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Biphasic homogeneous hydrogenation of sorbic acid with water soluble ruthenium catalysts – aspects of mass transfer

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Abstract

We synthesized a new water soluble ruthenium complex which contains the hydrophilic ligand tris(3-hydroxypropyl)phosphane. This compound catalyzes the regioselective biphasic hydrogenation of sorbic acid to yield 4-hexenoic acid with 82% selectivity and with turnover frequencies of up to 200 h^{-1}. Some thermodynamic and kinetic aspects of this biphasic reaction in water/ethyl acetate were studied. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Biphasic hydrogenation; Ruthenium; Tris(3-hydroxypropyl)phosphane; Kinetic aspects

1. Introduction

Catalysis in liquid/liquid biphasic systems is of great interest because it provides an attractive solution to the problem of separation of products from expensive transition metal catalysts. The two-phase system consists of two immiscible solvents, e.g. an aqueous phase containing the catalyst and an organic phase containing the products. The general setup for a two-phase reactor with separator is shown in Fig. 1.

The two phases which contain the catalyst, the reactants and the products are mixed thoroughly with an appropriate stirrer. As a result, the two phases form little bubbles, and the resulting surface, which is very high, is needed to allow for the diffusion of compounds from one phase to the other. After the reaction, the mixture is transferred to a separator. The catalyst phase is separated and can be used again immediately without any further treatment. This is one of the major advantages of the two-phase technique over one-phase reactions. The product phase is worked up using conventional techniques such as distillation.

For industrial syntheses of fine chemicals such as pharmaceuticals, vitamins and fragrances, unsaturated compounds especially unsaturated acids are interesting starting materials. They can be obtained by the hydrogenation of α,β-unsaturated compounds such as sorbic acid **1**. However, only selective hydrogenations are useful, and many studies on heterogeneously and homogeneously catalyzed hydrogenations of **1** have been carried out. The reaction can result in the formation of the three main products: 4-hexenoic acid **2**, 2-hexenoic acid **3** and hexanoic acid **4** (Eq. (1)), but only **2** and **3** are desired.9

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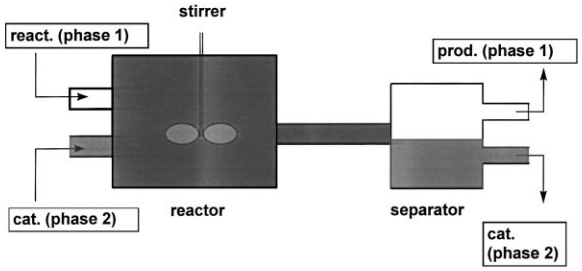
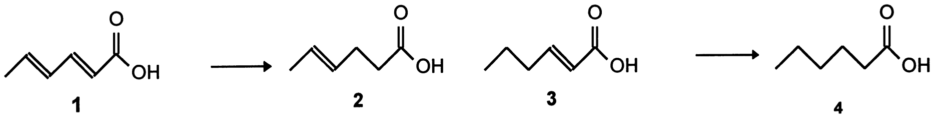


Fig. 1. Schematic illustration of a two-phase reactor and separator.



(1)

In addition it is necessary to obtain **2** or **3** selectively. Employing hetereogeneous Pd-, Pt-, Rh- and Ru-catalysts led always to the formation of **3** as the main product [1–3]. In homogeneously catalyzed hydrogenations of **1** different product distributions were obtained: Kameda and Igarashi [4] reported the formation of **3** and **4** using a Rh-complex whereas Alper and Lee [5] obtained **3** in 75% selectivity, when $[HCo(CN)_5]^{3-}$ was the catalyst. Cole-Hamilton [6] used $[RhCl(PPh_3)_3]$ as catalyst and found **4** to be the only product.

The formation of undesired hexanoic acid **4** might be the result of two subsequent hydrogenations. If the reaction is carried out in a biphasic system with the catalyst being present only in one phase, it might be possible to transfer the product of the first hydrogenation to the second phase and thus prevent it from being hydrogenated twice. We have used this method to avoid consecutive reactions successfully in telomerizations [7], and we believe that this method adds a further advantage to the two-phase technique: if the extraction step is fast enough, one might be able to react bi- or multifunctional reactants selectively without having to introduce protecting groups or even choose a completely different reaction sequence. Here we report our results on the biphasic hydrogenation of **1** with a water soluble ruthenium catalyst, which we synthesized for the first time.

2. Results

2.1. Catalyst preparation and characterization

We studied the synthesis of the new water soluble ruthenium complex **5**, which contains the hydrophilic ligand tris(3-hydroxypropyl)phosphane $[P(CH_2CH_2\text{-}CH_2OH)_3]$ [8]. Most of the water soluble transition metal complexes studied so far contain sulfonated phosphane ligands, but less studies have been carried out using other hydrophilic ligands. Therefore we concentrated on the mentioned hydroxyalkylphosphane. It was possible to synthesize **5** using two different routes (Eqs. (2) and (3)).

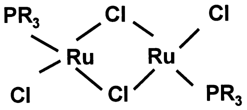
$$2\ RuCl_3\ aq. + 4\ P[(CH_2)_3OH]_3 \rightarrow \underset{\mathbf{5}}{[RuCl_2[P[(CH_2)_3OH]_3]_2} + 2\ OP[(CH_2)_3OH]_3 + 2\ HCl \qquad (2)$$

$$2\ RuCl_2(PPh_3)_3 \ + \ 2\ P[(CH_2)_3OH]_3 \ \rightarrow \ \underset{\mathbf{5}}{[RuCl_2[P[(CH_2)_3OH]_3]_2} \ + \ 6\ PPh_3 \qquad (3)$$

The redox reaction (Eq. (2)) starting from Ru(III)chloride was done in water. Whereas the substitution reaction (Eq. (3)) was done in a biphasic system toluene/water.

^{31}P-NMR-spectra of the reaction mixture obtained via Eq. (2) showed three signals at δ=60, 41 and -30 ppm, which were assigned to the phosphane oxide, **5** and free phosphane, respectively. Further characterization was done using ^{1}H- and ^{13}C-NMR-spectroscopy as well as IR-spectroscopy [^{1}H-NMR: δ=3.45 (*s*, 6 H, CH_2OH), 1.74–1.62 (*m*, 12 H PCH_2CH_2)]. Elemental analysis for $Ru_2Cl_4P_2$-$C_{18}O_6H_{42}$ [%]: Calc. C 28.73, H 5.22; found C 28.44, H 5.52. The peak of the molecular ion in SIMS-spectra (*m*/*z*=764.2) confirmed **5** to be a dinuclear complex. The following structure may be possible, which is in agreement with the analytical data obtained so far.

Possible structure of complex **5**



2.2. *Catalysis*

The hydrogenations were carried out in a biphasic system containing **5** dissolved in an aqueous buffer solution (pH=7), ethyl acetate as the second phase and sorbid acid. Hydrogen was added to the autoclave (50 bar) and then the reaction was started by stirring. Table 1 summarizes the results.

The results clearly show that **5** catalyzes the reaction with good activities and good selectivities to 4-hexenoic acid **2**. In fact this is the highest regioselectivity observed so far. Interestingly the in situ system (no. 2) does neither lead to the high conversion observed with **5** (no. 1) nor does it show a selectivity as good as the one obtained with **5**. The addition of the phosphane oxide (no. 3), which is formed during the syntheses of **5** leads to a somewhat higher conversion. If the phosphane itself is present (no. 4), the conversion decreases drastically. If the catalyst phase is recycled (no. 5 and 6), the selectivity for **2** and the conversion increase slightly. The formation of the 2-hexenoic acid **3** was not observed.

Subsequent experiments with the isolated complex **5** (no. 1) showed that the variation of the temperature also has a major influence on the conversion and a somewhat less pronounced effect on the selectivities. At 60°C only 5% conversion were observed (TOF=9) and the selectivities for **2** and **4** were 87.5 and 12.5, respectively. At 100°C the conversion was 99% (TOF=298) but the selectivity for **2** dropped to 66% and increased for **4** to 34%.

2.3. *Aspects of mass transfer and kinetics*

We studied thermodynamic data, fluid dynamics and kinetic parameters of this reaction in order to gain more information about the kinetics and the mechanism of the reaction.

We determined the concentrations and the behavior of the solubilities of compounds present in this system and set up the corresponding distribution curves. From these examinations, it follows that at reaction conditions sorbic acid **1**, 4-hexenoic acid **2** and hexanoic acid **4** are partly soluble in the aqueous phase. The distribution of the compounds in the two phases depends on the total amount of each compound present in the reaction system, i.e. the distribution coefficients are not constant. The solubility of all compounds in the organic phase is up to 20 times higher than their solubility in water.

Obviously, the solubility of the aqueous buffer solution in ethyl acetate cannot be neglected. In fact we found that the mole fraction of the aqueous buffer solution in the organic phase to be 0.27, which means that a significant amount of the buffer solution is dissolved in ethyl acetate. However, this result has little influence on the catalytic reaction, because the amount of catalyst present in the organic phase at reaction conditions was shown to be only 5.64% of the total amount of catalyst (18.53% of the aqueous buffer solution are dissolved in ethyl acetate at reaction conditions). The solubility of the catalyst in the

Table 1
Results of the hydrogenation of **1** in a biphasic solvent system[a]

No.	Catalyst system	Conversion (%)	TON	TOF (h^{-1})	$S_{\text{hexanoic acid 4}}$ (%)	$S_{\text{4-hexenoic acid 2}}$ (%)
1	**5**	92	368	105	16	81
2	*in situ*	81	240	103	34	62
3	**5**+P=O	96	384	192	22	78
4	**5**+PR_3	5	20	10	20	80
5	Recycling (1)	8	32	11	11	89
6	Recycling (2)	9	36	18	10	90

[a] *Reaction conditions*: T=80°C, pH_2=50 bar, buffer solution (pH=7), ethylacetate, 150 mmol sorbic acid; (2) 0.1 mmol $RuCl_33H_2O$\0.4 mmol $P[(CH_2)_3OH]_3$; (3) 0.025 mmol **5**\0.72 mmol *tris*(3-hydroxypropyl)phosphane oxide; (4) 0.025 mmol **5**\0.42 mmol $P[(CH2)_3OH]_3$; (5) 0.025 mmol **5**\0.25 mmol $P[(CH_2)_3OH]_3$\0.15 mmol phosphane oxide. S=selectivity; TON=mol product/mol catalyst; TOF=mol product/mol catalyst h.

organic phase thus does not show the same behavior as the aqueous buffer phase. To prove that the small amount of catalyst, which is present in the organic phase, does not influence the result of the reaction significantly, we studied the reaction under the same conditions, but without using the aqueous buffer phase. The observed conversion was 1%, and can thus be neglected. This result complements the observation that in pure water (i.e. no organic solvent nor buffer compound present) the reaction does not take place at all. Obviously neither the organic solvent nor water are able to develop the active form of the catalyst or the active form of the reactant: the pH-value of seven might either be necessary for the active catalyst species to develop a structure, which is capable of coordinating sorbic acid and/or it is needed because the anion of the sorbic acid is coordinated in the first step.

We determined the conversion with respect to the stirring velocity (Fig. 2).

Velocities of as low as 150 rpm give good selectivities, which do not vary significantly upon increasing the stirring velocity to 1000 rpm. However, the system is completely dispersed at stirring velocities above 1400 rpm, which was determined experimentally. We have thus chosen a stirring velocity of 2500 rpm for determining kinetic parameters, since the influences of the degree of intermixing and the mass transfer can only be neglected in completely dispersed systems, which means that the rate law is not depending on mass transfer phenomena.

In Fig. 3 the amount of **2** is plotted versus time.

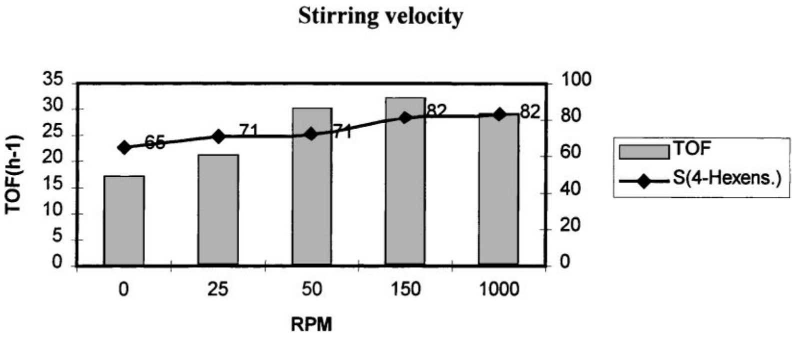


Fig. 2. Selectivity for 4-hexenoic acid S_2 and TOF versus stirring velocity.

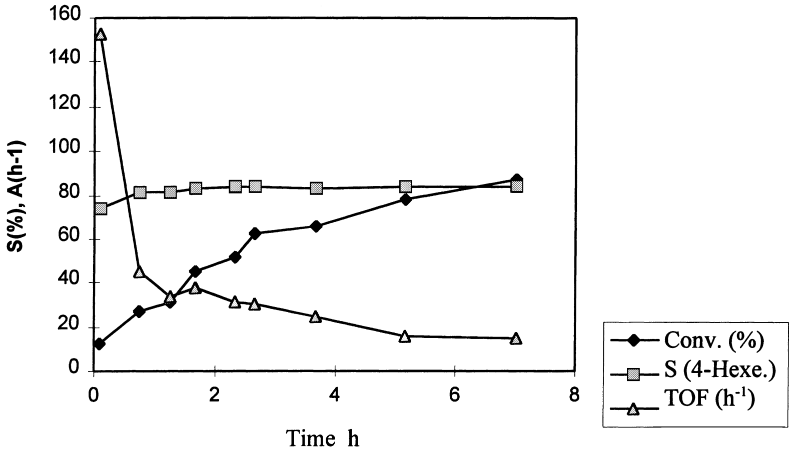


Fig. 3. Selectivity to 4-hexenoic acid versus time.

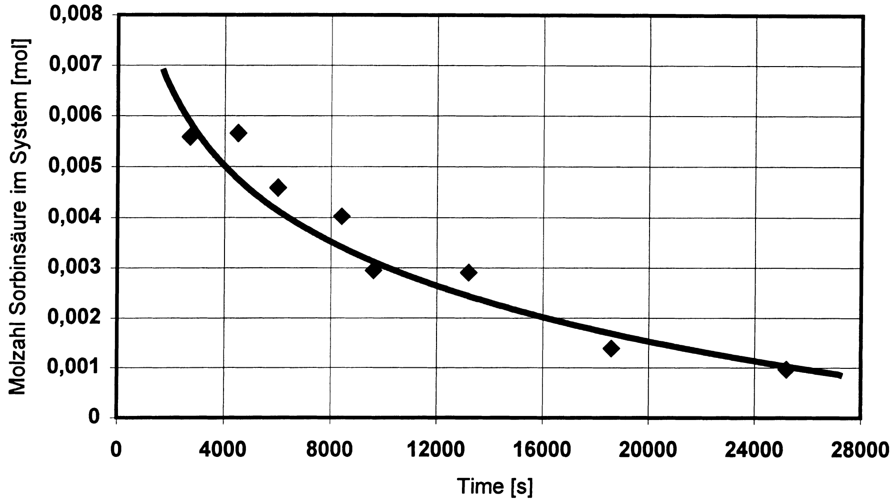


Fig. 4. Molar consumption of sorbic acid versus time.

The amounts of **2** and **4** increase at the beginning of the reaction, but the formation of 4-hexenoic acid **2** is strongly favored. The amount of hexanoic acid **4** is only increasing when sorbic acid has been reacted completely to give 4-hexenoic acid **2**. In order to deduce a rate law for the consumption of sorbic acid we made the following assumptions:

1. The velocity of the reaction is proportional to the concentration of the catalyst and the reactants (sorbic acid and hydrogen).
2. The concentration of the catalyst is constant during the reaction.
3. The concentrations of hydrogen and sorbic acid vary with time, but the amount of hydrogen consumed is so small under the reaction conditions, that the concentration of hydrogen can also be considered as being constant.
4. Thus, the reaction can be treated as pseudo-first-order, so that the rate law should have the simplified form (Eq. (4)):

$$n(\text{sorbic acid}) = n_0(\text{sorbic acid}) \cdot \exp(-kt) \qquad (4)$$

The calculation of k-values using the known values n_0 and n of sorbic acid led to the result, that k is not constant at the beginning of the reaction, while for reaction times larger than ca. 2700 s (ca. 45 min) k is constant and could be fitted to a value of $k=-0.00008$.

The modified rate law $[n_{(\text{sorbic acid})}=0.0064 \exp(-0.00008(t-2700))]$ takes into account reaction times larger than 2700 s, and the experimental data and the calculated curve are shown in Fig. 4.

Since the calculated values are in good agreement with the experimental data, the consumption of sorbic acid in the biphasic catalytic hydrogenation is indeed a pseudo-first-order reaction. We ascribe the deviation from the rate law, that is observed for the first 45 min of the reaction, to the fact, that this time is needed for the catalyst to turn into a homogeneously distributed active form. This assumption was checked by a preconditionning of the catalyst in a non-reactive system.

3. Summary

In summary we have synthesized and characterized the ruthenium complex $[RuCl_2\{P[(CH_2)_3OH]_3\}]_2$ **5** containing the tris(3-hydroxypropyl)phosphane ligand and studied its catalytic performance in the regioselective biphasic hydrogenation of sorbic acid for the first time. Complex **5** selectively catalyzes the reaction to form 4-hexenoic acid **2** with selectivities of up to 82%. The formation of 2-hexenoic acid **3** was not observed. We determined the solubilities and kinetic parameters of the reaction and found the consumption of sorbic acid to be a pseudo-first-order reaction, for which we determined the rate law. We believe that the good selectivities for the formation of 4-hexenoic acid encourage the study of catalytic reactions with other bi- or multifunctional substrates and investigations of this kind are carried out at present.

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