Dramatic Pressure Effects on the Selectivity of the Aqueous/Organic Biphasic Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by Water-Soluble Ru(II)-Tertiary Phosphane Complexes

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Abstract: In a water/chlorobenzene biphasic reaction, the hydrogenation of *trans*-cinnamaldehyde, catalyzed by water-soluble Ru(II)-phosphane complexes at pH 3.04 (phosphate buffer), produces a 61:39 mixture of cinnamyl alcohol and dihydrocinnamaldehyde at 1 bar H_2; however, the selectivity is increased to 93:7 by increasing the hydrogen pressure to 8 bar.

Keywords: alcohols; aldehydes; allylic compounds; hydrogenation; regioselectivity; ruthenium complexes

Aqueous/organic biphasic reactions are increasingly attractive in view of catalyst recycling and clean product isolation.[1,2] Earlier, one of us has reported[3,4] the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols with aqueous sodium formate as hydrogen source and $[\{RuCl_2(m\text{TPPMS})_2\}_2]$ + excess *m*TPPMS as catalyst (*m*TPPMS = *meta*-monosulfonated triphenylphosphane). This aqueous/organic biphasic method allowed facile preparation of allylic alcohols in close to quantitative yields. The outstanding selectivity was rather unexpected, since one of the hydrogenation products of $[\{RuCl_2(m\text{TPPMS})_2\}_2]$, namely $[RuClH(m\text{TPPMS})_3]$, had been previously found to be an active catalyst for the hydrogenation of olefins.[5] Detailed NMR spectroscopic studies have revealed that in the presence of excess phosphane the hydrogenation of $[\{RuCl_2(m\text{TPPMS})_2\}_2]$ yields $[RuClH(m\text{TPPMS})_3]$ at low pH (<6) and *cis*-$[RuH_2(m\text{TPPMS})_4]$ at high pH (>8).[6] It was also established that at atmospheric H_2-pressure $[RuClH(m\text{TPPMS})_3]$ catalyzed the selective hydrogenation of olefinic C=C bonds, while *cis*-$[RuH_2(m\text{TPPMS})_4]$ proved to be a selective catalyst for the hydrogenation of the C=O unit in aldehydes.[7]

In addition to allowing the mild reduction of unsaturated aldehydes with a *pH-controlled selectivity*, the above findings also gave rationale to the selectivity observed with aqueous sodium formate as reductant, in which case the solutions typically had a pH around 8. Nevertheless, these observations were somewhat inconsistent with other literature reports. Namely, Grosselin and Mercier,[8,9] as well as Hernandez and Kalck[10] have found that crotonaldehyde and *trans*-cinnamaldehyde could be hydrogenated to crotyl and cinnamyl alcohol, respectively, with a selectivity up to 96% in *unbuffered* aqueous-organic biphasic systems. The catalyst was either prepared *in situ* from $RuCl_3 \cdot 3\,H_2O$ and *m*TPPTS, or added as $[RuClH(m\text{TPPTS})_3]$ and *cis*-$[RuH_2(m\text{TPPTS})_4]$, respectively [*m*TPPTS = tris(*m*-sulfonatophenyl)phosphane]. Since metal ion hydrolysis and the reduction of Ru(III) to Ru(II) by *m*TPPTS result in proton formation, unbuffered solutions of the *in situ* prepared Ru- *m*TPPTS complexes are always somewhat *acidic*, usually in the pH range of 3–5 depending on the metal concentration. According to the results of our combined pH-potentiometric/NMR spectroscopic studies, in this pH range the formation of $[RuClH(m\text{TPPTS})_3]$ and, consequently, that of the saturated aldehyde products could be expected. (This conclusion relies on the close similarity in the coordination ability of *m*TPPMS and *m*TPPTS, which – at least in the case of hydridophosphaneruthenium(II) complexes – seems well established.[11,12]) The only major difference in the reaction parameters was in the hydrogen pressure: our studies were done at 1 bar, while those in the literature at 30 and 40 bar, respectively. We suspected that at sufficiently high pressures the increased hydrogen concentration in the solution can shift the equilibria of Equation (1) and Equation (2) in favour of the formation of *cis*-$[RuH_2(m\text{TPPMS})_4]$ even in spite of the acidic conditions, and by this, promote the formation of unsaturated alcohols.

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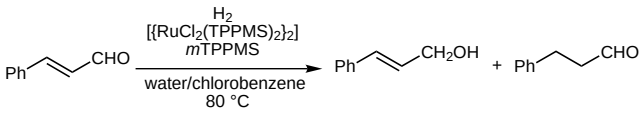
$$\tfrac{1}{2}\,[\{RuCl_2(m\text{TPPMS})_2\}_2] + m\text{TPPMS} + H_2 \rightleftharpoons [RuClH(m\text{TPPMS})_3] + H^+ + Cl^- \quad (1)$$

$$[RuClH(m\text{TPPMS})_3] + m\text{TPPMS} + H_2 \rightleftharpoons \textit{cis}\text{-}[RuH_2(m\text{TPPMS})_4] + H^+ + Cl^- \quad (2)$$

Based on this assumption, the selectivity of the hydrogenation of *trans*-cinnamaldehyde in water/chlorobenzene biphasic reactions was studied as the function of the hydrogen pressure at constant pH (phosphate buffer) in the acidic region. The pH-dependence of the reaction was also reinvestigated, not only at 1 bar, but at 10 bar H_2, as well. In all cases the reactions yielded only cinnamyl alcohol and dihydrocinnamaldehyde, and no formation of the fully saturated product was observed (Scheme 1).



Scheme 1.

The pH-dependence measurements showed the expected trend, i.e., an increasing yield of the unsaturated alcohol and a decreasing yield of the saturated aldehyde with the increase in the pH. This trend was much more expressed at 10 bar, where already at pH 2.9 more than 90% of the products was represented by cinnamyl alcohol. At the same pH, but at 1 bar H_2, the concentration of cinnamyl alcohol (alc) and dihydrocinnamaldehyde (ald) were roughly the same (51% and 49%). The effect of pressure on the selectivity, defined as $S\% = 100[(alc - ald)/(alc + ald)]$ at $pH = 3.04$ is shown on Figure 1.

It is seen that the selectivity readily increases with the increasing pressure and already at 8 bar the product mixture contains 93% cinnamyl alcohol (S = 86%). This shows that a relatively small increase in the pressure changes the selectivity of this hydrogenation dramatically and makes a highly selective reaction from a non-selective one.

Marked pressure effects on selectivity are not unusual, especially in enantioselective hydrogenations.[13,14] However, these effects are mainly observed in a wider pressure range. In our case, as well, one possible explanation could be a different pressure dependence of the rate of C=C hydrogenation, catalyzed by $[RuClH(m\text{TPPMS})_3]$ and that of C=O hydrogenation, catalyzed by *cis*-$[RuH_2(m\text{TPPMS})_4]$. However, both olefin[3] and aldehyde[15] hydrogenations showed first

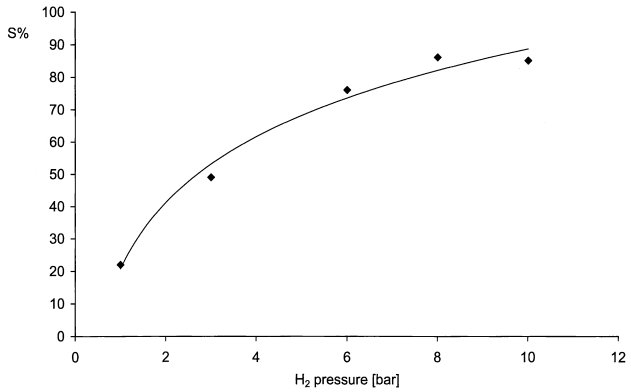


Figure 1. The selectivity (S%) of the biphasic hydrogenation of *trans*-cinnamaldehyde as a function of hydrogen pressure. pH of the aqueous phase: 3.04, other parameters as in Experimental Section. $S\% = 100[(alc - ald)/(alc + ald)]$, alc = cinnamyl alcohol, ald = dihydrocinnamaldehyde.

order dependence on $P(H_2)$ with related catalysts. It is more conceivable, therefore, that the increase in hydrogen pressure changes the molecular distribution of ruthenium among its various hydride species, as shown, for example, in reactions (1) and (2). At the reaction temperature (80 °C), the solubility of H_2 in water under 1 – 10 bar pressure is approximately 0.7 – 7 mM,[16] which is in the range of the proton concentration in the solution at pH 3, so changes of the pressure can easily effect a mobile equilibrium. Indeed, the cherry-red solution at 1 bar H_2, containing $[RuClH(m\text{TPPMS})_3]$, becomes yellow at 10 bar, and *cis*-$[RuH_2(m\text{TPPMS})_4]$ also has a strong yellow colour. UV-visible spectrophotometric measurements in the range of 400 – 600 nm under increasing hydrogen pressure confirmed the reaction of $[RuClH(m\text{TPPMS})_3]$ and H_2.

This deceptive coincidence of colours, UV-vis spectra, equilibria and reactivity notwithstanding, the product of the reaction is *not cis*-$[RuH_2(m\text{TPPMS})_4]$. ^{1}H NMR spectra of $[\{RuCl_2(m\text{TPPMS})_2\}_2]$ + excess *m*TPPMS under > 5 bar hydrogen pressure did not show the characteristic signal of *cis*-$[RuH_2(m\text{TPPMS})_4]$ ($\delta = -10.3$ ppm, pseudo-quartet), instead, a new signal appeared, which could be best interpreted assuming a *trans*-$[RuH_2(m\text{TPPMS})_4]$ structure[17] (^{1}H $\delta = -7.7$ ppm, quintet, $J_{P\text{-}H} = 8.6$ Hz; ^{1}H{^{31}P} $\delta = -7.7$ ppm, s; ^{31}P{^{1}H} $\delta = 58.5$ ppm, br s). Despite many efforts, at present we do not have any definitive structural evidence for this compound, except that it does not seem to be a non-classical Ru-hydride (T_1/400 MHz 430 ms at 40 °C). Further studies of this new compound are underway, and the results will be reported in due course. Nevertheless, based on the pressure effect, it cannot be excluded that minor species containing molecular H_2, such as, e.g., $[RuH(H_2)(\text{TPPMS})_4]^+$, play role either in the *cis*/*trans* isomerization of $[RuH_2(m\text{TPPMS})_4]$ or in the catalysis of *trans*-cinnamaldehyde hydrogenation itself. Non-

classical phosphane-ruthenium(II) hydrides have been already suggested to be involved in the selectivity changes with H_2 pressure in the hydrogenation *vs.* reductive imination of nitriles, albeit no such complexes were characterized in that system.[18]

In conclusion, we have shown, that the selectivity of *trans*-cinnamaldehyde hydrogenation in aqueous-organic biphasic systems with water-soluble Ru(II)-phosphane catalysts is strongly sensitive to the hydrogen pressure and that this sensitivity depends on the pH of the aqueous phase. Such effects are due to the low solubility of H_2 in water and the acid-base equilibria of transition metal hydrides in this solvent. The results call attention to the special phenomena which may be observed in aqueous organometallic catalysis in comparison with related reactions in purely organic solvents.

Experimental Section

General Remarks

*m*TPPMS and [{$RuCl_2$(*m*TPPMS)$_2$}$_2$] were prepared according to published procedures.[19] *trans*-Cinnamaldehyde and chlorobenzene (both from Aldrich) were distilled prior to use. Doubly distilled water was used throughout. H_2 and Ar were acquired from Messer. ^{1}H and ^{31}P NMR spectra were recorded on Bruker AM360 and DRX400 instruments in D_2O or D_2O/H_2O mixtures, using a thick-wall glass NMR tubes with a teflon valve (Aldrich; up to 10 bar) or medium-pressure sapphire NMR tubes (up to 100 bar). Chemical shifts are referenced to 3-(trimethylsilyl)-1-propanesulfonic acid Na salt (TSPSA, Fluka) and 85% H_3PO_4, respectively. GC analyses of hydrogenation product mixtures were carried out on a Chrom 5 chromatograph (2 m Carbowax 20M on 80/100 Chromosorb/3.5% KOH column, FID).

Hydrogenation Experiments

19 mg ($2 \cdot 10^{-5}$ mol) [{$RuCl_2$(*m*TPPMS)$_2$}$_2$] and 22.8 mg ($5.7 \cdot 10^{-5}$ mol) *m*TPPMS were placed into a home-made heavy-walled glass reactor equipped with a gas inlet, pressure gauge and an inlet/sampling port. After closing the reactor it was deoxygenated with several evacuation/refill (Ar) cycles. Then 3.0 mL of an aqueous phosphate buffer of the desired pH were injected through the inlet port, followed by 100 μL of *trans*-cinnamaldehyde dissolved in 3.0 mL of chlorobenzene. The reactor was evacuated and filled with H_2 of the desired pressure at room temperature, then placed into an oil bath of 80 ^{0}C, the temperature of which was controlled by a Lauda K4R circulator. The reactions were started with starting the magnetic stirring, and in typical experiments were run for 2 hours. Depending on the pH and pressure, conversions of *trans*-cinnamaldehyde were obtained in the 5 – 70% range, however, complete conversions could be obtained in longer reaction times. No 3-phenyl-1-propanol was detected. At the end of the reaction the reactor was cooled in ice/water, and the product mixture was analyzed by gas chromatography of the organic phase. Occasional use of an internal standard (naphthalene) showed that no loss of material occurred.

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