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Pablo J. Baricelli

pbaricel@uc.edu.ve

Universidad de Carabobo

Daniela Sánchez

Universidad de Carabobo

Adriana Rivolta

Universidad de Carabobo

Lissette Jiménez

Universidad de Carabobo

Maria Modroño-Alonso

Universidad de Carabobo

Merlín Rosales

Universidad de Cartagena. Cartagena de Indias

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Aqueous-biphasic hydrogenation of 1-hexene, styrene, 2-pentene, and their mixtures catalyzed by $RuH_2(CO)(o\text{-TPPTS})_3$: Catalytic performance, kinetic Studies and catalyst recycling

Pablo J. Baricelli[a]*, Daniela Sánchez[a], Adriana Rivolta[a], Lissette Jiménez[a], Maria Modroño-Alonso[a] and Merlín Rosales[b].

[a] Centro de Investigaciones Químicas, Facultad de Ingeniería, Universidad de Carabobo, Valencia, Venezuela.
[b] Grupo de Química Bioorgánica, Facultad de Ciencias Exactas y Naturales and Instituto de Matemáticas Aplicadas, Universidad de Cartagena. Cartagena de Indias, Colombia.

Abstract

The water soluble complex $RuH_2(CO)(o\text{-TPPTS})_3$ [o-TPPTS = $P(o\text{-}C_6H_4SO_3Na)_3$] was used as precatalyst in the aqueous-biphasic hydrogenation of a series de alkenes, such as 1-hexene, styrene and 2-pentene. In first instance, 1-hexene was used as model substrate in order to obtain the best operational parameters for the hydrogenation reaction, which correspond to T = 100 °C (373.15 K), P = 900 psi of H_2 (62.1 atm), stirring speed = 800 rpm, substrate/catalyst ratio = 100/1 and t = 4 h. Likewise, it could be demonstrated that the sulfonation of phosphine in the *ortho* position had no influence on the conversion of 1-hexene to hexane, and no steric hindrance was evident that influenced the kinetics of the reaction. Under these conditions, the activity trend observed for hydrogenation of the different alkenes was: 1-hexene > styrene > 2-pentene. However, when a mixture of them is used, the order changes (styrene > 1-hexene > 2-pentene), possibly due to styrene's greater coordination ability. The recycling of the catalytic phase was performed three successive times without observing loss on the activity of the catalytic precursor, which is indicative that all metal remains in the aqueous phase during the hydrogenation reaction. The mercury test in independent experiments, showed no interference of the Hg with the evolution of the reaction, demonstrating that the catalytic reactions were performed by molecular species.

Keywords: Aqueous biphasic catalysis, ruthenium, tri(*o*-sulfonated phenyl)phosphine, alkenes

*Corresponding author's mail: pbaricel@uc.edu.ve

1. Introduction

Hydrogenation is one of the most important classes of catalytic reactions, which can be carried out with molecular hydrogen (***direct hydrogenation***) or through the acceptance of hydrogen from other molecules known as hydrogen donors (***transfer hydrogenation***). Although the first studies on hydrogenation were carried out through heterogeneous catalysis (metals like Ni, Pd and Pt on various supporting systems) [1-3], homogeneous hydrogenation has been successful over time because it favors selectivity. In particular, hydrogenation of alkenes by transition metal complexes has been an area of continuously growing interest, which has proved to be important in several industrial applications and has played a key role in the fundamental understanding of the organometallic catalytic reactions [1,4]. Since the discovery of Wilkinson's catalyst 60 years ago [5], the hydrogenation of alkenes has been studied by using by various types of catalysts, such as “frustrated Lewis pairs”, organic catalysts, enzymes, main group catalysts and transition metal complexes, including scandium and yttrium, as well as f-block element complexes (lanthanides and actinides) [6].

In homogeneous catalytic process, catalyst recovery and recycling could be a serious problem [4], so some strategies have been used to overcome this difficulty, among which is aqueous-biphasic catalysis [7-9]. The synthesis of the water-soluble ligand tri(sodium-*m*-sulfonated-triphenylphosphine (trisulfonated triphenylphosphine, *m*-TPPTS) [10-12], and its applications in the Ruhrchemie/Rhone-Poulenc [13] and Kuraray [14] processes gave a noticeable and definitive boost to academic and industrial knowledge on the uses of aqueous-organic biphasic catalysis. In this sense, very interesting special issues on advances in catalysis in green aqueous media were edited by Papadogianakis and Sheldon in 2015 [15] and more recently in 2025 [16], in which hydrogenation, hydroformylation and other organic reactions with academic and industrial concepts and applications, extremely important in our research area were reported.

The first studies on aqueous-biphasic catalysis were carried out precisely in the hydrogenation of alkenes and other unsaturated compounds (aldehydes, ketones), which were reviewed by Toth and Joo [17] and Nomura [18]. In recent years, several groups of researchers have been working on the use of biphasic catalysis in a series of innovative applications in which the importance of this type of systems is demonstrated, such as the use of phosphine-containing core-shell water-soluble polymers as nanoreactors in the hydrogenation of styrene and 1-octene by Manoury et al. [19] reported the use of ethylene glycol-toluene systems as selective and recyclable precatalysts without appreciable loss in its activity in the chemo selective semi-hydrogenation of alkynes by Bhanage et al. [20]. The hydrogenation of biomass-derived substrates reported by Papadogianakis et al. [21] in the hydrogenation of renewable biomass-derived levulinic acid in aqueous media and the hydrogenation of biomass derivate, catalyzed by ruthenium [II] complexes containing phosphorous-nitrogen ligands under mild conditions by Aguirre et al. [22].

The hydrogenation of alkenes and their mixture are reactions of great interest as a technological tool in connection with the improvement of fuels, area in which our research groups have been strongly involved. In this sense, hydrogenation of alkenes (1-hexene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, styrene, allyl-benzenes and other C_6-C_{10} alkenes) and their mixtures have been performed by using tungsten [23,24], ruthenium [25] and rhodium [26] complexes as precatalysts. These and other papers have recently been reviewed by some of us [27].

Recently, our research group reported for the first time the application of a very active and recyclable ruthenium catalyst $Ru(H)_2(CO)(o\text{-TPPTS})_3$ for the biphasic hydrogenation of naturally occurring olefins, such as allylbenzenes, eugenol estragole and safrole [28]. The purpose of the present research paper is to understand and compare the hydrogenation rates of some model olefins such as 1-hexene, 2-pentene, and styrene relative to some natural olefins such as allylbenzene, eugenol, estragole, and safrole, which possess

a combination of terminal and cyclic olefins that could nourish the knowledge acquired during the study of catalytic processes where there are mixtures of olefins with different types of substituent such as those found in the hydrogenation of biomass.

2. Experimental section

2.1 General procedure

All manipulations were performed under nitrogen using standard Schlenk techniques [29]. Prior to use, all organic solvents and alkenes were purified by distillation over standard agents and deoxygenated. $RuCl_3 \cdot 3H_2O$, 1-hexene, styrene, heptane, ethanol, 2-pentene, 2-methoxy ethanol, were obtained from Aldrich. All other chemicals were commercial products and were used without further purification. All gases were purchased from AGA Gases (Venezuela). Infrared spectra were recorded in a Perkin-Elmer 1000 FTIR spectrometer using samples pressed as KBr disks. NMR data were obtained on a Bruker AVANCE 300 spectrometer. GC analyses were performed on a Hewlett Packard 5890 Series II chromatograph with a flame ionization detector and ultra 2.5% phenyl methyl silicone, 25 m, 320 µm column. Quantification was achieved by using naphthalene as the internal standard and all peaks were identified by comparison with pure samples or by GC/MS on a HP 5890/5971 coupled system using a Quadrex PONA 5% phenyl methyl silicone, 25 m, 320µm column. UV-Vis spectra were measured in a diode array Hewlett Packard 8452 spectrometer.

Complex $Ru(H)_2(CO)(o\text{-TPPTS})_3$ was synthesized from $RuCl_3.xH_2O$ and the water-soluble phosphine *o*-TPPTS as reported recently and characterized by mean of FT-IR and NMR spectroscopy [30].

2.2. Catalytic hydrogenation

In a typical experiment, a solution of the catalyst precursor $RuH_2(CO)(o\text{-}TPPTS)_3$ (0.024 mmol) in water (15 mL) and the corresponding alkene or alkene mixture (1.96 mmol) in n-heptane (15 mL) were introduced into a glass-lined stainless-steel autoclave (Parr, 50 ml) fitted with internal mechanical stirring, temperature control unit and sampling valve. The solution prepared was purged three times with hydrogen and then charged to the required pressure and heated to the desired temperature. Samples of the reaction mixture were periodically extracted and the total pressure was adjusted via a high-pressure reservoir. The samples were cooled, the phases separated and the organic phase analyzed by GC/MS. The reaction temperature was varied from 80 to 110 ºC (353-383 K); hydrogen pressure varied from 600 to 900 psi (41-61 atm); the substrate/catalyst ratio varied from 20/1 to 120/1 and the stirring speed was kept constant at 800 rpm. 1-Hexene was used as a model substrate to determine the best operational conditions The TOF values were calculated by dividing the moles of products obtained per mole of catalyst obtained in the reaction (turnover number, TON) by the time (in hours) in which 100 % conversion was achieved.

2.3. Catalytic recycling experiments

The recycling experiments were conducted to evaluate the stability of the catalytic precursor after sequential experiments by using a general procedure like that described in the prior section. Once the samples were extracted, they were strictly handled under anaerobic conditions. The aqueous catalytic phase was mixed with a fresh organic phase that contained the corresponding alkene (1.96 mmol) in n-heptane (15 mL), introduced again into the autoclave, and purged three times with hydrogen. Then, the autoclave was charged at the required pressure and heated to the desired temperature, for the procedure to be re-initiated.

3. Results and discussion

3.1. Aqueous biphasic alkene hydrogenation

The ruthenium complex $RuH_2(CO)(o\text{-}TPPTS)_3$ was examined as catalyst precursor for the biphasic hydrogenation of some alkenes, such as 1- hexene, styrene and 2-pentene (Scheme 1). 1-Hexene was used as model substrate in order to obtain the best operational parameters above specified, for which three parameters were varied in a controlled manner: pressure, temperature and substrate to catalyst ratio (S/C).

Scheme 1 here, please

Figure 1 shows the behavior of $RuH_2(CO)(o\text{-}TPPTS)_3$ in the hydrogenation of 1-hexene varying the hydrogen pressure from 600 to 900 psi (41.4-62.1 atm) indicating a total conversion to 1-hexane in approximately 2h (120 min). As can be seen, the catalytic activity increases as the hydrogen pressure increases. The analysis of conversion rate and the products distribution indicated that 900 psi (62.3 atm) is the best pressure for the hydrogenation because it presents the highest activity towards hydrogenation, with a percentage of isomerization of less than 5% in 120 minutes and it is completely converted to 1-hexane in 150 min.

Fig. 1 here, please

Figure 2 shows the reaction profiles for the 1-hexene conversion varying the temperature from 80 to 110 ºC (353-383 K). All profiles showed similar tendencies during the hydrogenation reaction. However, at 80 ºC, the apparent induction period observed during the first hour of reaction corresponds to the time required to form the catalytic active specie in appreciable concentrations. Similar observations were reported by our group for the rhodium-catalyzed hydroformylation of C_6 olefins in homogeneous and biphasic systems [31]. Analysis of the experimental results (conversion and products distribution) indicated that although slightly higher activity is obtained at 110 °C than at 100 °C after 2.5 hours

(99.5% versus 95.4%, respectively), 100 ºC was the selected temperature to prevent possible thermal decomposition of the catalyst and, furthermore, because only about 4,5% remain as isomers which are finally converted to hexane.

Fig. 2 here please

Figure 3 shows the reaction profiles for the substrate/catalyst ratio varied from 20/1 to 400/1 and clearly can be observed the tendency of the increase the hydrogenation rate from the diluted to more concentrated solutions. The conversion and the products distribution were analyzed and the 100/1 S/C ratio was selected because at 120 min all the 1-hexene has been converted to hexane.

Fig. 3 here please

Subsequently, with the best operating conditions of the system [T = 100 ºC (373.15 K), P = 900 psi of H_2 (62.1 atm), stirring speed = 800 rpm, substrate/catalyst ratio = 100/1 and t = 4 h], the hydrogenation of 1-hexene was carried out, obtaining a total conversion to 1-hexane in approximately 2 hours of reaction (Figure 4a). Finally, the total conversion of 1-hexene was compared using the analogous complex $Ru(H)_2(CO)(m\text{-}TPPTS)_3$ under the same reaction conditions (Figure 4b), finding that there is no substantial difference between the catalytic activity of the complex with the *ortho*-sulfonated phosphine and that of the *meta*-sulfonated phosphine. Once again, as with the hydrogenation of allylbenzenes, a higher conversion to the isomers of 2-hexene is achieved when using the ruthenium system with the sulfonated phosphine in the meta position (Fig. 4c).

Figure 4 here please

Finally, when the well-known mercury test was carried out in order to detect the presence of any amalgam specie, the hydrogenation of 1- hexene was carried out in the presence of mercury, under the best operational parameters found for the biphasic hydrogenation of 1- hexene. The reaction profile was essentially the same as in the absence of mercury, indicating that there is no participation of metallic particles or colloids in the

catalysis, under our reaction conditions [32].

3.2 Kinetics of aqueous hydrogenation of individual alkenes

Kinetics studies of the hydrogenation of individual alkenes were performed by using the integral method [33,34]. For these reactions, the rate equation may be written as eq. 1, where *r* and k_{cat} are the reaction rate and the rate constant, respectively, whereas α, β and γ are the reaction orders on catalyst, alkene and dissolved dihydrogen concentrations, respectively:

$$r = \frac{d[Alkene]}{dt} = k_{cat}[Ru]^{\alpha}[Alkene]^{\beta}[H_2]^{\gamma} \quad (1)$$

If the concentrations of the ruthenium precatalyst and the hydrogen concentration remain constant, then the rate expression (equation 1) can be rewritten as follows:

$$r = \frac{d[alkene]}{dt} = k_{obs}[Alkene]^{\beta} \quad (2)$$

Assuming that the rate equation is first order on alkene concentration (β = 1) and reorganizing it, equation 2 is transformed to equation 3; by integrating equation 3, equation 4 was obtained, which corresponds to a straight line.

$$\frac{d[Alkene]}{[Alkene]} = k_{obs}dt \quad (3)$$

$$-ln\frac{[Alkene]}{[Alkene]_o} = k_{obs}t \quad (4)$$

With equation 4, curves of *ln* ($[Alkene]/[Alkene]_o$) as a function of time for the hydrogenation of alkenes were plotted, in order to calculate the observed rate constant (k_{obs}) and confirm that the catalytic reactions were first order on substrate concentration.

Taking all these factors into account, the biphasic hydrogenation of the individual alkenes, 1-hexene, styrene and 2-pentene, were conducted at the best operational parameters [T = 100 ºC (373.15 K), P = 900 psi of H_2 (62.1 atm), stirring speed = 800 rpm,

substrate/catalyst ratio = 100/1 and t = 4 h] in order to determine both the order of reaction with respect to the concentration of the alkene and the corresponding rate constant; the experimental results are shown in Figure 5 and Table 1.

Figure 5 and Table 1 here, please

The results and data showed in Figure 5a and Table 1 show that 1-hexene is hydrogenated 86% in 2h with 94.5 % of selectivity toward the formation of hexane, whereas the 2-hexenes was formed in 5%. Also, 2-pentene was hydrogenated in 86%, possibly due to the expected isomerization reaction to 1-pentene and subsequent hydrogenation. The styrene substrate, was selectively hydrogenated to ethyl benzene with 100% conversion in 4 h. The inductive effect of the benzene ring and the impossibility to form structural isomers are operating in this substrate. The styrene, is easily hydrogenated because the phenyl group stabilizes the secondary carbon, leaving the doublet bond exposed to a moderated hydrogenation which reach conversion of 100 % in 3.5 h of reaction. Similar explanation has been reported by Wilkinson et al. [5].

On the other hand, all of the reactions of individual alkenes showed kinetics of first order with respect to alkene concentration (Figure 5b), the constant rates are summarized in Table 2. The order of reactivity obtained for this complex during the olefin hydrogenation was found as follows: 1-hexene > styrene > 2-pentene.

Table 2 here, please

Analysis of these results indicates that 1-hexene, an aliphatic alkene, hydrogenates approximately five times faster than the aromatic alkene (styrene), while the internal alkene (2-pentene) hydrogenates more slowly, most likely because it must first isomerize to 1-pentene before hydrogenating. Just as with the hydrogenation of 1-hexene, the homogeneous nature of the hydrogenation of styrene and 2-pentene were also confirmed by the mercury test.

3.3. Kinetics of aqueous hydrogenation of alkene mixtures

To evaluate the performance of the $RuH_2(CO)(o\text{-}TPPTS)_3$ catalyst precursor in the aqueous-biphasic hydrogenation of an alkene mixtures, the reaction was carried out using the equimolar combination of each component: 1-hexene, 2-pentene and styrene (0.043 M of each one of their, total alkene concentration of 0.13 M). The results are summarized in Figure 6 and Table 3.

Figure 6 and Table 3 here, please

As it is shown in Table 3, the hydrogenation of each substrate in the mixture showed first-order kinetics for each olefin. However, conversely to the results found for individual alkene, the equimolar mixture of all the alkenes led to a different order of reactivity for the hydrogenation reaction. Now, styrene has a higher hydrogenation rate constant than 1-hexene (styrene > 1-hexene > 2-pentene). As may be observed, there is an induction period of approximately 30 min, which can be attributed to the time required to reach thermal equilibrium, as well as the competition for the active sites of the catalyst and the formation of the catalytically active species in appreciable concentrations. This can be explained by the different coordination strengths of the substrates. Thus, for example, although styrene has a lower activity than 1-hexene individually (approximately 5 times smaller), it coordinates preferentially to the complex due to the electronic properties of the phenyl ring attached to the carbon-carbon double bond, promoting the formation of a stronger synergetic bond than in the case of 1-hexene. Styrene is now nearly twice as reactive as 1-hexene. Finally, 2-pentene has the lowest coordinating ability because it is an internal alkene therefore presenting a greater steric hindrance.

3.4. Mechanism of olefins hydrogenation

In order to gain further understanding of the mechanisms of the olefins hydrogenation with the Ru complex sulphonated in *ortho* position and despite the impossibility of obtaining

solid or crystalline species, since the mechanism seem to involve rapid equilibria between closely related labile species. The presence of free phosphine ligand by $^{31}P\{^{1}H]$ NMR was observed [25,35,36], which allows us to assume that the active species is formed by dissociation of a phosphine ligand, but dissociated phosphine can be re-coordinated in some of the cycle's elementary steps. Based on the kinetic experiments conducted in this study and those previously published by some of us, we have proposed simple catalytic cycles for both the hydrogenation and isomerization of alkenes, catalyzed by the ruthenium system in an aqueous-biphasic system (Scheme 2). The precatalyst, $RuH_2(CO)(o\text{-TPPTS})_3$ (**1**), loses a phosphine ligand to produce the catalytic coordinatively unsaturated intermediate $RuH_2(CO)(o\text{-TPPTS})_2$ (**2**), considered as the catalytically active species. Coordination of the corresponding alkene generates the Ru-olefin intermediate (**3**). Migration of the hydride ligand to the alkene produces two ruthenium-alkyl intermediates: the linear metal-alkyl intermediate (**4**) and the branched metal-alkyl intermediate. The migratory insertion of hydride and alkene to yield the linear alkyl intermediate may be assisted by coordination of the third phosphine, which then reacts with a dihydrogen molecule to yield the corresponding product (alkane) and regenerate the catalytic precursor (**1**). Complex **1** is in equilibrium with the active specie (**2**), which allows to restart the catalytic cycle.

Scheme 2 here, please

On the other hand, the migratory insertion of the hydride and the alkene, which leads to the branched metal-alkyl intermediate, may or may not be assisted by the coordination of the third phosphine. If the third phosphine coordinates to the metal center, it leads to the hydrogenation product (it was omitted for ease of viewing), and if it does not coordinate, it can lead to the isomerization of the corresponding alkene, via β-hydrogen elimination of the carbon atom adjacent to the R group and dissociation of the corresponding isomer.

We suggest that the hydrogenation of 1-hexene occurs primarily via the hydrogenation mechanism (sequence 1 → 2 → 3 → 4 → 1) with some of isomerization (sequence 3 → 5 → 6 → 2), whereas the hydrogenation of 2-pentene occurs via the initial isomerization of 2-pentene to 1-pentene (sequence 1 → 2 → 6 → 5 → 3), followed by the hydrogenation of the latter (3 → 4 → 1). Obviously, the hydrogenation of styrene follows the conventional hydrogenation cycle

3.5. Reusing of the aqueous biphasic hydrogenation catalyst

One of the principal characteristics of the aqueous biphasic catalysis is the possibility of recovering and reusing the catalytic precursor during the reaction [7-9]. The capability of reusing our catalytic precursor $RuH_2(CO)(o\text{-}TPPTS)_3$ was confirmed with four consecutive experiments using the best operational conditions above reported and 1-hexene as model molecule. The aqueous phase containing the catalyst was maintained during the experiment and the organic phase containing 1-hexene was replaced every 240 min for 4 consecutive experiments without any indication of dropping the total conversion. The results are summarized in Table 4.

Table 4 here please

Also, we can infer from Table 4 that the presence of 2-hexene in the final product, could be related with a small loss of the catalyst activity of the $RuH_2(CO)(o\text{-}TPPTS)_3$ complex due to the air exposure in each recycle, which may have led to the transformation of the active species into another species.

4. Conclusions

The complex $RuH_2(CO)(o\text{-}TPPTS)_3$ showed to be an efficient catalyst precursor for the biphasic hydrogenation of different types of olefins like, 1-hexene, 2-pentene and styrene.

The mercury test for the hydrogenation reactions of alkenes shows that the reactions proceed through the formation of molecular species rather than ruthenium nanoparticles. On the other hand, the performance of the $RuH_2(CO)(o\text{-}TPPTS)_3$ catalyst in the aqueous-biphasic hydrogenation of the individual olefin (1-hexene, styrene and 2-pentene) and their equimolar mixture was also evaluate from a kinetic point of view. When individual hydrogenation of each olefin is performed, 1-hexene was hydrogenated quicker than styrene. However, when we analyze the olefin mixture, styrene hydrogenates faster than 1-hexene; in both cases, 2-pentene is the alkene that exhibits the least activity towards hydrogenation. This is because there is competition for the active sites of the catalyst and the formation of catalytically active species in appreciable concentrations, so that styrene, the alkene which has the greatest coordination ability, is now hydrogenated more rapidly than 1-hexene. Also was demonstrate that this complex can be recycle for three times without significant decrease of its activity, as long as the ruthenium remains in the aqueous phase. However, only the isomerization products were obtained in the fourth recycling cycle.

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Caption for Schemes and Figures

Figure 1. Effect of hydrogen pressure on the biphasic hydrogenation of 1-hexene in water/n-heptane by use of $H_2Ru(CO)(o\text{-TPPTS})_3$ at 100 ºC and S/C = 100: (a) Reaction profile at 600 psi (41.4 atm) of H_2; (b) Reaction profile at 800 psi (55.2 atm) of H_2; (c) Reaction profile at 900 psi (62.1 atm) of H_2 d) Distribution products at different hydrogen pressures at 2 h. At the end of reaction, the percentage of isomers was less than 2.0%.

Figure 2. Effect of temperature on the biphasic hydrogenation of 1-hexene in water/*n*-heptane by use of $H_2Ru(CO)(o\text{-}TPPTS)_3$ at 900 psi H_2 and S/C = 100: (a) Reaction profile at 80 ºC; (b) Reaction profile at 90 ºC; (c) Reaction profile at 100 ºC; (d) Reaction profile at 110 ºC; (e) Distribution products at different temperatures at 2 h. At the end of the reaction (4 hours), the percentage of isomers remained between 1.0% and 2.0%.

Figure 3. Effect of substrate/catalysts ratio (S/C) on the biphasic hydrogenation of 1-hexene in water/*n*-heptane by use of $H_2Ru(CO)(o\text{-}TPPTS)_3$ at 100 ºC and 900 psi H_2: (a) Reaction profile at S/C of 20/1; (b) Reaction profile S/C of 40/1; (c) Reaction profile at S/C of 80/1; (d) Reaction profile at S/C of 100/1; (e) Reaction profile at S/C of 400/1; (f) Distribution products at different substrates/catalyst ratio at 2 h. At the end of the reaction, the percentage of isomers was less than 1.5%.

Figure 4. Comparison of catalytic activities and product distribution of the water soluble complexes $Ru(H)_2(CO)(o\text{-}TPPTS)_3$ and $Ru(H)_2(CO)(m\text{-}TPPTS)_3$ in the hydrogenation of 1-hexene with the best operational condition parameters [T = 100 ºC (373.15 K), P = 900 psi of H_2 (62.1 atm), stirring speed = 800 rpm, substrate/catalyst ratio = 100/1 and t = 4 h]: (a) Reaction profiles; (b) Distribution products at different substrates/catalyst ratio at 2 h. At the end of the reaction, the percentage of isomers was less than 2.0%.

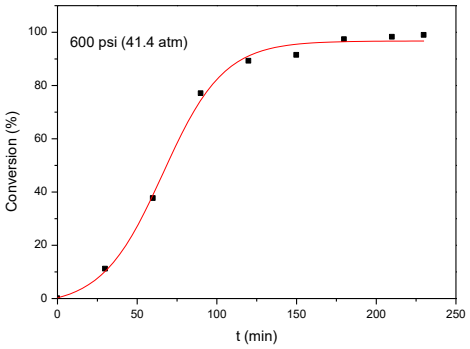
Figure 5. Biphasic hydrogenation of individual alkenes by use of $H_2Ru(CO)(o\text{-}TPPTS)_3$. Conditions: [1-hexene] = 0.13 M; [cat] 1.3 mM; reaction time: 4 h; P = 900 psi (62.1 atm); T= 100°C; S/C = 100/1 stirring speed = 800 r.p.m; C_A/C_{Ao}: $[Alkene]/[Alkene]_o$.

Figure 6. Biphasic hydrogenation of a equimolar alkenes mixture by use of $H_2Ru(CO)(o\text{-}TPPTS)_3$. Conditions: [1-hexene] = [styrene] – {2-pentene = 0.043 M; [cat] 1.3 mM; reaction time: 4 h; P = 900 psi (62.1 atm); T= 100°C; S/C = 100/1 stirring speed = 800 r.p.m; C_A/C_{Ao}: $[Alkene]/[Alkene]_o$.

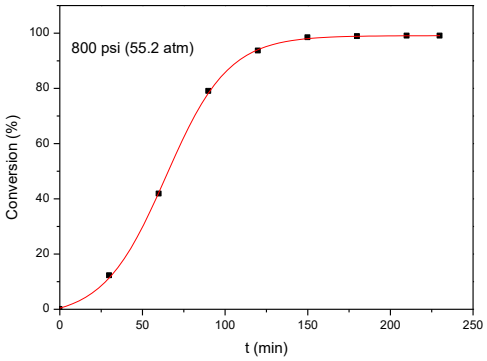
Scheme1. Aqueous-biphasic hydrogenation of tested olefins and their expected products.

Scheme2. Proposed catalytic cycle for alkene hydrogenation and isomerization catalyzed by $H_2Ru(CO)(o\text{-}TPPTS)_3$ in the heptane/water biphasic system.

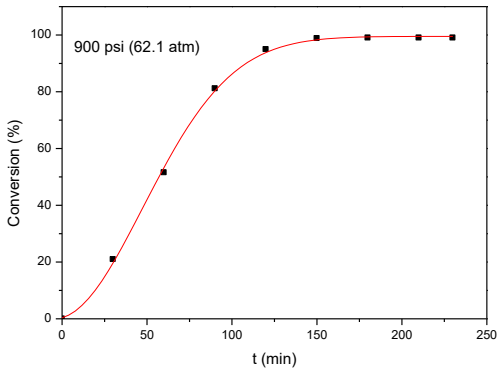
Figure 1



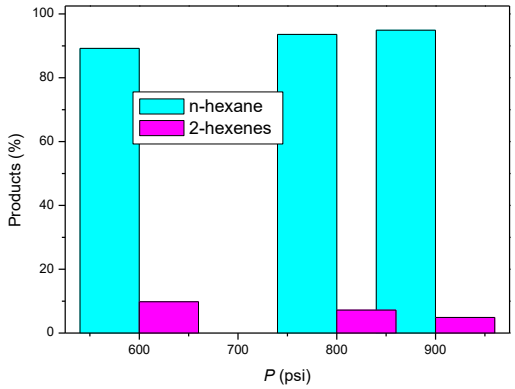
(a)



(b)

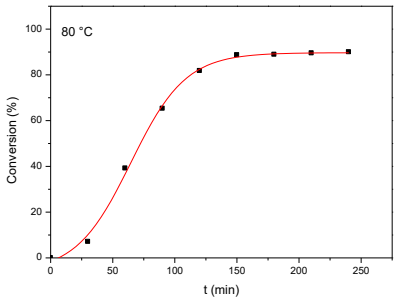


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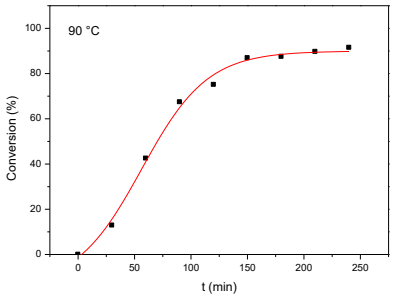


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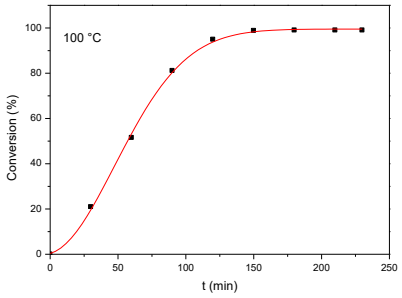
Figure 2



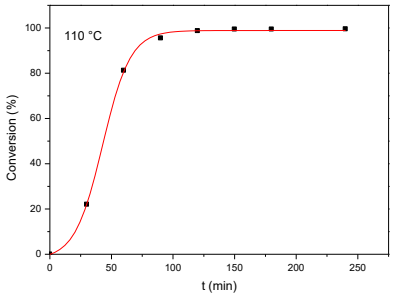
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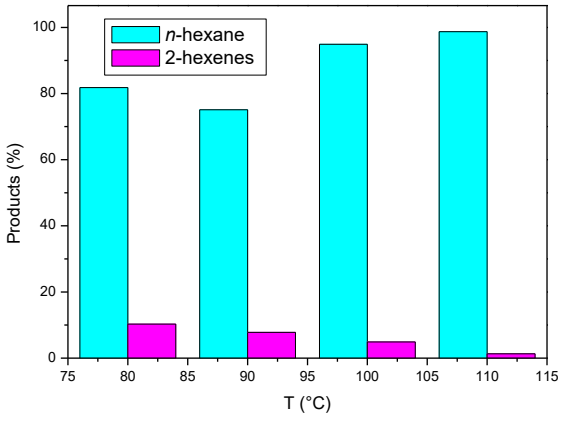
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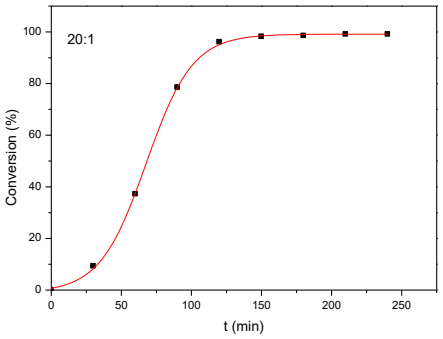


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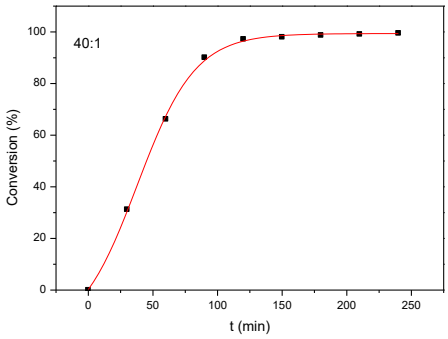


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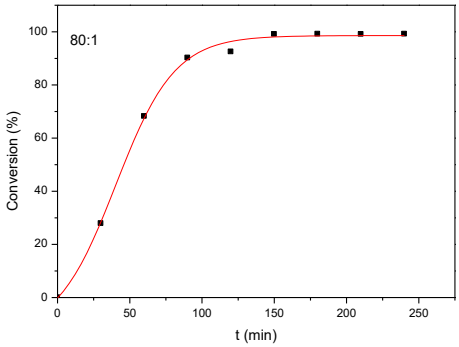
Figure 3



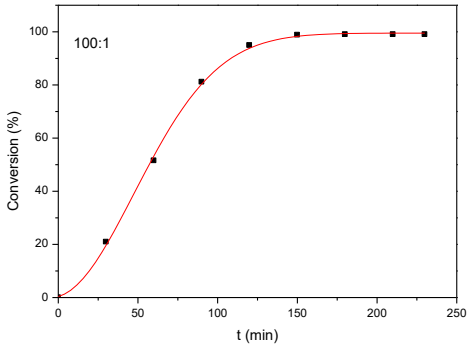
(a)



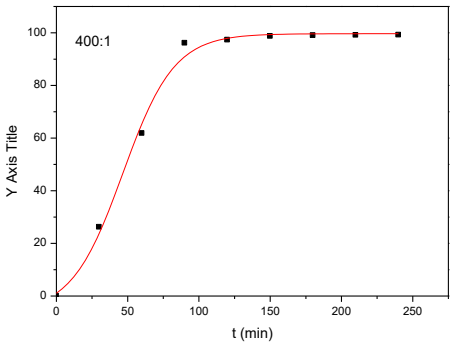
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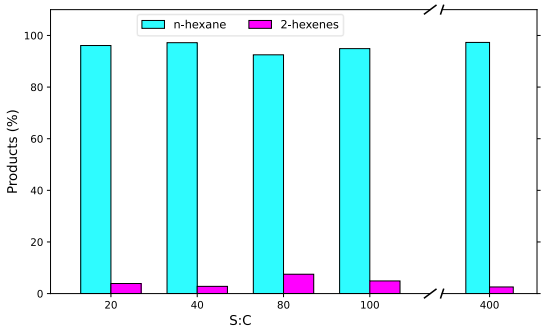
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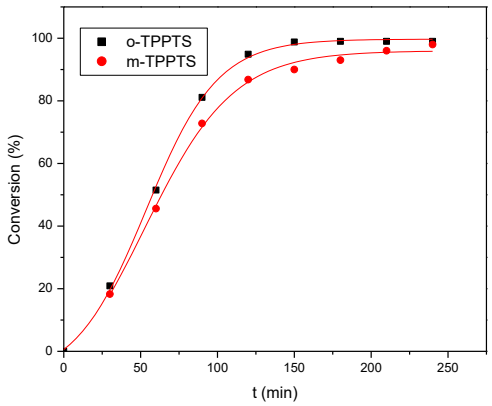


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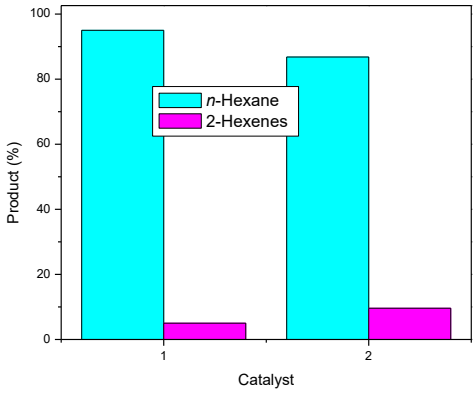


(f)

Figure 4

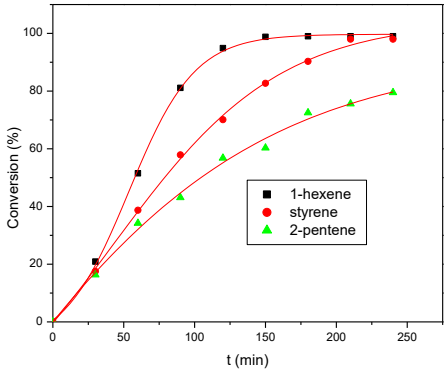


(a) Reaction profile using ruthenium complexes with *ortho* and *meta*-TPPTS

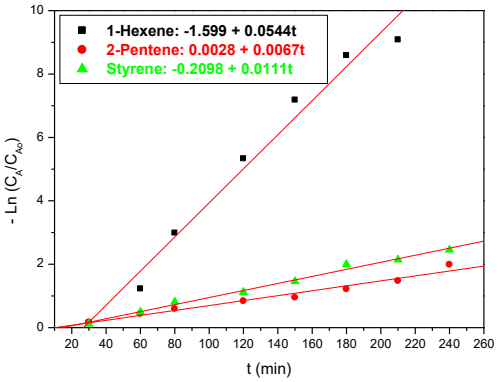


(b) Distribution of products using ruthenium complexes with *ortho* (1) and *meta*-TPPTS (2).

Figure 5

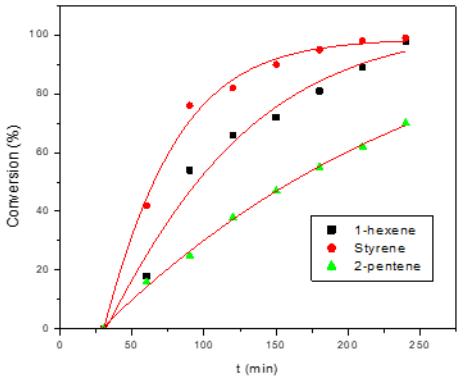


(a) Reaction profiles

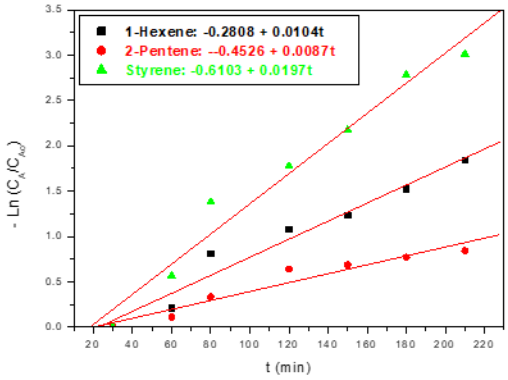


(b) Plots of ln (C_A/C_{Ao}) *versus* time

Figure 6

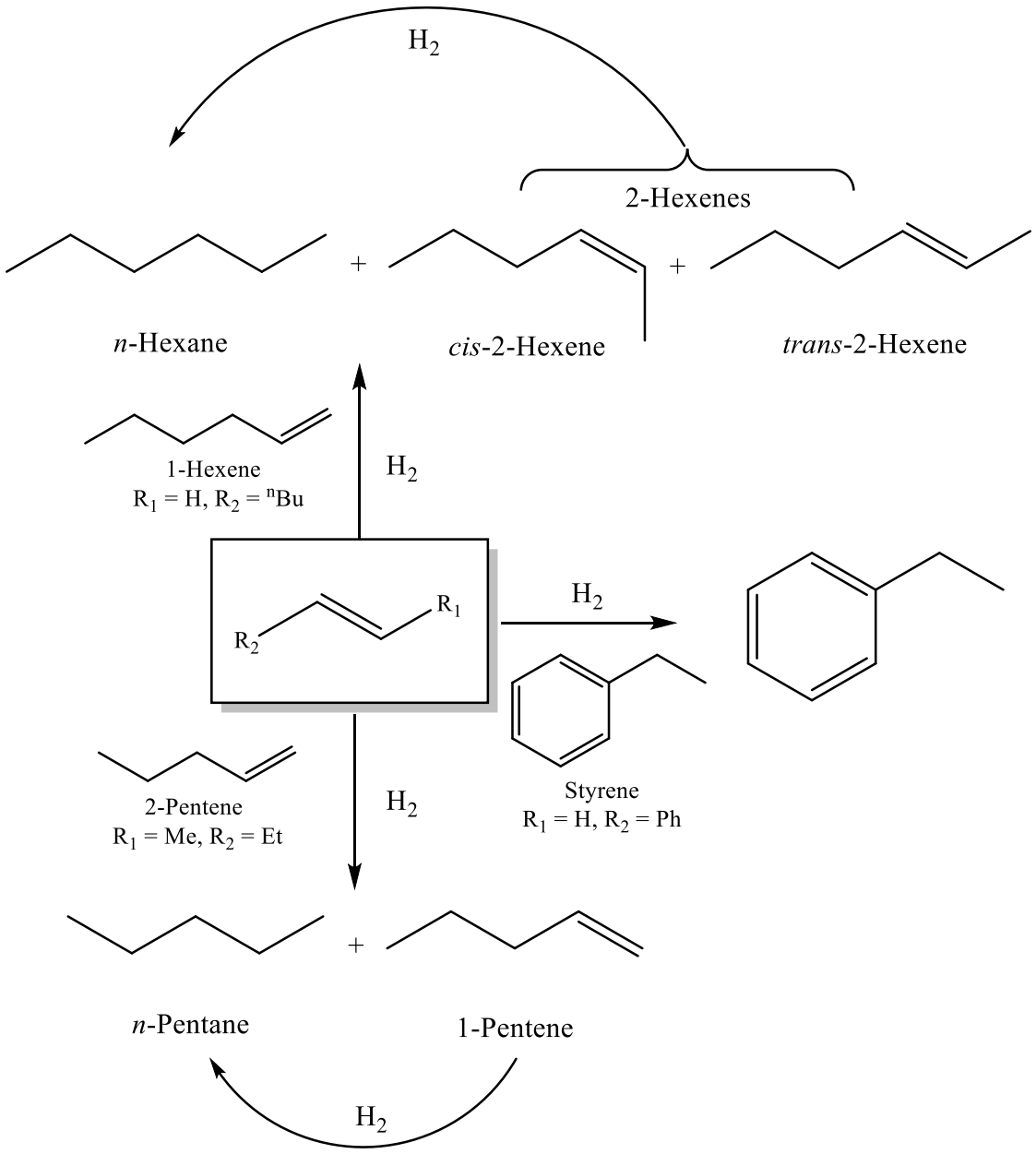


(a) Reaction profiles

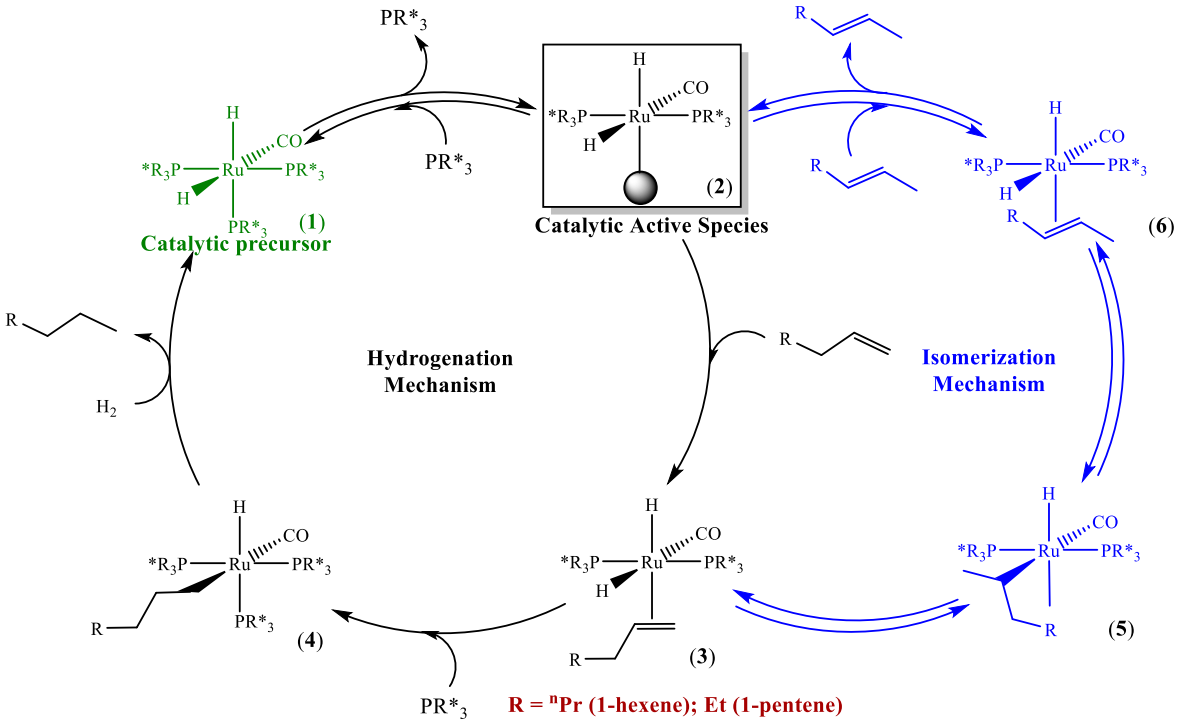


(b) Plot of ln (C_A/C_{Ao}) *versus* time

Scheme 1


H2
2-Hexenes
+
+
n-Hexane
cis-2-Hexene
trans-2-Hexene
1-Hexene
R1 = H, R2 = nBu
H2
R1
R2
H2
Styrene
R1 = H, R2 = Ph
2-Pentene
R1 = Me, R2 = Et
H2
+
n-Pentane
1-Pentene
H2

Scheme 2


PR*3
H
CO
*R3P
Ru
PR*3
H
PR*3
(1)
Catalytic precursor
(2)
Catalytic Active Species
R
(6)
Hydrogenation
Mechanism
Isomerization
Mechanism
H2
(4)
(3)
(5)
R = nPr (1-hexene); Et (1-pentene)

Supplementary Files

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