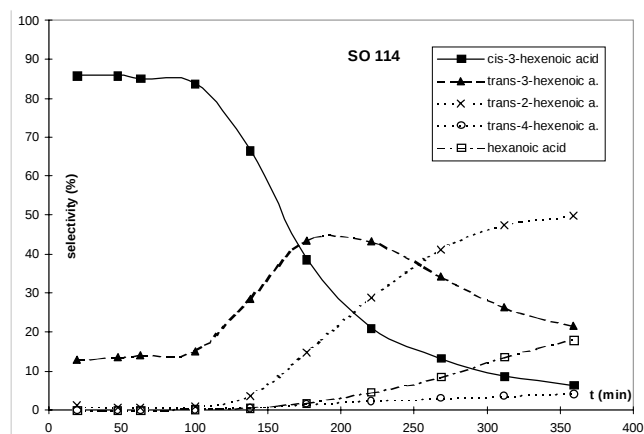


Fig. 2 Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL MTBE, 30 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂, 34 °C, 0.0824 mmol cat.; Dependence of product selectivities from reaction time

The concentration/time-diagrams obtained were evaluated with a rate law based on the Michaelis-Menten-equation. A mathematics description was only possible for the sorbic acid consumption but not for the product generation because the concentration of *cis*-3-hexenoic acid is influenced by several consecutive reactions. The kinetic data obtained experimentally were evaluated by integration. We looked for a function that is capable to describe the measured concentration-time-profile.

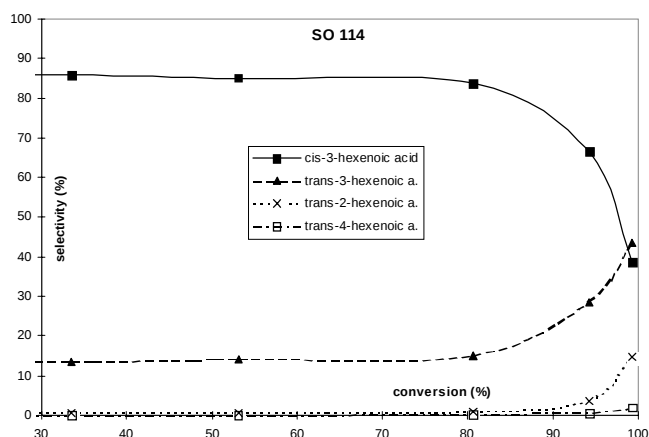


Fig. 3 Product selectivities in dependence of conversion; Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL MTBE, 30 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂, 34 °C, 0.0824 mmol cat.

The amounts of compounds in the organic phase analyzed by GC were calibrated so that the sum of these amounts was identical with the weight of sorbic acid introduced in the reaction. Therefore the following equation was used (eq. 1).

$$n_{\text{calib.}} = \frac{n_{\text{sorb.-weight}}}{\sum n_{\text{GC}}} \cdot n_{\text{i,GC}} \quad (\text{eq. 1})$$

$n_{\text{calib.}}$ = calibrated amount

$n_{\text{sorb.-weight}}$ = initial weight of sorbic acid

$\sum n_{\text{GC}}$ = sum of all amounts, all compounds detected by GC

From these amounts obtained experimentally we calculated the corresponding concentrations [mol/l]. The catalyst concentration, the concentrations of sorbic acid and the concentrations of the products refer to the total volume of ionic liquid and the second phase (0.134 l). For determination the integrated form of the rate law was used (eq. 4). This is possible because the hydrogen concentration was kept constant ($[\text{H}_2] = [\text{A}_2]_0 = \text{const.}$) during the reaction. The rate laws and equations are given in eq. 2 and eq. 3.

Michaelis-Menten rate law (eq. 2):

$$-d[\text{sorb}]/dt = \frac{k_2[\text{C}]_0[\text{Sorb}][\text{H}_2]}{K_m + [\text{Sorb}]} \quad (\text{eq. 2})$$

$$\text{Michaelis function: } K_m = \frac{(k_{-} + k_2[\text{H}_2])}{k_{+}} \quad (\text{eq. 3})$$

Integrated rate law:

$$K_m \ln ([\text{Sorb}]/[\text{Sorb}]_0) + ([\text{Sorb}]/[\text{Sorb}]_0) = -k_2[\text{C}]_0[\text{H}_2]_0 t \quad (\text{eq. 4})$$

Equation 4 cannot be reduced to the concentration of sorbic acid [Sorb] but to the reaction time t . Thus equation 5 can be set up which allows for the calculations of

the values of reaction time for given concentrations. This profile is in good agreement with the experimental values (Figures 4–7).

$$t = -\frac{K_m \ln([Sorb]/[Sorb]_0)}{k_2[C]_0[H_2]_0} - \frac{[Sorb] - [Sorb]_0}{k_2[C]_0[H_2]_0} \quad (\text{eq. 5})$$

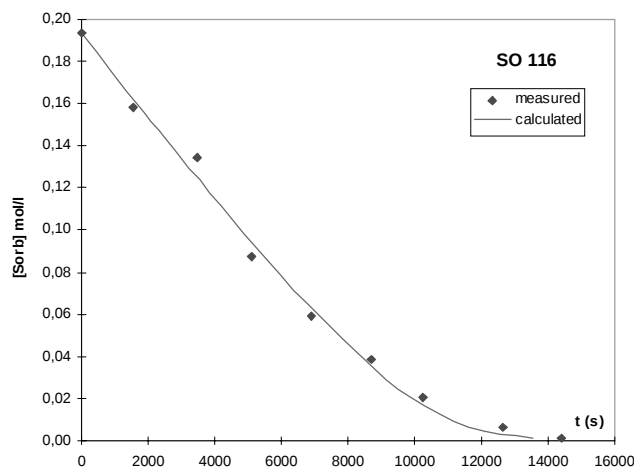


Fig. 4 Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂; concentration-time-diagram; [cat] = 4.83×10^{-4} mol/l; $T = 34^\circ\text{C}$; $k_2 [H_2]_0 = 0.0462$ 1/s; $K_m = 0.021$ mol/l

To confirm this behaviour we carried out further experiments with different catalyst concentrations and at different temperatures. The rate constant k_2 and the Michaelis function K_m were adapted for different reaction temperatures so that the calculated concentration-time-profiles (eq. 5) were in good agreement with the experimental values. The concentration/time-curves at lower temperatures had in general a smaller curvature than those at higher temperatures. The smaller K_m is, the course of the curve is brought more into line with a

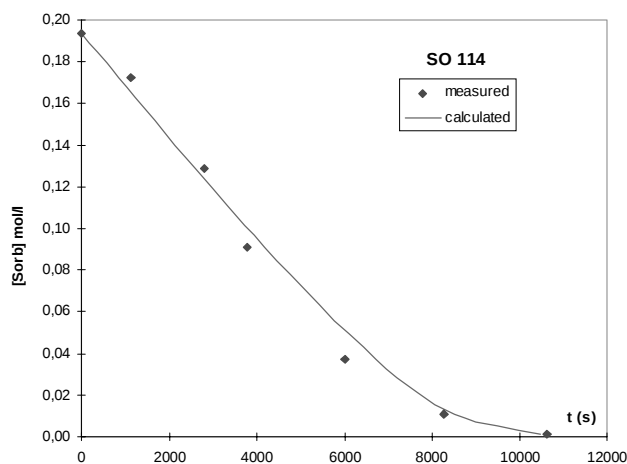


Fig. 5 Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL MTBE, 30 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂, experiment SO 114; [cat] = 6.15×10^{-4} mol/l; $T = 34^\circ\text{C}$; $k_2 [H_2]_0 = 0.0462$ 1/s; $K_m = 0.021$ mol/l

course describing a zero order reaction regarding sorbic acid. Therefore, the increase of curvature was taken into account with lightly increasing K_m values (from 0.01 to 0.03 mol/l). The used values of k_2 and K_m are mentioned in the footnotes of the diagrams.

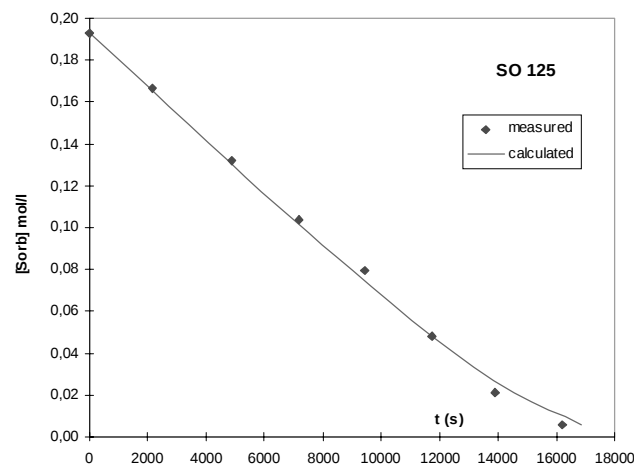


Fig. 6 Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL MTBE, 30 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂, experiment SO 125; [cat] = 4.90×10^{-4} mol/l; $T = 30^\circ\text{C}$; $k_2 [H_2]_0 = 0.0285$ 1/s; $K_m = 0.014$ mol/l

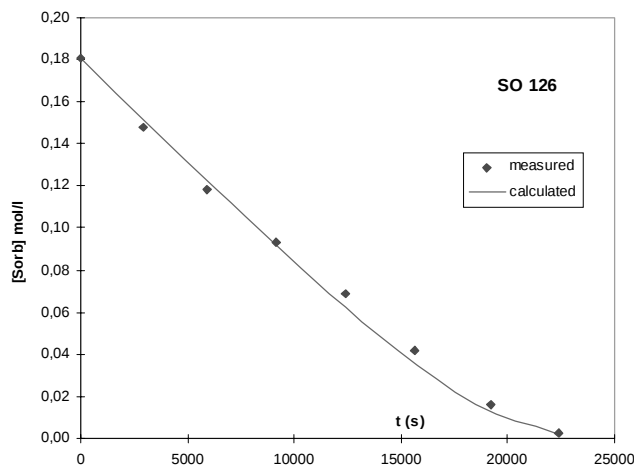


Fig. 7 Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL MTBE, 30 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂, experiment SO 126; [cat] = 3.77×10^{-4} mol/l; $T = 30^\circ\text{C}$; $k_2 [H_2]_0 = 0.0285$ 1/s; $K_m = 0.014$ mol/l

With catalyst concentrations smaller than 3×10^{-4} mol/l, the catalytic activities decrease drastically. In summary the rate law with the constants K_m and $k_2[H_2]_0$ determined is only valid for catalyst concentrations between 3.7×10^{-4} and 6.15×10^{-4} mol/l.

We checked if the determined values of $k_2[H_2]_0$ (Figures 4–7) show a temperature dependence following the arrhenius law. The temperature dependence of a rate constant k is defined in the arrhenius law (equation 6).

$$k = A \cdot e^{-E_a/RT} \quad \text{oder} \quad \ln k = \ln A - \frac{E_a}{RT} \quad (\text{eq. 6})$$

We assume that the hydrogen concentration is constant between 28 and 40 °C and the hydrogen concentration $[H_2]_0$ does not need to be known to calculate the activation energy E_a . But the preexponential factor A cannot be determined without knowing the value of $[H_2]_0$.

We determined the activation energy in the arrhenius diagram where the y axis is $\ln(k_2[H_2]_0)$ and the x axis is $1/T$ (Figure 8). The slope of this straight line is equal to $-E_a/R$, and the activation energy determined from this is 78 ± 5 kJ/mol in this case.

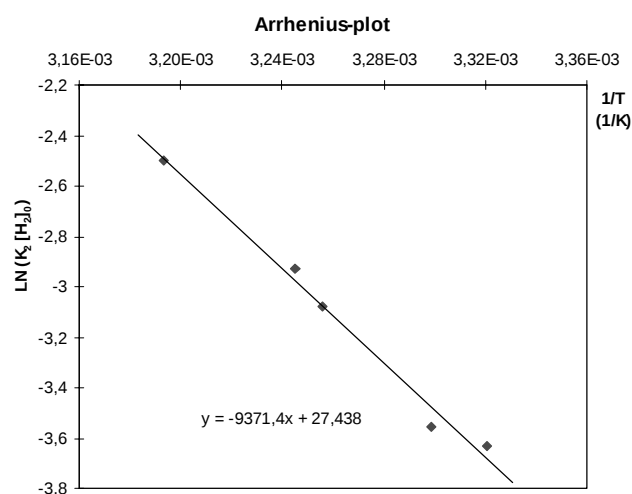


Fig. 8 Hydrogenation of sorbic acid, 44 mL bmim PF₆, 60 mL MTBE, 30 mL dibutyl ether, 25 mmol sorbic acid, 16 bar H₂; Temperature dependence of $k_2 [H_2]_0$

To the best of our knowledge the only activation energy determined for hydrogenations in ionic liquids was measured for the hydrogenation of an acrylnitrile–butadiene polymer with $[RuHCl(CO)(PCy_3)_2]$ as catalyst in bmim BF₄ [10]. The rate constants were determined between 100 and 160 °C and the activation energy for the total process was 47 ± 3 kJ/mol. This is a quite lower activation energy compared to the activation energy of 78 kJ/mol that the same catalyst has in homogeneous hydrogenations in other solvents [11]. Our value of the activation energy for the whole process is in the same range compared to literature.

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Experimental

All procedures were carried out under an atmosphere of dry argon using standard Schlenk techniques. The argon was deoxygenated by BASF catalyst R-3-11 and dried using mole-

cular sieve Linde 4 A. Solvents were freshly distilled under argon atmosphere and dried by standard procedures. Air and moisture sensitive solutions and reagents were handled using syringe techniques. The catalyst **7** was synthesized as described in [8]. Hydrogenation experiments under pressure were carried out in 100 ml stainless steel autoclaves equipped with special stirrers for two-phase-catalysis. Sorbic acid was purchased from Aldrich. The hydrogen used had a purity of 99.9%.

Hydrogenation Reactions

In a typical experiment, the catalyst phase consists of 44 ml bmim PF₆ and the organic phase contains 60 ml MTBE and 30 ml Dibutylether. The GC standard and sorbic acid are dissolved in the organic phase. We determined the distribution of all compounds between the two phases and found that about 90% of the sorbic acid, the products and the GC standard are solved in the organic phase. All reactions were performed in a specially designed autoclave with a high-pressure sampling valve. The system was stirred with a 6-blade-stirrer kept at constant rpm for all experiments. We stopped the stirrer for ten seconds before taking the sample so that the two phases could separate. All reactions were run at 16 bar hydrogen pressure and at different temperatures. The temperature control was realized with a thermal element which was in contact with the reaction mixture. The autoclave was stirred and heated up to reaction temperature before the hydrogen was added. Right after the hydrogen addition, the stirrer is started and the reaction time is counted. The hydrogen pressure was kept constant. Each sample was cooled in an ice bath and the two phases were separated. The MTBE phase containing the products was analyzed by GC [CP-Wax-58-(FFAP)-CB (50 m)].

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