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Hydroformylation of natural olefins with the $[Rh(COD)(\mu\text{-}OMe)]_2$/TPPTS complex in BMI-$BF_4$/toluene biphasic medium: Observations on the interfacial role of CTAB in reactive systems

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The complex $[Rh(COD)(\mu\text{-}OMe)]_2$ in presence of TPPTS (TPPTS = triphenylphosphinetrisulfonate) was evaluated as catalyst precursor for the *in situ* hydroformylation of natural olefins (eugenol, estragole and safrole) in biphasic media BMIm-BF_4/toluene. Under moderate reaction conditions, the substrates showed the following reactivity order: eugenol > estragole > safrole. The rhodium system showed a high activity and selectivity towards the desired aldehydes. It was found that the use of cetyltrimethylammoniun bromide (CTAB) as phase transfer agent inhibits the hydroformylation reaction. The catalytic phase can be recycled up to four times without evident loss of activity or selectivity. In this work we report the use of an ionic liquid with hydrophilic character, without using water in the reaction medium.

1. Introduction

The hydroformylation of naturally occurring olefins such as eugenol, estragole, safrole and others allylbenzenes readily available from biomass is a very important method to obtain oxygenated products like aldehydes and alcohols of high added value, relevant in flavor, cosmetic and pharmacy industries [1–4]. Several groups have studied the homogeneous hydroformylation of allylbenzenes over the last years. Kalck et al. [5] studied the hydroformylation of eugenol, estragole and safrole with the system $[Rh(\mu\text{-}SR)_2(CO)_2L_2]$ where L = PPh_3, $P(OPh)_3$ and $P(OMe)_3$ and obtained high regioselectivity towards the linear aldehydes (80–96 %). Dos Santos et al. [3] reported a very interesting study about the hydroformylation of allylbenzenes and propenylbenzenes using the system $[Rh(COD)(OAc)]_2$/L, where L = mono- and diphosphines. When monophosphines were used, the activity and regioselectivity of the reaction depended of the basicity of the ligand whereas with diphosphines, the regioselectivity depended on the bite angle, favoring the formation of the lineal aldehyde when wide angled ligand is used. Claver et al. [6] reported the hydroformylation of *trans*-anethole and estragole by the system $[Rh(acac)(CO)_2]$ with carbohydrate derived diphosphite. A very good yield in branched aldehydes was observed during the hydroformylation of *trans*-anethole and moderate regioselectivity with estragole. Paganelli et al. [7] reported the hydroformylation of *m*-diisopropenylbenzene in homogeneous, heterogeneous and biphasic systems as the first step in the preparation of the mono-aldehyde Florhydral, using rhodium as catalyst precursor and sodium tri(*m*-sulfonatephenyl)phosphine (TPPTS, commonly known as triphenylphosphinetrisulfonate) or the biopolymer HSA (human serum albumin) as auxiliary ligands; they reported the best results using the high water soluble ligand TPPTS. Recently, Melean et al. [8] have been involved in the functionalizing of naturally occurring olefins like allylbenzenes (eugenol, estragole, safrole and *trans*-anethole). The hydroformylation of allylbenzenes was achieved for the first time with water-soluble catalyst precursors of Rh and Ru in biphasic media, which represents an interesting new alternative to obtain aldehydes of high added value. In this order of ideas, Baricelli and dos Santos research groups [9] reported the hydroformylation of eugenol, estragole and safrole in rhodium aqueous biphasic system promoted by mono- and diphosphines. The ratio linear to branch aldehydes (l/b) can be controlled by the nature of water-soluble phosphorous ligands. The

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conventional TPPTS ligand provided the preferential formation of the lineal aldehydes, while with the tetrasulfonate diphosphines (DPPETS and DPPPTS) the regioselectivity was switched to the branched isomer. In biphasic catalysis, CTAB has been used as a phase transfer agent. In the toluene/water systems the presence of the surfactant increases the conversion. However, the role and mechanism of action on the interaction of surfactant and system components is not well understood. In our group, we have focused to study a very interesting alternative in biphasic catalysis, which is the system organic and ionic liquids phase. Baricelli et al. [10] reported the activity and selectivity of the biphasic ionic liquid/toluene system using the catalytic precursor $[Rh(CO)(Pz)(TPPMS)]_2$ in the modification of naturally occurring olefins in the hydroformylation of terpenes and allylbenzenes, as well as in the hydrogenation of α,β-unsaturated aldehydes. This catalyst showed good behavior during it reuse up to five times without any loss of the activity or selectivity.

In the present work we report for the first time the *in situ* hydroformylation of natural olefins (eugenol, estragole and safrole) in biphasic media $BMIm\text{-}BF_4$/toluene with $[Rh(COD)(\mu\text{-}OMe)]_2$ in presence of TPPTS as the catalytic precursor. Additionally, we conducted interaction studies between the CTAB and the components present in the catalytic system in aqueous media by means of surface tension measurements. We intend to do a first approach about the interfacial phenomena related to the role of CTAB like as agent mass transfer.

2. Experimental

2.1. General procedure

All manipulations were carried out under nitrogen using standard Schlenk techniques [11]. Organic solvents were dried and purified by distillation over standard agents under N_2 or Ar prior to use. All other chemicals were commercial products and were used without further purification. All gases were of high purity (99.99 %) and were purchased from Aga-Gases (Venezuela).

$[Rh(COD)(\mu\text{-}OMe)]_2$ [12] and TPPTS [13] were prepared according to published procedures. Eugenol, estragole and safrole were purchased from Aldrich and bubbled with argon or nitrogen prior to use. Toluene was refluxed with sodium/benzophenone and cetyltrimethylammoniun bromide (CTAB) was purchased from Aldrich and used as received.

Infrared spectra were recorded in a Perkin Elmer Spectrum 1000 FTIR using samples as KBr disks. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 500 MHz spectrometer, using deuterated solvents. All chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (^1H) or 85 % H_3PO_4 (^{31}P). GC analyses were performed on a Hewlett Packard 5971 Pluss Series II chromatograph with a flame ionization detector in an ultra-1, DB-1, (10 % dimethyl polixilosane), 25 m, 0.32 mm, 0.52 μm column to separate the products. Quantification was achieved by using n-heptane as the internal standard and all peaks were identified by GC/MS on a Digital Technology 5890/5971 coupled system using a Quadrex PONA 10 % dimethyl polixilosane, 25 m, 0.52 μm.

2.2. Biphasic hydroformylation of natural olefins

In a typical experiment, the catalyst precursor $[Rh(COD)(\mu\text{-}OMe)]_2(0.25 \times 10^{-5}$ mol) in 1 mL of ionic liquid $BMI\text{-}BF_4$ and the solution of the corresponding substrate eugenol, estragole or safrole (10 mmol) in 1 mL of toluene and TPPTS (5×10^{-5} mol), were introduce into a stainless steel reactor (Parr instruments, 5 mL) equipped with a magnetic stirring bar. The system was purged three times and loaded to the required syn-gas (CO/H_2, 1:1) pressure; then the reactor was submerged in a glycerin bath and adjusted to the desired temperature. When the reaction was completed, the reactor was cooled and slowly vented, the phases were separated and the organic phase was analyzed by GC and GC–MS techniques.

2.3. Surface tension measurement

Surface tension of the different systems was determined at room temperature using a Cole Palmer Model 21 tensiometer and du Noüy ring method with a platinum-iridium ring with a circumference of 6 cm. All solutions were allowed to stand for 24 h to achieve equilibrium. Surface tension was obtained by plotting surface tension *versus* the logarithm of the solute concentration. Aqueous 10 % (w/v) stock solutions were prepared for the samples TPPTS, TPPMS, rhodium complex, rhodium complex-H_2/CO-TPPTS, cetyltrimethylammonium bromide (CTAB), as well as 1:1 wt ratio mixture of TPPTS/CTAB and TPPMS/CTAB. Diluted solution was prepared from stock solution on concentration interval of 0,099 and 2,0 %.

2.4. Catalytic recycling experiments

The catalytic phase was reused from 2 to 5 times. The general procedure for the recycling experiments is similar to that described in the prior section. Once the samples were extracted, they were cooled, the phases separated under *aerobic* condition and the organic phase analyzed. The catalytic ionic liquid phase was mixed with a fresh organic phase that contain the substrate (10 mmol) in toluene (1 mL), introduced again into the autoclave purged three times with syn-gas (1:1 $CO + H_2$), then charged with the required pressure and heated to the desired temperature, and finally the procedure re-started.

3. Results and discussion

3.1. Biphasic hydroformylation of eugenol

A preliminary study was conducted in order to determine the best operational conditions for the biphasic hydroformylation of eugenol as model molecule using the binuclear water-soluble catalytic system $[Rh(COD)(\mu\text{-}OMe)]_2$/TPPTS. Similar reaction conditions than those used for our group in aqueous biphasic systems [9] were employed for ionic liquid/toluene biphasic medium, except pressure and temperature, which were determinate and obtaining new values of 110 °C and 55 bars, respectively, and thus completing the best operational parameters. The $BMIm\text{-}BF_4$ was selected due to its hydrophilic properties, which let a very good solubility of the catalytic precursor and TPPTS in the ionic liquid phase. Once the reaction conditions were determined, the hydroformylation of eugenol was studied. The reproducibility of this reaction was also confirmed; the results are summarized in Table 1.

As it can be seen from runs I—IV in Table 1, the conversion and reproducibility of the hydroformylation of eugenol is very good with 99 % of total conversion and 94 % of selectivity towards the aldehydes (70 % lineal and 30 % branched, l/b ≈ 2.3), obtaining a turnover frequency (TOF) of (32 ± 1) TON min^{-1} [TON = 1920 in 1 h, TON (turnover number) = mol products/mol catalyst]. These results are very similar to those reported for our groups for aqueous biphasic system [9]. However, in our $BMIm\text{-}BF_4$ system, no cetyltrimethylammoniun bromide (CTAB) as phase transfer agent was used because completely inhibits the hydroformylation reaction probably due to the stabilization of the ionic species from the ionic liquid interacting with the ones from the CTAB in the interphase of the system and hindering the interaction ionic liquid-catalytic precursor-substrate [10]. In other words, the catalytic activity of the system $[Rh(COD)(OAc)]_2$/L was lost completely. However, the hydroformylation of eugenol could be performed in aqueous biphasic system as was reported by our group [9]; in this case, the addition of small amounts of CTAB accelerated the reaction significantly, promoting a complete conversion of eugenol in only 20 min with excellent selectivity (95 %) for aldehydes. In our study showed in Fig. 1, the amount of CTAB was varied from 0 until 1×10^{-2} M, in order to establish the maximum reaction rate in our system. The used amount of CTAB was 1×10^{-3} M. Similar results were published by dos Santos et al. [14] and Chen et al. [15] for aqueous similar systems. However, our

Table 1
Hydroformylation of eugenol with $[Rh(COD)(\mu\text{-}OMe)]_2$/TPPTS in $BMI.BF_4$/toluene biphasic system.

Run	Conversion (%)	TOF[a] (TON min^{-1})	Rate (bar/min)	Aldehyde Selectivity (%)	Branched Aldehyde (%)	Lineal Aldehyde (%)	l/b[b]
I	99	33	0.23	94	31	69	2.2
II[c]	99	32	0.23	94	31	69	2.2
III[c]	99	30	0.23	94	30	70	2.3
IV[c]	99	34	0.23	94	30	70	2.3

Reaction conditions: Eugenol (10 mmol), $[Rh(COD)(\mu\text{-}OMe)]_2$ (0.25×10^{-5} mol), Rh (0.5×10^{-5} mol), TPPTS (5×10^{-5} mol) Temperature: 110 °C, Pressure: 55 bar (H_2/CO: 1:1), Volume $BMI.BF_4$: 1 mL, Volume toluene: 2 mL; time: 120 min.

[a] TON: mol of products/mol catalyst.

[b] l/b: linear to branched ratio.

[c] The hydroformylation of eugenol was performed four times in order to assure the reproducibility of the reaction.

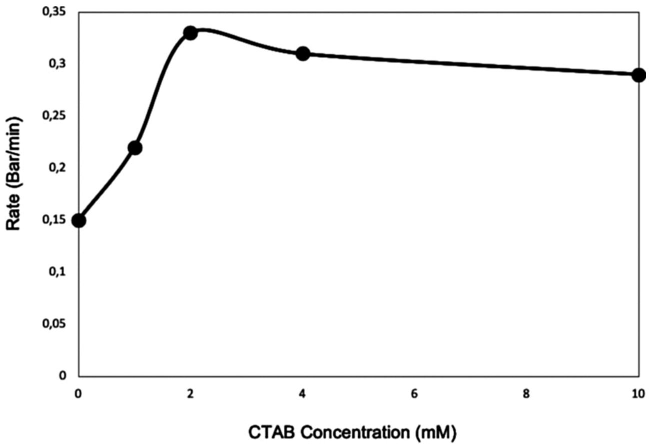

Fig. 1. Variation of CTAB concentration during eugenol biphasic hydroformylation.

$BMI.BF_4$ /toluene medium, behave completely different.

The good conversion and selectivity of the catalytic precursor can be attribute to the formation of very active mononuclear rhodium species in solution like $[HRh(CO)(TPPTS)_2]$ or $[HRh(CO)_2(TPPTS)]$, due to the rupture of the initial $[Rh(COD)(\mu\text{-}OMe)]_2$ dimer in the presence of the phosphine. By comparison with the published and very interesting similar complexes and observations [16–18], the formation of mononuclear rhodium species is mainly responsible of the hydroformylation reaction in this kind of systems. Other examples about the formation of this mononuclear species has been reported by Joó and Alper [19] in the biphasic reduction of nitro compounds using bimetallic $[(1,5\text{-}HD)RhCl]_2$(1,5-HD: 1,5-hexadiene) and chlorodicarbonylrhodium (I) dimer, the $[1,5\text{-}HDRhCl]_2$ was converted to mononuclear specie $Rh(CO)_2Cl$ which corresponded to the nitro-amine conversion. However, no reaction was observed when a phase transfer catalyst was present [dodecyltrimethyl-ammonium chloride (DTAC), tetrabutylammonium chloride, tetra-butylammonium hydroxide]. Similar observation also were reported by our group when a rhodium binuclear complex $[Rh(CO)(\mu\text{-}Pz)(TPPTS)]_2$ was used in the hydroformylation of 1-hexene [20]. Finally, we wish to mention that non any solid complex was observed during the hydroformylation reaction in our catalytic systems in the above used reaction conditions.

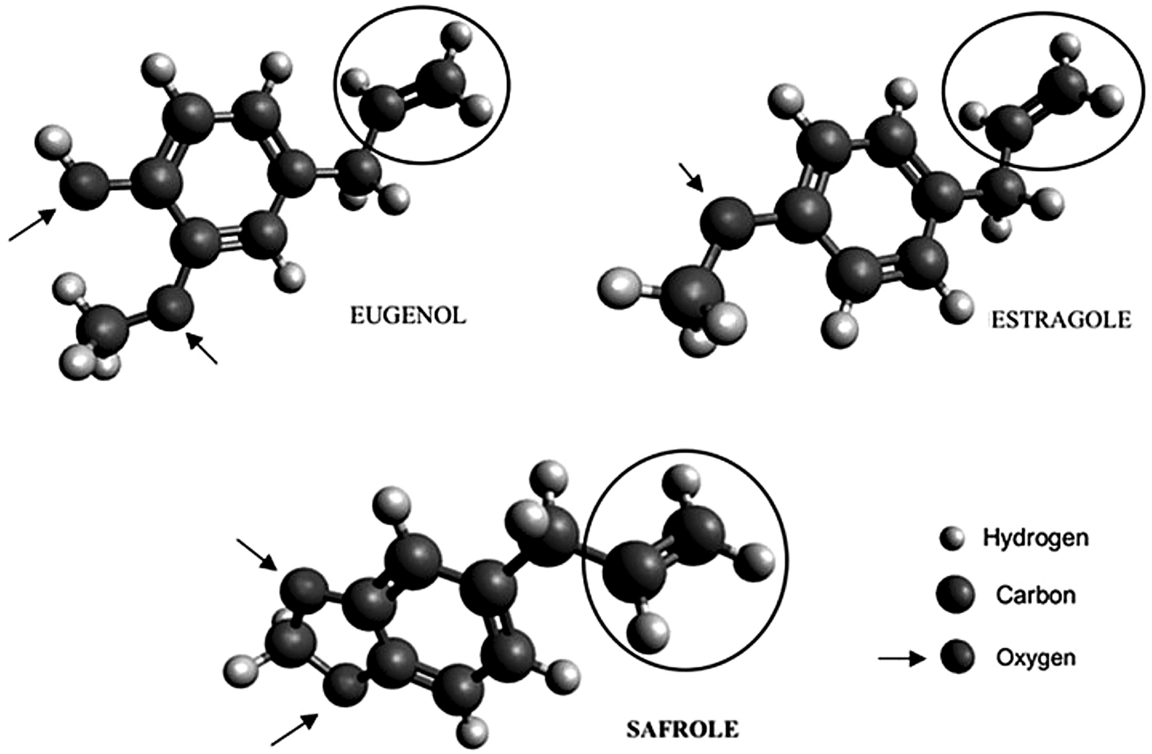

Fig. 2. Optimized structures of different allybenzenes.

3.2. Biphasic hydroformylation of allylbenzenes

Even when eugenol, estragole and safrole belong to the same allylbenzenes family, they have shown a very different conversion profile related with the rate of hydroformylation reaction because of their marked structural differences. We can observe in Fig. 2 that all molecules, have an aromatic ring connected to the allylic chain. The reactivity of the terminal double bond will depend of the chemical environment and of the substituent on the aromatic ring and also the orientation of the double bond according with the π electronic density of the aromatic ring.

In order to study the behavior of others allylbenzenes molecules, the hydroformylation reaction of estragole and safrole were carried out, using the same reaction condition than the above for eugenol. As shown in Fig. 3, eugenol (**1**), can undergo several competing transformation under the reaction conditions used in our experiments: hydroformylation to give the lineal (**2**) and branched aldehydes (**3** and **4**), hydrogenation to form the saturated product (**5**) and isomerization to yield (**6**), which can be also hydroformylated to form branched aldehydes (**3** and **4**).

Similarly, in Figs. 4 and 5, are specified the corresponding products from the hydroformylation reaction of estragole and safrole.

As it can be seen from runs I-III (Table 2), the hydroformylation of estragole and safrole [TOF of 27 and 5 TON min^{-1} (TON = 1620 and 320 in 1 h), respectively] occur more slowly than eugenol (TOF = 32 TON min^{-1}, TON = 1920); the regioselectivities are 1.9 for safrole and 2.0 for estragole. These results can be explained because eugenol have better solubility on the ionic liquid phase due to the hydroxyl group present on its aromatic ring which is lacking on estragole and safrole. Both reached quantitative conversion in 140 min while safrole required 900 min evidencing the eugenol hydrophilic character, which is according with its bigger hydroformylation rate in the BMI-BF$_4$/toluene biphasic system. Under the reaction conditions studied in our experiments, the rhodium system showed a high activity and selectivity towards the desired aldehydes, especially to the lineal isomer.

3.3. Surface tension measurement in aqueous system

Biphasic catalysis is based on the conversion of the reactants at the interface. Only some technique can make measures that will permit to known and deeping of this phenomenon. Surface tension measures have a broad use in surface and colloidal chemistry for many industrial and academics applications. Self-assembly and adsorption phenomena have been understanding through of the interpretation of these measures. For this reason, it is important to know the different interfacial activities of the components involved such as catalyst, ligand, surfactants, among others. The systems were evaluated in aqueous phase as a first approach to understand the formation of complexes and their effect on interfacial adsorption. Water is a universal solvent and the hydrophobic effect act as a driving force on the species present in the aqueous phase.

In Fig. 6, the plot of surface tension as a function of the concentration of different substances is observed. The chart includes the CTAB for comparative purposes, as cationic surfactant represents the substance with greater interfacial activity. The values below the line indicate species with higher interfacial activity than the CTAB. Likewise, the species that are above this reference line correspond to species with lower interfacial activity.

The Rh complex [Rh(COD)(μ-OMe)]$_2$ is the one that showed the greatest interfacial activity of the substances. This is indicative that the complex has a suitable hydrophilic-lipophilic balance (HLB) to be adsorbed at the interface. This is reasonable according to its action as a catalyst in the two-phase system.

Regarding the TPPTS and TPPMS ligands, it is evident that greater concentration than CTAB is required to achieve a decrease in the surface tension of the water. TPPMS is the one that shows greater interfacial activity because its structure has less sulfonic groups, which give it the hydrophilic character. For TPPTS, the higher sulfonic group content gives it greater solubility in water and therefore decreases its adsorption at the interface. In the case of the CTAB-TPPTS and CTAB-TPPMS mixtures, a significant variation in the surface tension of the ligands can be observed, which indicate the formation of a complex between both species. Due to the ionic nature of both species, it is logical to expect the formation of a complex by attracting opposite charges which causes that the species increase its hydrophobic character and therefore increase its adsorption at the interface. The mechanism of surfactant in biphasic catalysis requires greater understanding in relation to its impact on the chemical reaction that takes place [21]. The catalyst with the metal center and the ligands (TPPMS and TPPTS) are anionic in nature. This property indicates affinity for water and permanence in the liquid, which reduces the interfacial activity and therefore, catalytic action. When the reaction is carried out in the ionic liquid, the driving force for the transfer of the catalyst towards the interface is electrical in nature; the catalyst is transported to the interface by the solvent ions [22]. Ionic liquids have the property of transporting ions in their environment; in the aqueous phase, this driving force is the hydrophobic effect. Since the surfactant forms a complex with the ligands of the catalyst, which is rejected by water. The hydrophobic effect is a consequence phenomenon mainly of entropic nature since the water molecules must be reorganized to interact with the present solute (catalyst surfactant complex). The properties of surfactants such as micelle formation and decrease in

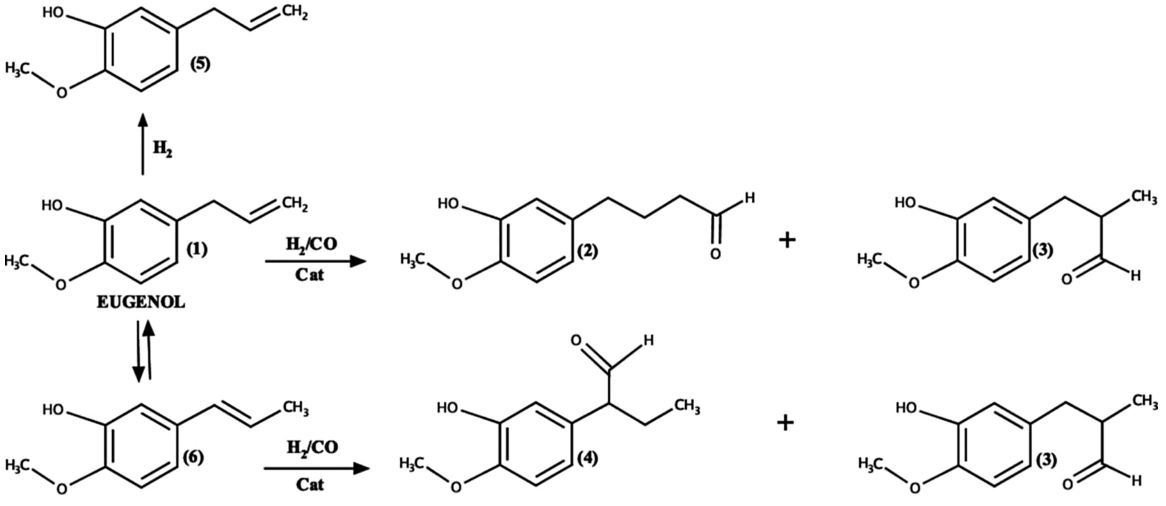

Fig. 3. Hydroformylation of Eugenol.

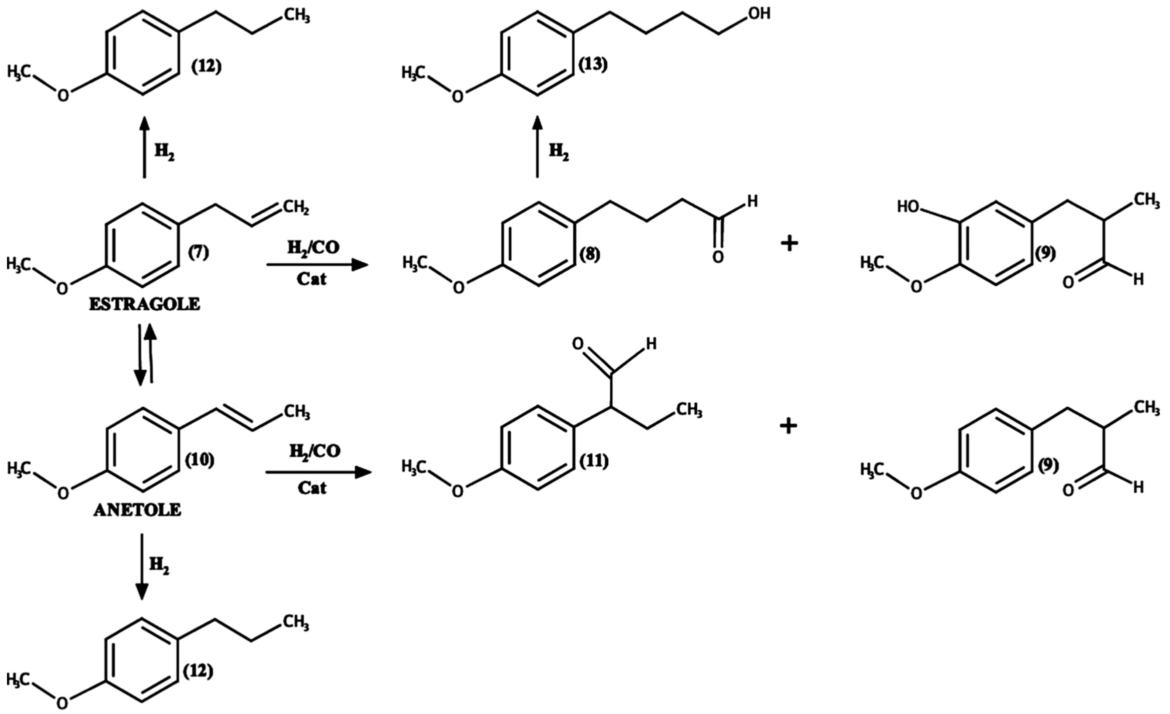

Fig. 4. Hydroformylation of Estragole.

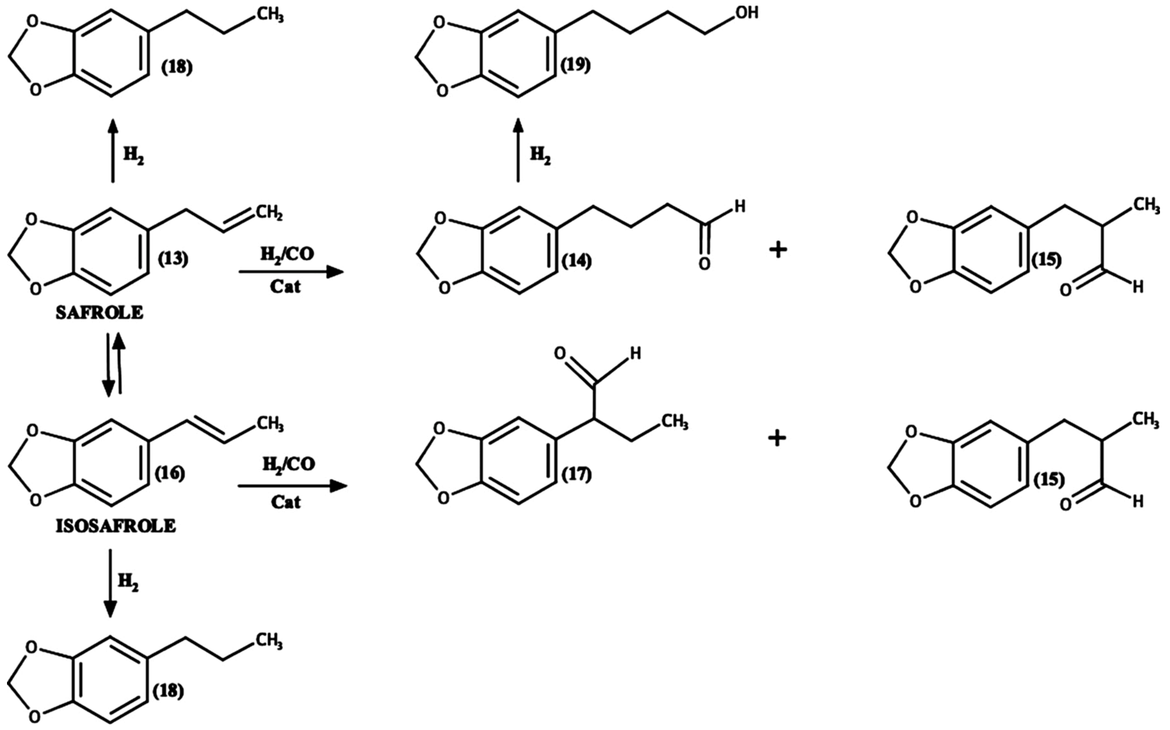

Fig. 5. Hydroformylation of Safrole.

surface tension are consequences of this effect [23].

Surface tension measurements in aqueous systems have been used to understand a large number of interfacial processes [24]. They have the advantage that the molecule with interfacial activity adsorbs on the surface from the bulk of the solution. The phenomena of partition towards the oil phase do not exist. Ionic liquids have a higher solvency capacity than water [25]. However, the phenomena are more difficult to interpret due to the variety of interactions that are present in ionic liquids. CTAB in ionic liquids can form micelles in the bulk and monolayers on the surface [26,27]. The solvophobic effect of ionic liquids on CTAB has been reported [28]. Therefore, we propose that the formation of the CATB monolayer inhibits the hydroformylation reaction, while the catalyst is solvated in the ionic liquid without be able to be adsorbed at the interface. In this way the CTAB do not function as a charge transfer agent, while in water the CTAB forms a complex due to the electrostatic forces that earn activity at the interface and also interfacial adsorption.

Table 2
Hydroformylation of differentallybenzenes with $[Rh(COD)(\mu\text{-}OMe)]_2$/TPPTS in BMI.$BF_4$/toluene biphasic system.

Run	Substrate	Time (min)	Conversion (%)	TOF[a] (TON min^{-1})	Rate (bar/min)	Aldehyde Selectivity (%)	Branched Aldehyde (%)	Lineal Aldehyde (%)	l/b[b]
I[c]	Eugenol	140	99	33	0.23	95	31	69	2.2
II[c]	Estragole	140	99	27	0.21	95	33	67	2.0
III[c]	Safrole	900	99	5	0.01	82	35	65	1.9

Reaction conditions: Substrate (10 mmol), $[Rh(COD)(\mu\text{-}OMe)]_2$ (0.25×10^{-5} mol), Rh (0.5×10^{-5} mol), TPPTS (5×10^{-5} mol) Temperature: 110 °C, Pressure: 55 bar (H_2/CO: 1:1), Volume BMI.BF_4 : 1 mL, Volume toluene: 2 mL.

[a] TON: mol of products/mol catalyst.

[b] l/b: lineal to branched ratio.

[c] The hydroformylation of these substrates was performed at leasttwice in order to assure the reproducibility of the reaction.

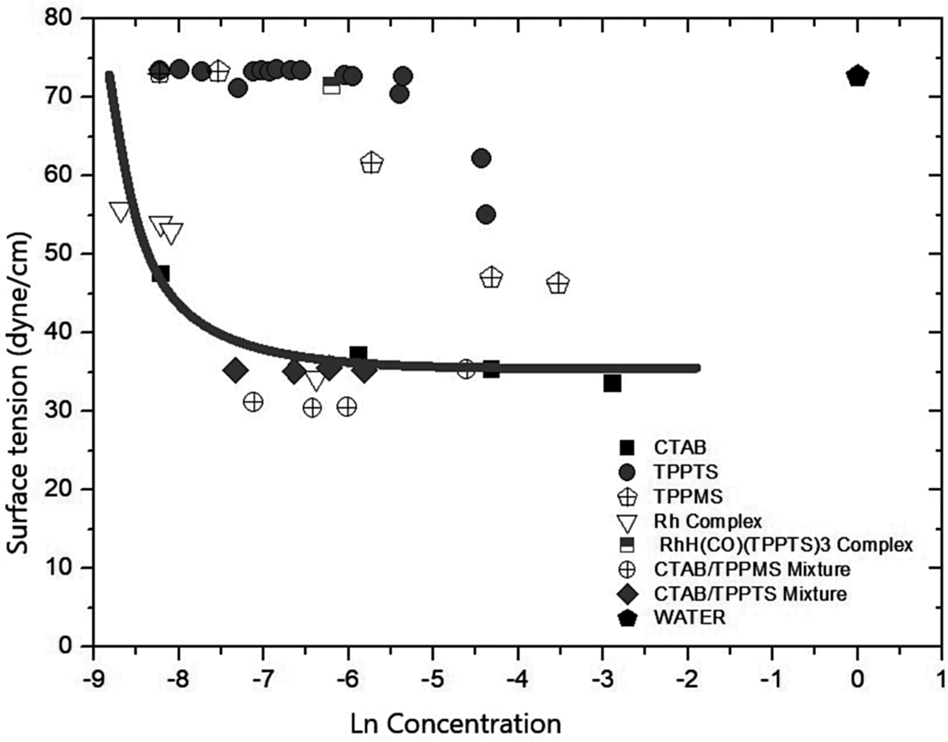

Fig. 6. Surface tension of amphiphilic molecules solutions.

3.4. *Catalyst recycling*

One aspect that is important to address in biphasic catalysis is the capability of reusing the catalyst precursor [29]. The BMI-BF_4/toluene system was investigated regarding recyclability of the catalytic precursor $[Rh(COD)(\mu\text{-}OMe)]_2$/TPPTS in the biphasic hydroformylation of eugenol. When the recycling experiments were carried out under aerobic conditions, the catalytic phase was used four consecutive times without significant loss of the activity and selectivity of the reaction, as it can be observed in Table 3. Also, the regioselectivity of the reaction favors the formation of the lineal isomer (**2**). However, from the four recycling a decrease in the conversion is expected probably due to the active specie is sensitive to the presence of air, leading probably their transformation in catalytically inactive specie. For the above reasons, a series of experiments in total anaerobic conditions are in progress in order to extend the recyclability of the active specie.

It is very important to emphasize the good performance in activity and selectivity that the system BMIm-BF_4/toluene showed in the

Table 3
Recycling of the catalytic phase in the hydroformylation of eugenol with $[Rh(COD)(\mu\text{-}OMe)]_2$/TPPTS in BMI.$BF_4$/toluene biphasic system.

Recycling	Conversion (%)	TOF[a] (TON min^{-1})	Rate (bar/min)	Aldehyde Selectivity (%)	Branched Aldehyde (%)	Lineal Aldehyde (%)	l/b[b]
–	99	33	0.23	94	31	69	2.2
I[c]	98	32	0.22	94	32	68	2.1
II[c]	98	30	0.19	92	31	69	2.2
III[c]	76	23	0.13	87	32	68	2.1
IV[c]	64	20	0.15	87	32	68	2.1

Reaction conditions: Eugenol (10 mmol), $[Rh(COD)(\mu\text{-}OMe)]_2$ (0.25×10^{-5} mol), Rh (0.5×10^{-5} mol), TPPTS (5×10^{-5} mol) Temperature: 110 °C, Pressure: 55 bar (H_2/CO: 1:1), Volume BMI.BF_4 : 1 mL, Volume toluene: 2 mL; time: 120 min.

[a] TON: mol of products/mol catalyst.

[b] l/b: lineal to branched ratio.

[c] Each reaction was performed at least twice in order to assure the reproducibility of the reaction.

hydroformylation reaction of eugenol and the others natural olefins, such as estragole and safrole, which open the possibility of to use a good biphasic system for the hydroformylation of natural olefins at industrial and academic setting.

4. Conclusions

The binuclear complex [Rh(COD)(μ-OMe)]$_2$ in the presence of TPPTS shows an excellent behavior in the biphasic hydroformylation of eugenol, estragole and safrole using the biphasic system BMIm-BF$_4$/toluene, which showed very good aldehydes conversion and also important activity and regioselectivity towards lineal aldehydes. The catalytic phase was reused until four times without significant loss of the activity and selectivity of the reaction. The use of phase transfer agent (CTAB) inhibits the hydroformylation reaction in our reaction conditions. As first vision, we proposed than the monolayer formation of CTAB at interface due solvophobic produced an effect in ionic liquids that block adsorption of catalyst inhibiting, as consequence, the hydroformylation reaction. However, in aqueous medium, the surface tension measurements show that the TPPMS ligand has the lowest surface tension. In the presence of CTAB, the formation of a complex with greater interfacial activity occurs, which would be responsible for the high conversion in aqueous systems.

Declaration of Competing Interest

The authors report no declarations of interest.

CRediT authorship contribution statement

Pablo J. Baricelli: Supervision, Project administration, Conceptualization. **Mariandry Rodríguez:** Investigation. **Luis G. Melean:** Investigation. **Margarita Borusiak:** Resources. **Isis Crespo:** Investigation. **Juan C. Pereira:** Investigation, Conceptualization. **Merlín Rosales:** Investigation, Conceptualization.

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References

[1] H. Siegel, W. Himmele, Angew. Chem. Int. Edu. 19 (1980) 178–183.

[2] (a) D.H. Grayson, Monoterpenoids, Nat. Prod. Rep. 5 (1988) 419–464, https://doi.org/10.1039/np9880500419;
(b) D.H. Grayson, Monoterpenoids, Nat. Prod. Rep. 15 (1998), https://doi.org/10.1039/a815439y, 449-475.H.

[3] A.C. da Silva, K.C.B. de Oliveira, E.V. Gusevskaya, E.N. dos Santos, Rhodium-catalyzed hydroformylation of allylbenzenes and propenylbenzenes: effect of phosphine and diphosphine ligands on chemo- and regioselectivity, J. Mol. Catal. A. Chem. 179 (2002) 133–141, https://doi.org/10.1016/S1381-1169(01)00408-3.

[4] (a) A.J. Chalk, in: W.M. Lawrence, B.D. Mookherjee, B.J. Willis (Eds.), Flavors and Fragances: A World Perspective. Proceeding 10th International Congress of Essential Oils, Fragances and Flavors, 1986, pp. 867–882. Washington D.C.;
(b) J. Chalk, in: P.N. Rylander, H. Greenfield, R.L. Agustine (Eds.), Catalysis of Organic Reactions, Vol 22, Marcel Dekker, New York, 1988, pp. 43–63.

[5] P. Kalck, D.C. Park, F. Serein, Influence of various parameters on the selectivity of the production of aldehydes starting from alkenes issued from the biomass and using the catalyst precursors Rh$_2$(μ-sr)$_2$(CO)$_2$(PA$_3$)$_2$, J. Mol. Catal. 36 (1986) 349–357, https://doi.org/10.1016/0304-5102(86)85091-X.

[6] M.R. Axet, S. Castillon, C. Claver, Rhodium-diphosphine catalysed hydroformylation of allybenzene and propenylbenzene derivatives, Inorg. Chim. Acta 359 (2006) 2973–2979, https://doi.org/10.1016/j.ica.2005.12.039.

[7] S. Paganelli, A. Ciappa, M. Marchetti, A. Scrivanti, U. Matteoli, Hydroformylation of *m*-di-isopropenylbenzene and 1-isopropyl-3-isopropenylbenzene for the preparation of the fragrance, Florhydral. J. Mol. Catal. A: Chem. 247 (2006) 138–144, https://doi.org/10.1016/j.molcata.2005.11.035.

[8] L.G. Melean, M. Rodríguez, M. Romero, M.L. Alvarado, M. Rosales, P.J. Baricelli, Biphasic hydroformylation of substituted allylbenzenes with water-soluble rhodium or ruthenium complexes, Appl. Catal. A Gen. 394 (2011) 117–123, https://doi.org/10.1016/j.apcata.2010.12.037.

[9] P.J. Baricelli, M. Rodriguez, L.G. Melean, M. Modrono-Alonso, M. Borusiak, M. Rosales, B. Gonzalez, K.C.B. de Oliveira, E.V. Gusevskaya, E.N. dos Santos, Rhodium catalyzed aqueous biphasic hydroformylation of naturally ocurring allylbenzenes in the presence of water-soluble phosphorus ligands, Appl. Catal. A Gen. 490 (2015) 163–169, https://doi.org/10.1016/j.apcata.2014.11.028.

[10] P.J. Baricelli, L.G. Melean, M. Rodríguez, M. dos Santos, M. Rosales, E. Escalante, Biphasic hydrogenation and hydroformylation of natural olefins with a binuclear rhodium complex in ionic liquid/toluene, J. Chem. Chem. Eng. 4 (2013) 299–305, https://doi.org/10.17265/1934-7375/2013.04.003.

[11] D.F. Shriver, The Manipulation of Air Sensitive Compounds, McGraw-Hill, USA, 1969.

[12] R. Usón, L.A. Oro, J.A. Cabeza, Dinuclear methoxy, cyclooctadiene, and barrelene complexes of rhodium(I) and iridium(I), Inorg. Synth. 23 (1985) 126, https://doi.org/10.1002/9780470132548.ch25.

[13] P.J. Baricelli, J. López, E. Lujano, F.J. López-Linares, Synthesis, characterization and catalytic applications in aqueous-biphasic system of a new tungsten complex W(CO)$_3$(CH$_3$CN)(TPPTS)$_2$, J. Mol. Catal. A 186 (2002) 57, https://doi.org/10.1016/S1381-1169(02)00066-3.

[14] H.J.V. Barros, B.E. Hanson, E.V. Gusevskaya, E.N. dos Santos, Biphasic hydroformylation of monoterpenes employing Rh/TPPTS/CTAC: the role of the substrate in the mass transfer between the phases, Appl. Catal. A: General 278 (2004) 57, https://doi.org/10.1016/j.apcata.2004.09.025.

[15] (a) H. Chen, Y. Li, J. Chen, P. Cheng, Y.E. He, X. Li, Micellar effect in high olefin hydroformylation catalyzed by water-soluble rhodium complex, J. Mol. Catal. A: Chem. 149 (1999) 1–6, https://doi.org/10.1016/S1381-1169(99)00165-X;
(b) H. Chen, Y. Li, J. Chen, P. Cheng, X. Li, Synergistic effect of TPPTS and TPPDS on the regioselectivity of olefin hydroformylation in two-phase catalytic system, Catal. Today. 74 (2002) 131–135, https://doi.org/10.1016/S0920-5861(01)00538-7.

[16] A. Aghmiz, A. Orejón, M. Diéguez, M.D. Miquel-Serrano, C. Claver, A.M. Masdeu-Bultó, D. Sinou, G. Laurenczy, Rhodium-sulfonated diphosphine catalyst in aqueous hydroformylation of vinyl arenes: high-pressure NMR and IR studies, J. Mol. Cat. A: Chem. 195 (2003) 113–124, https://doi.org/10.1016/S1381-1169(02)00544-7.

[17] B.R. James, D. Mahajan, Bis(ditertiaryphosphine) complexes of rhodium(I). Synthesis, spectroscopy, and activity for catalytic hydrogenation, Can. J. Chem. 57 (1979) 180–187, https://doi.org/10.1139/v79-030.

[18] (a) R. Davis, J.W. Epton, T.G. Southern, Hydroformylation of alkenes catalysed by [Rh(SR)(CO)PR′$_3$]$_2$: evidence for a mononuclear active species, J. Mol. Catal. A: Chem. 77 (1992) 159–163, https://doi.org/10.1016/0304-5102(92)80196-N;
(b) M. Dieguez, A. Ruiz, C. Claver, M.M. Pereira, M.T. Flor, J.C. Bayón, M.E. S. Serra, A.Md'A. Rocha Gonsalves, Synthesis, reactivity and catalytic properties of rhodium complexes of (R,R)-1-benzyl-3,4-dithioetherpyrrolidines, Inorg. Chim. Acta 295 (1995) 64–70, https://doi.org/10.1016/S0020-1693(99)00309-6.

[19] F. Joó, H. Alper, Novel coincidence effects in a bimetallic phase transfer catalyzed reaction. Biphasic reduction reactions catalyzed by rhodium carbonyl metallate clusters, Can. J. Chem. 63 (1985) 1157–1160, https://doi.org/10.1139/v85-196.

[20] P.J. Baricelli, F. López-Linares, S. Rivera, L.G. Melean, V. Guanipa, P. Rodriguez, M. Rodriguez, M. Rosales, Influence of the addition of thiophenes on the catalytic activity of the rhodium binuclear complex [Rh(CO)(μ-Pz)(TPPTS)]$_2$ during the biphasic hydroformylation of 1-hexene, J. Mol. Catal. A: Chem 291 (2008) 12–16, https://doi.org/10.1016/j.molcata.2008.05.010.

[21] T. Pogrzeba, M. Schmidt, N. Milojevic, C. Urban, M. Illner, J.-U. Repke, R. Schomäcker, Role of nonionic surfactants during catalysis in micro emulsion systems on the example of rhodium-catalyzed hydroformylation, Ind. Eng. Chem. Res. 56 (2017) 9934–9941, https://doi.org/10.1021/acs.iecr.7b02242.

[22] K. Ueno, M. Watanabe, From colloidal stability in ionic liquids to advanced soft materials using unique media, Langmuir 27 (2011) 9105–9115, https://doi.org/10.1021/la103942f.

[23] J.N. Israelachvili, Intermolecular and Surface Forces, third ed., Academic Press, USA, 2011.

[24] M.J. Rosen, Surfactants and Interfacial Phenomena, third. ed., John Wiley and Sons, Inc., New York, 2004.

[25] J.L. Anderson, J. Ding, T. Welton, D.W. Armstrong, Characterizing ionic liquids on the basis of multiple solvation interactions, J. Am. Chem. Soc. 124 (2002) 14247–14254, https://doi.org/10.1021/ja028156h.

[26] L.G. Chen, H. Bermudez, Solubility and aggregation of charged surfactants in ionic liquids, Langmuir 28 (2012) 1157–1162, https://doi.org/10.1021/la2040399.

[27] L.G. Chen, H. Bermudez, Probing the interface of charge surfactants in ionic liquids by XPS. Ionic Liquids: Science and Applications, American Chemical Society, 2012, https://doi.org/10.1021/bk-2012-1117.ch014. Chapter 4.

[28] J.L. Anderson, V. Pino, E.C. Hagberg, V.V. Sheares, D.W. Armstrong, Surfactan solution effects and micelle formation in ionic liquids, Chem. Commun. (2003) 2444–2445, https://doi.org/10.1039/B307516H.

[29] D. S.Bhaduri, Mukesh, Homogeneous Catalysis: Mechanism and Industrial Application, Wiley/Interscience, 2000. Chapt.1.