

The regioselective biphasic hydrogenation of *trans*-cinnaldehyde by *meta* sulfonatophenyl-diphenylphosphine (TPPMS) Ru(II) and Os(II) species. The influence of ionic strength, ligand tensoactivity and metal nature in the selective production of the unsaturated alcohol

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Abstract

The hydrogenation of *trans*-cinnamaldehyde was studied, using as catalyst precursor the complexes $MCl_2(CH_3CN)_4$, where $M = Ru(II)$ and $Os(II)$, stabilized with the water-soluble ligand, *meta*-sulfonatophenyl-diphenylphosphine, in its sodium salt form, (TPPMS). The Ru(II) system showed better activity and selectivity than its Os(II) analogue, under biphasic catalysis. For the ruthenium system an enhancement of the selectivity to the unsaturated alcohol was obtained by increasing substrate to catalyst ratio, salt concentration and ligand tensoactivity. © 1999 Elsevier Science B.V. All rights reserved.

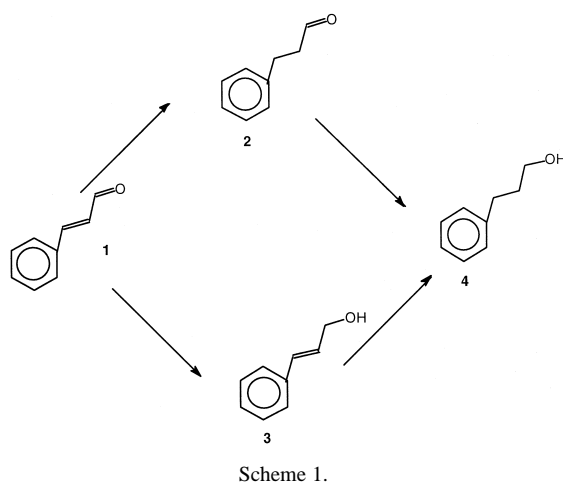
Keywords: Regioselective biphasic hydrogenation; *Trans*-cinnaldehyde; Unsaturated alcohol

1. Introduction

The industrial development of the biphasic (aqueous–organic) hydroformylation process, established in 1984 by Rhone-Poulenc/Ruhrchemie [1], has given a considerable impetus to the progress of the area of organometallic chemistry and catalysis in water [2]. The use of a

two-phase (aqueous/organic) system has the advantage of having the catalyst dissolved in a solvent which is immiscible with that of the substrate, facilitating the recovering and recycling of the catalytic precursor, which in most cases consists of a precious metal complex [2]. In general, the transition metal is held in the aqueous phase by coordinating to the appropriate water-soluble ligand. Some of the most useful hydrosoluble ligands are TPPTS (tri-sodium salt of tris-*meta*-sulfonatophenylphosphine) [1]

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and TPPMS (Sodium salt of *meta*-sulfonylphenyldiphenylphosphine) [3].

This biphasic concept has been elegantly extended to non-aqueous liquid biphasic systems by using fluorinated ‘pony-tails’ ligands and solvents [4]. Although these systems are important for the transformation of many organic molecules, the ligands are very expensive and the fluorinated medium requires careful handling. However, in the case of water-soluble biphasic catalysis, the aim is to continue through a further development; because water is the most abundant solvent, it is inexpensive [5] and environmentally friendly [6].

One of the most documented applications of biphasic catalysis in the literature relates to the selective hydrogenation of unsaturated organic molecules [2]. Work in this field covers a wide range of research, which goes from the simple reduction of olefins [7,8] and heteroaromatics [9,10], through the controlled transformation of lipids in biomembranes and living cells [11].

Amongst the most interesting and useful hydrogenation research carried out, the regioselective reduction of the carbonyl moiety in aldehydes and α,β -unsaturated aldehydes stands out [10,12–17]. This regioselective reduction process of aldehydes is of interest because of its importance in the synthesis of fine chemicals, and they are starting material for plastifiers [18]. In the oil industry, the study of regioselective hydrogenation is of importance in controlling the hydroprocessing of hydrocarbons selectively to avoid waste production and unwanted reaction pathways [9,10].

Trans-Cinnamaldehyde (3-phenyl-2-propenal, CNA, **1**), has been one of the most studied substrates from the group of α,β -unsaturated aldehydes, using biphasic catalysis (Scheme 1). Aspects dealing with the reduction of this compound, especially the selectivity to the unsaturated alcohol (Cinnamyl alcohol or Cinnamol, **3**) are summarized in Table 1 [10,12–17].

Table 1
Hydrogenation of *trans*-cinnamaldehyde using water-soluble organometallic complexes

Catalyst precursor	Time (h)	Temperature (°C)	$P(\text{H}_2)$ (bar)	% Conversion	% Selec.	Ref.
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/6\text{TPPMS}$	3	100	30.1	100	90	[10]
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/6\text{TPPTS}$	3	100	30.1	100	95	[12,13]
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/5\text{TPPTS}$	3	35	20	99	98	[14]
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/5\text{TPPTS}$	3	40	20	100	96	[12]
$\text{RuCl}_2(\text{TPPMS})_2$	5	80	NaO_2CH	98	92	[15]
$[\text{RuCl}_2(\text{TPPMS})_2]_2$	3	100	30.1	100	83	[16]
$[\text{RuHCl}(\text{TPPMS})_2]_2$	3	100	30.1	100	54	[16]
$\text{RuHCl}(\text{CO})(\text{TPPMS})_3$	8	100	17	90	23	[13]
$\text{RuHCl}(\text{CO})(\text{TPPTS})_3$	8	100	17	87	30	[13]
<i>cis</i> - $\text{RuCl}_2(\text{PTA})_4$	3	80	NaO_2CH	21	100	[17]
$[\text{RuCl}(\mu\text{-Cl})(\text{TPPTS})_2]_2$	3	40	20	100	91	[12,16]
$\text{RuH}(\text{Cl})(\text{TPPTS})_3$	3	40	20	100	96	[12]
$\text{RuH}_2(\text{TPPTS})_4$	3	40	20	100	95	[12]
$\text{RuH}(\text{OAc})(\text{TPPTS})_3$	3	40	20	100	96	[12]

Some points of interest from Table 1 are worth mentioning:

1. The ruthenium catalyst precursors prepared in situ, from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with either TPPMS or TPPTS, tend to give better conversions and better selectivity to **3** than their respective aqueous organometallic complexes.
2. For the aqueous complexes of ruthenium, having either TPPMS or TPPTS as ligands, the latter ligand promotes a more efficient selectivity of **1** to the unsaturated alcohol, **3**, as compared to TPPMS.
3. Ruthenium complexes having carbonyls as ligands, showed a low selectivity of **1** into **3** ([13]).
4. It has been stated that a water solution of $\text{MCl}_3 \cdot 3\text{H}_2\text{O}$ /TPPTS or TPPMS, ($\text{M} = \text{Ru}$ or Rh) in the presence of activated olefins induces the formation of phosphonium salt species under acidic conditions [12,19].

In order to compare the results observed in Table 1, regarding the selective transformation of CNA (**1**) to Cinnamyl alcohol (**3**) using Ru(III) species, with those of Ru(II) and Os(II) catalytic systems; the latter two M(II) species were investigated, in the presence of the water-soluble ligand TPPMS. Some influence of reaction conditions such as: pressure, temperature, substrate to catalyst ratio and salt addition, were examined. The effect of ionic strength, ligand tensoactivity and nature of the metal on the regioselective transformation of **1** into **3**, in a two-phase system, will be reported.

The formation of phosphonium salts was also examined. Using high-pressure and normal NMR systems and will be reported separately.

2. Experimental

All manipulations were carried out using standard Schlenck techniques under dry argon or nitrogen. Solvents were purified by conventional procedures. GC-MS was done with a HP

5890 system, HP-1 column (50 M, split injection of 1:50, $T_i = 60^\circ\text{C}$, time of two minute for organic compounds, program of $10^\circ\text{C}/\text{min}$, $T_f = 120^\circ\text{C}$). GC chromatograms were run in a Varian 3400 with FI detector, Megabore type capillary column (15 mts, DB-5 phase, 1.5u FT, J and W Scientific). Quantification was achieved by using the internal standard (cyclooctane) method; the peaks were identified by comparison with authentic samples and with the results of the GC/MS. Infrared spectra were taken in a Perkin-Elmer 1600 FTIR coupled to a Digital Computer DEC Station 316SX and a HP color-pro Printer, using KBr. NMR were run in a Bruker AMX 400 MHz spectrometer, using deuterated solvents. H_3PO_4 and TMS were used as external standards.

2.1. Materials

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (Aldrich), $\text{OsCl}_3 \cdot n\text{H}_2\text{O}$ (Strem) and triphenylphosphine (Strem) were used without further purification. Acetonitrile was dried over CaH_2 and distilled prior to use. Toluene, *trans*-cinnamaldehyde, Cinnamol, Hydrocinnamaldehyde, 3-phenyl-1-propanol and diethyl ether were obtained from Aldrich Chemical. The TPPMS ligand was prepared according to the literature procedure [3]. Purification was achieved by recrystallization in water and ethanol, until the ^{31}P NMR showed only one singlet (relative to phosphoric acid) at -5.99 (TPPMS). $\text{MCl}_2(\text{CH}_3\text{CN})_4$ complexes ($\text{M} = \text{Ru}$ and Os) were prepared according to published procedures [20,21].

2.2. Catalytic experiments

Catalytic runs were carried out by using the following conditions: The reactor was an autoclave from PARR Instruments (300 ml, 316SS, Glass Liner) fitted with an internal stirring system, temperature controlled thermowell unit and sampling valve. Reaction temperature was varied from 80°C to 140°C (353 K to 413 K),

hydrogen pressure varied from 100 psi (7 bar) to 450 psi (31 bar), stirring rate was set at 630 rpm for a time period of 8 h. Samples from the reactions were taken periodically via the sampling valve, layers were separated and the organic phases were immediately analyzed by gas chromatography. The gas chromatograph was calibrated to calculate concentrations on a mol percent basis, against an internal standard (cyclooctane). Total volume of the mixture was 100 ml (1:1 toluene/water).

3. Results and discussion

The systems consisting of $MCl_2(CH_3CN)_4$ ($M = Ru(II)$ and $Os(II)$) and 3 equiv. of TPPMS were used as catalyst precursors in the selective hydrogenation of *trans*-cinnamaldehyde (CNA) in a biphasic medium, consisting of equal volumes of water and toluene, according to these initial experimental conditions: 100°C, 250 psi H_2 , 630 rpm, S/C ratio 50:1, 8 h, 100 ml.

Under the above conditions, the percentage conversions of CNA were 87 and 16% for the Ru(II) and the Os(II) systems, respectively. After the catalysis, the only products obtained, as determined from the GC-MS analyses, were: Hydrocinnamaldehyde (**2**), Cinnamol (**3**) and 3-phenyl-1-propanol (**4**), in the following percentage ratios: Ru(II); 23:21:43 and Os(II); 9:4:3; for **2**, **3** and **4** respectively. These results indicated that both systems, under the initial reaction conditions given, are not selective in the biphasic reduction of CNA. The ruthenium system is a more active catalyst precursor for the hydrogenation of CNA than its osmium analogue.

In an attempt to force the hydrogenation process to go exclusively by the formation of the unsaturated alcohol product, (**3**), using both, the Ru(II) and the Os(II) systems, studies of the influence of reaction conditions such as pressure, temperature, substrate to metal ratio and salt concentration were carried out.

3.1. Effect of the temperature

Under the same reaction conditions (250 psi, 630 rpm, S/C: 50, toluene/water: 1:1) the effect of temperature in the conversion of CNA to Cinnamol (**3**) is differently for the Ru(II) and Os(II) systems. In the case of the ruthenium system, a low temperature (80°C) favors the very slow transformation of **1** into **3**. As the temperature increases (100, 120 and 140°C) the

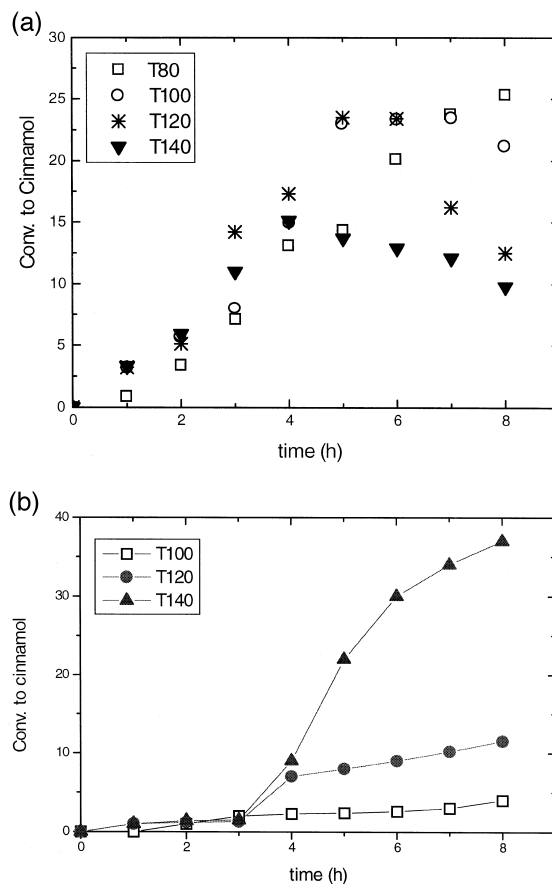


Fig. 1. a. Reaction profiles for the regioselective conversion of CNA to Cinnamol as a function of temperature (°C), using the catalytic system consisting of $RuCl_2(CH_3CN)_4 + 3TPPMS$, in a two-phase (water/toluene) medium. ($[Ru] = 3.0 \times 10^{-3}$ M; $[TPPMS] = 9.0 \times 10^{-3}$ M; $[CNA] = 1.5 \times 10^{-1}$ M; 250 psi, 630 rpm, S/C 50). b. Reaction profiles for the regioselective conversion of CNA to Cinnamol as a function of temperature, using the catalytic system consisting of $OsCl_2(CH_3CN)_4 + 3TPPMS$, in a two-phase (water/toluene) medium. ($[Ru] = 3.0 \times 10^{-3}$ M; $[TPPMS] = 9.0 \times 10^{-3}$ M; $[CNA] = 1.5 \times 10^{-1}$ M; 250 psi, 630 rpm).

transformation of **1** into **3** increases slowly, while the conversion of **3** into **4** follows quickly (see Fig. 1a). As temperature increases, a fast reduction of **3** into **4** is observed.

For the osmium system, as the temperature increases (from 100 to 140°C) the transformation of **1** into **3** follows slowly (Fig. 1b). A long induction period is observed for this catalyst system before the hydrogenation begins. Presumably, the formation of the catalytically active species for this metal forms more slowly than that of ruthenium, under similar two-phase conditions.

For both catalytic systems, the temperature has a minor influence in the selective transformation of CNA to Cinnamol and does not deserve further comment.

3.2. The effect of the pressure

The behavior described for both systems with increasing temperature is similarly observed when the pressure is incremented from 100 to 450 psi, maintaining constant temperature. For the ruthenium system, higher pressure favors a shift in product yield from **3** to **4**. In the case of the osmium system, there is a small increment of **3** with increasing hydrogen pressure.

3.3. The effect of increasing substrate to metal ratio

An interesting effect is observed as one decreases substrate to metal ratio, as observed in Fig. 2, using the Ru(II) system. The reaction profiles for the transformation of **1** into **3**, with decreasing S/C ratio are depicted, using the conditions of 100°C, 630 rpm, 250 psi, toluene/water, 100 ml. As the S/C ratio changes from 100 to 25, the selectivity and conversion towards the unsaturated alcohol is increased; the conversion and selectivity reaches a maximum of 90% at S/C = 25. Another point of interest is that on decreasing the S/C ratio, the initial induction period is drastically reduced. Presumably, it is possible that when a

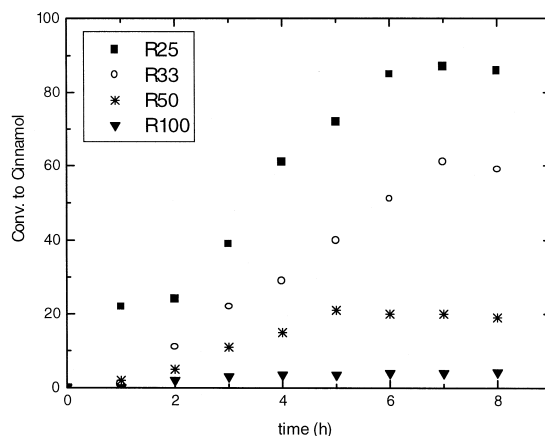


Fig. 2. Reaction profiles for the regioselective hydrogenation of CNA into Cinnamol, as a function of substrate to catalyst ratio, using as catalyst system $\text{RuCl}_2(\text{CH}_3\text{CN})_4 + 3\text{TPPMS}$, in a two-phase (water/toluene) medium ($\text{R100} = \text{S/C } 100$, $\text{R50} = \text{S/C } 50$, $\text{R33} = \text{S/C } 33$, $\text{R25} = \text{S/C } 25$); 100°C, 630 rpm, 250 psi H_2 .

large amount of metal and water-soluble phosphine are present in the medium, a better stability and faster ability to transform the CO moiety is given to the catalytically active species. This behavior may be the result of the influence of salt concentration and increment in tensoactivity; because in every case the concentration of the water-soluble TPPMS ligand, in its sodium salt form, is increased relative to that of the substrate [22,23].

A further interesting observation with the ruthenium system is that, after the catalysis, the organic phases remain completely clear, a possible indication that the metal complex is confined totally in the aqueous phase, even at S/C ratio of 25.

For the osmium(II) system there is no improvement in the regioselective hydrogenation of the CO moiety of the CNA in the two-phase medium when decreasing the S/C ratio. Further studies are required before giving a plausible answer to this observation.

3.4. The effect of ionic strength in the selectivity

It has been stated that the “ionic strength of the aqueous medium affects both the reaction

rate and the reaction selectivity” [22,23]. Based on this statement and in order to determine if this is the factor responsible for improving the selectivity when there is a decrease in the S/C ratio, using the Ru(II) systems; a study on the effect of increasing salt concentration in the aqueous phase was carried out.

Fig. 3 shows the reaction profiles for these experiments. Under standard reaction conditions (100°C, 250 psi, 630 rpm; S/C 50), it is observed that as the concentration of sodium sulfate is increased from S1 (no salt added) to S4 ([salt] = 2.0×10^{-1} M), there is a marked increase in the regioselectivity to the Cinnamol (**3**) product. With increasing salt concentration there is also an increase in the initial reaction rate which goes from 2.00 (S1) to 26.5 [mmol **3** (mmol Ru)⁻¹ h⁻¹] (see profile S4). This is a clear demonstration that the ionic strength plays an important role in the increment of the rate and in the selectivity to the unsaturated alcohol, when the reaction is carried out in a two-phase system. What the exact role is of the high ionic strength in orienting the formyl group to a position of better interaction with the catalyst is still a matter of speculation that requires more careful work. However, it is known that

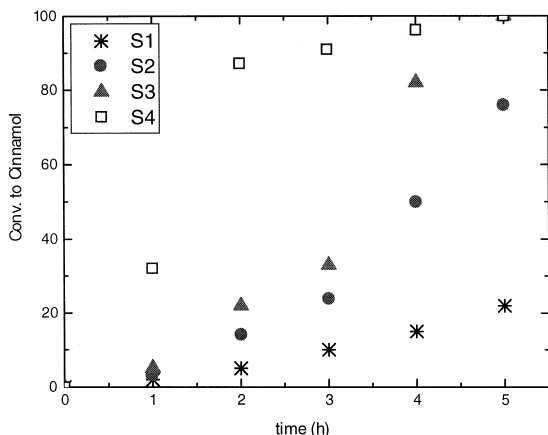


Fig. 3. Reaction profiles for the conversion to Cinnamol as a function of salt concentration, using the $\text{RuCl}_2(\text{CH}_3\text{CN})_4 + 3\text{TPPMS}$ catalyst system in a two-phase medium. (S1: [salt] = 0; S2: [salt] = 2.0×10^{-3} M, S3 [salt] = 2.0×10^{-2} M, S4: [salt] = 2.0×10^{-1} M; salt = Na_2SO_4 ; 100°C, 250 psi, 630 rpm; S/C 50).

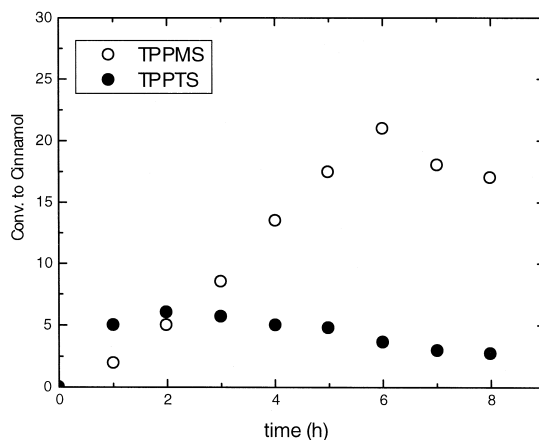


Fig. 4. Reaction profiles of studying the effect of phosphine tensoactivity in the selectivity to the unsaturated alcohol during the hydrogenation of CNA using the catalyst system consisting of $\text{RuCl}_2(\text{CH}_3\text{CN})_4 + 3\text{P}$ (P = TPPMS (Tensoactive) and TPPTS (non-tensoactive)), in a two-phase medium. ([Ru] = 3.0×10^{-3} M; [TPPMS] = 9.0×10^{-3} M; [CNA] = 1.5×10^{-1} M; 100°C, 250 psi, 630 rpm, toluene/water: 1:1).

high salt concentration may help tensoactive molecules to aggregate in micelle formation; these formations may play a fundamental role in orienting the catalytically active species and the formyl group in such a way as to promote a faster reaction conversion and better selectivity [23].

When the hydrogenation of CNA is carried out with the ruthenium(II) complex, in the presence of 3 equiv. of TPPMS (Tensoactive) or 3 equiv. of TPPTS (non tensoactive), under the same reaction conditions and without addition of salt, as shown in Fig. 4; the tensoactive phosphine plays a much better role in promoting the production of **3**. Thus, tensoactivity is also important in helping the selectivity though the effect is much less pronounced than the one observed for the ionic strength. Although this observation appears to contradict point 2 in the introduction (Table 1). Where it is stated that TPPTS showed better conversion and selectivity for transforming **1** into **3**; it is possible that pressure and metal nature also play a important role in the hydrogenation. Most of the experiments shown in Table 1 have been carried out at

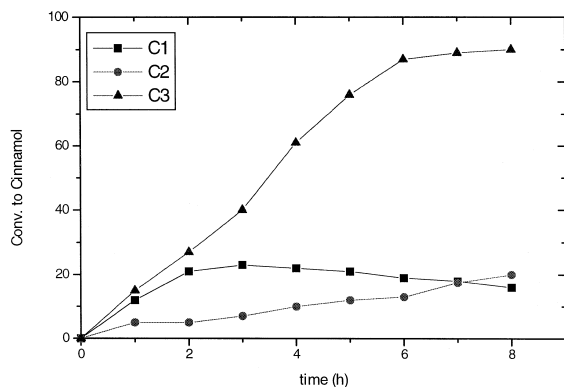


Fig. 5. Reaction profiles for the two-phase hydrogenation of CNA and its selective conversion to **3**, using different types of ruthenium catalytic precursors (C1: $\text{HRuCl}(\text{CO})\text{TPPMS}_3$; C2: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + 3\text{TPPMS}$; C3: $\text{RuCl}_2(\text{CH}_3\text{CN})_4 + 3\text{TPPMS}$). ($[\text{Ru}] = 3.0 \times 10^{-3}$ M; $[\text{TPPMS}] = 9.0 \times 10^{-3}$ M; $[\text{CNA}] = 1.5 \times 10^{-1}$ M; 100°C , 250 psi, 630 rpm, S/C = 25; toluene/water: 1:1).

higher pressure than the one observed in this experiment [10,12–17].

3.5. The effect of metal catalyst precursor in the selectivity

Using one of the best conditions (100°C , 250 psi, 630 rpm, $[\text{salt}] = 0$, S/C = 25) to orient the selectivity in the hydrogenation of CNA to the formation of Cinnamol (**3**), a study was carried out using the following ruthenium catalytic systems: (C1: $\text{HRuCl}(\text{CO})\text{TPPMS}_3$ [24], C2: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + 3\text{TPPMS}$; C3: $\text{RuCl}_2(\text{CH}_3\text{CN})_4 + 3\text{TPPMS}$).

The reaction profiles for C1, C2 and C3 are shown in Fig. 5. It follows that the nature of the metal catalyst precursors have a special role in the conversion process; Ru(II) being more active than Ru(III), when the catalyst precursor is prepared in situ. It is presumed that in the case of the water soluble complex $\text{HRuCl}(\text{CO})(\text{TPPMS})_3$, the dissociation of the phosphine ligand is slow at the temperature of the reaction; therefore, a slow transformation of the CNA molecule is observed [22]. Also, is it possible that the presence of the carbonyl retard the effective process of hydrogenation, as it has been observed in Table 1.

From the point of view of economics, it is less expensive to improve selectivity to the unsaturated alcohol based upon the addition of tensoactive ligands or incrementing salts concentration, rather than increasing metal concentration or controlling, via buffers, the pH of the reaction medium.

4. Conclusions

From the work presented in this article, it has been observed that tensoactivity of the ligand, ionic strength of the aqueous medium and nature of the metal ion, all play an important role in the regioselective transformation of cinnamaldehyde to the unsaturated alcohol in a two-phase system.

The catalytic system consisting of Ru(II) and the water-soluble tensoactive ligand TPPMS is more active in the hydrogenation and transformation of cinnamaldehyde to Cinnamol than its Os(II) analogue.

This work has important implications in the regioselective conversion of aldehydes into unsaturated alcohols, of importance in the industry of fragrances and flavor chemistry [25].

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