# Mobile phase effects in Rh/sulfonated phosphine/molten salts catalysed the biphasic hydroformylation of heavy olefins

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Rh(acetylacetonate)$(CO)_2$/sulfonated-Xantphos dissolved in pure 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid catalyses the hydroformylation of heavy olefins ($C_8$–$C_{12}$) with selectivities (up to 99% in *n*-aldehydes). The selectivity is strongly influenced by the nature of the ionic phase and co-solvent.

**KEY WORDS:** hydroformylation; ionic liquids; molten salts; rhodium; biphasic catalysis

## 1. Introduction

The hydroformylation of light alkenes catalysed by rhodium complexes associated with sulfonated phosphines is one of the most important and investigated reactions of aqueous biphasic catalysis [1]. This biphasic reaction mode is highly effective in catalyst separation and recycling [2] and it is employed industrially for the hydroformylation of light alkenes ($C_2$–$C_5$ olefins) [3]. However, the main drawbacks of this aqueous biphasic systems are the low reaction rates due to the phase-transfer limitations caused by poor substrate solubility in the aqueous phase such as those encountered in the hydroformylation of heavier alkenes ($C_8$–$C_{14}$ olefins) [4]. There are an increasing number of studies involving the development of other catalytic systems that would circumvent the phase-transfer limitations, such as supported aqueous-phase catalysis [5,6] and biphasic fluorous-phase catalysis [7]. Moreover, biphasic organometallic catalysis employing room temperature molten salts (ionic liquids) [8–10] as the mobile phase is now emerging as an important alternative for the immobilisation of transition-metal catalyst precursors. Indeed, this medium has been successfully used in the rhodium-catalysed hydroformylation of simple alkenes [11–13] and methyl-3-pentanoate [14]. We wish to report here our preliminarily results on the use of Rh(acac)$(CO)_2$/sulfonated Xantphos [15] (acac = acetylacetonate) immobilised in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (BMI.$PF_6$) [16] (scheme 1) catalytic system in the biphasic hydroformylation of heavy olefins (1-octene, 1-decene and 1-dodecene).

## 2. Experimental

### 2.1. General information

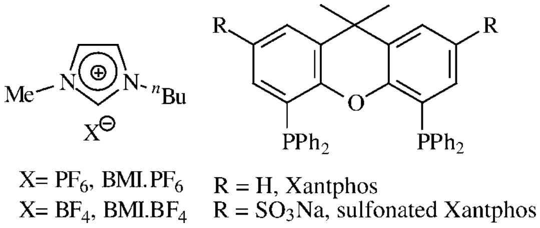
All catalytic reactions were carried out under an argon or nitrogen atmosphere in an oven-dried 100 ml capacity stainless-steel reaction vessel using a magnetic stirrer (300–350 rpm). Solvents were dried with adequate drying agents and distilled under argon prior to use. The Xantphos ligands [15] and the BMI.$PF_6$ ionic liquid [16] were prepared according to literature procedures. All the other chemicals were purchased from commercial sources (Strem or Aldrich) and used without further purification. Mass spectra were obtained using a GC/MS Shimadzu QP-5050 (EI, 70 eV). Gas chromatography analyses were performed with a Varian gas chromatograph with a FID and 30 m long capillary column with a dimethylpolysiloxane stationary phase and using di-*n*-butyl ether as standard. The organic compounds were characterised by CG-MS and by comparison of their CG retention times with those of authentic samples.

### 2.2. Immobilisation of the catalyst

The catalyst was immobilised by mixing Rh(acac)$(CO)_2$ (5 mg, 0.0194 mmol) with different concentrations of the phosphines in methanol at room temperature and adding to the BMI.$PF_6$ ionic liquid followed by evaporation of the volatiles at 40 °C under reduced pressure during 1 h affording a light yellow ionic liquid catalyst solution.

### 2.3. Catalytic experiments

Catalytic experiments were performed in a 100 ml capacity stainless-steel reaction vessel. The liquid ionic catalyst solution was previously prepared and the desired substrates (19.4 mmol) were transferred under argon to the reaction



Scheme 1.

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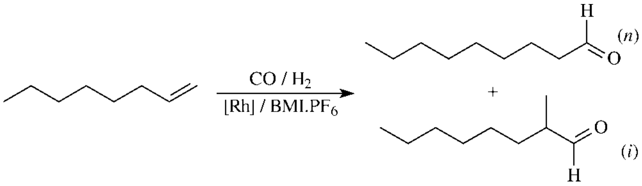
vessel. Thereafter, the reaction vessel was pressurised with $CO/H_2$ to the desired pressure. The reaction was initiated by placing the reaction vessel into a temperature-controlled oil bath preheated to the desired temperature. Catalytic reactions were terminated by removing the vessel from the oil bath and despressurising after cooling in an ice bath. In all cases the organic layer was readily separated from the ionic liquid layer after the reaction. The reaction products were analysed by gas chromatography.

## 3. Results and discussion

The hydroformylation of 1-octene (equation (1)) was performed with Rh/phosphine complexes immobilised in $BMI.PF_6$ under different reaction conditions and the results are summarized in tables 1 and 2.



(1)

It is clear from the data on table 1 that the catalytic system formed by the immobilisation of $Rh(acac)(CO)_2$/xantphos (1 : 1 molar ratio) in $BMI.PF_6$ is highly active giving to turnover numbers (TOF) up to 245 $h^{-1}$ at 99% 1-octene conversion and superior to those obtained with sulfonated Xantphos under similar reaction conditions (compare entries 1 and 4, table 1). However, this system is not suitable for catalyst recycling since most of the rhodium complex is removed in the organic phase after the first recycle (the conversion drops from 99 to 60%, compare entries 2 and 3, table 1). On the other hand, Rh/sulfonated Xantphos form a recyclable catalytic system (compare entries 5–8, table 1). Moreover, almost complete 1-octene conversion with little isomerisation is attained by increasing the reaction time from 4 to 24 h. The catalytic selectivity is maintained to the order of 80% by employing phosphine/Rh ratios up to 5. The same trend was observed in reactions performed in homogeneous conditions using thixantphos as the ligand [17].

The influence of the reaction temperature and syngas pressure on the catalyst activity and selectivity has been investigated and the observed results are presented in table 2.

The reaction temperature and syngas pressure has significant effects on the reaction rate and selectivity. The selectivity in $n$-nonanal and the 1-octene conversion drops with increasing of the syngas pressure from 15 to 35 atm (see entries 1–4, table 2). The 1-octene conversion increases with the augmentation of the reaction temperature whereas the selectivity increases with a rise in the temperature from 60 to 100 °C, then a continuous drop was observed (compare entries 5–9, table 2).

With these optimised reaction conditions (15 atm of syngas, 100 °C and phosphine/Rh ratio of 4) the hydroformylation of 1-octene using different mobile phases and 1-decene, 1-dodecene and 1-octadecene were investigated (table 3).

Table 1

Catalytic activity and selectivity in the hydroformylation of 1-octene by Rh/phosphine complexes immobilised in $BMI.PF_6$ under various reaction conditions.[a]

| Entry | Rh(phosphine) [cycle] | L/Rh ratio | $t$ (h) | Conversion (%) | TOF ($h^{-1}$) | $n/i$ | Isomer.[b] (%) |
|---|---|---|---|---|---|---|---|
| 1 | Rh(Xantphos) [1] | 1 | 4 | 98 | 245 | 2.1 | 9 |
| 2 | Rh(Xantphos) [1] | 1 | 6 | 99 | 164 | 2.1 | 8 |
| 3 | Rh(Xantphos) [2] | 1 | 6 | 60 | 97 | 2.2 | 19 |
| 4 | Rh(XantphosSulf) [1] | 1 | 4 | 18 | 47 | 2.2 | 28 |
| 5 | Rh(XantphosSulf) [1] | 1 | 24 | 99 | 41 | 1.7 | 4 |
| 6 | Rh(XantphosSulf) [2] | 1 | 24 | 99 | 41 | 1.7 | 4 |
| 7 | Rh(XantphosSulf) [3] | 1 | 24 | 99 | 41 | 1.8 | 8 |
| 8 | Rh(XantphosSulf) [4] | 1 | 24 | 99 | 41 | 1.9 | 12 |
| 9 | Rh(XantphosSulf) [1] | 2 | 24 | 93 | 39 | 3.5 | 18 |
| 10 | Rh(XantphosSulf) [1] | 3 | 24 | 87 | 36 | 4.5 | 23 |
| 11 | *Rh(XantphosSulf) [1]* | *4* | *24* | *90* | *37* | *4.8* | *15* |
| 12 | Rh(XantphosSulf) [1] | 5 | 24 | 18 | 7 | 4.1 | 33 |
| 13 | Rh(XantphosSulf) [2] | 5 | 24 | 39 | 16 | 4.1 | 25 |
| 14 | Rh(XantphosSulf) [3] | 5 | 24 | 41 | 17 | 4.0 | 32 |
| 15 | Rh(XantphosSulf) [4] | 5 | 24 | 41 | 16 | 4.0 | 42 |
| 16 | Rh(XantphosSulf) [5] | 5 | 24 | 37 | 15 | 3.5 | 34 |

[a] Catalysis performed at 80 °C and 50 atm $CO–H_2$ (1 : 1) using 3 ml $BMI.PF_6$ and 1-octene to Rh ratio of 1000. Turnover frequencies were calculated as mol of 1-octene converted per mol of catalyst per hour.

[b] Percent isomerisation of 1-octene.

Table 2

Effects of syngas pressure an reaction temperature over the system using Rh(XantphosSulf) immobilised in $BMI.PF_6$.[a]

| Entry | $P$ (atm) | $T$ (°C) | Conv. (%) | TOF ($h^{-1}$) | $n/i$ | Isomer.[b] (%) |
|---|---|---|---|---|---|---|
| 1 | 5 | 80 | 61 | 25 | 4.5 | 37 |
| 2 | 15 | 80 | 90 | 37 | 4.8 | 15 |
| 3 | 25 | 80 | 66 | 28 | 3.1 | 22 |
| 4 | 35 | 80 | 60 | 23 | 2.6 | 21 |
| 5 | 15 | 60 | 5 | 2 | 2.6 | 21 |
| 6 | 15 | 80 | 90 | 37 | 4.8 | 15 |
| 7 | *15* | *100* | *77* | *32* | *13.1* | *21* |
| 8 | 15 | 120 | 86 | 36 | 8.9 | 25 |
| 9 | 15 | 140 | 94 | 39 | 7.4 | 29 |

[a] Catalysis performed using 3 ml $BMI.PF_6$ and 1-octene to Rh ratio of 1000. Ligand to catalyst ratio is 4. Turnover frequencies were calculated as mol 1-octene converted per mol of catalyst per hour. Total time of all reactions is 24 h.

[b] Percent isomerisation of 1-octene.

The first aspect that should be emphasised is that no alkene hydrogenation side reaction was observed. It is evident that the $n/i$ ratio and chemoselectivity in the hydroformylation of 1-octene is related to the nature of the mobile phase. The higher $n/i$ ratios (up to 13.1) and chemoselectivity were attained using pure $BMI.PF_6$ (hydrophobic) [18] than in reactions performed in water, pure $BMI.BF_4$ (hydrophilic), $BMI.PF_6$ saturated with water or using toluene as co-solvent. This behaviour might be related to the changes in the structure of the ionic liquids when in the presence of the co-solvents.

Pure ionic liquids such as $BMI.PF_6$ are well-organised liquids possessing a polymeric structure of weak interactions. However, “wet” ionic liquids are best described as

Table 3

Hydroformylation of heavy olefins by Rh(acac)(CO)$_2$/phosphine (Rh : phosphine 1 : 4, A = Xantphos and B = sulfonated Xantphos; 1/1000 (Rh/olefin)) dissolved in different mobile phases at 100 °C and 15 atm syngas initial pressure during 24 h.

| Entry | Mobile phase (ml) | Ligand | Olefin | Conversion (%) | TOF[a] (h$^{-1}$) | *n*/*i* | Isomer[b] (%) |
|---|---|---|---|---|---|---|---|
| 1 | BMI.PF$_6$ (3) | B | 1-octene | 77 | 32 | 13.1 | 21 |
| 2 | BMI.PF$_6$ (6) | B | 1-octene | 82 | 34 | 14.8 | 17 |
| 3 | BMI.PF$_6$ (3)/H$_2$O[c] | B | 1-octene | 99 | 41 | 1.7 | 20 |
| 4 | BMI.PF$_6$ (3)/PhMe (3) | B | 1-octene | 82 | 34 | 1.7 | 51 |
| 5 | BMI.BF$_4$ (3) | B | 1-octene | 98 | 41 | 2.4 | 74 |
| 6 | H$_2$O (4) | B | 1-octene | 93 | 39 | 1.8 | 45 |
| 7 | PhMe (4) | A | 1-octene | 98 | 41 | 2.2 | 16 |
| 8 | BMI.PF$_6$ (3) | A | 1-octene | 99 | 41 | 1.7 | 18 |
| 9 | *BMI.PF$_6$ (3)* | *B* | *1-decene* | *79* | *33* | *61.0* | *6* |
| 10 | H$_2$O (3) | B | 1-decene | 99 | 42 | 6.9 | 19 |
| 11 | BMI.PF$_6$ (3) | B | 1-dodecene | 79 | 33 | 10.2 | 21 |
| 12 | BMI.PF$_6$ (3)[d] | B | 1-octadecene | 34 | 14 | 49 | 42 |
| 13 | BMI.PF$_6$ (3)/PhMe (3) | B | 1-octadecene | 76 | 32 | 3.6 | 67 |

[a] Turnover frequencies were calculated as mol alkene converted per mol of catalyst per hour.

[b] Percent isomerisation of 1-octene.

[c] The salt was saturated with water (around 12.1 wt%) [19].

[d] The solid product was extracted with toluene.

"nano-structured" with polar and non-polar regions [19]. This type of nano-inhomogeneity allows neutral molecules to reside in the less polar regions and facilitating the diffusion of polar species in the more polar or wet regions. This of course dramatically changes the partial miscibility of the alkenes, syngas and the hydroformylation products in the ionic catalytic phase. Studies to determine the influence of the co-solvents in the partial miscibility of alkenes and syngas in the ionic liquids and the consequences on the hydroformylation reaction mechanism and kinetics are currently under investigation.

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