High pressure infrared and nuclear magnetic resonance studies of the rhodium-sulfoxantphos catalysed hydroformylation of 1-octene in ionic liquids

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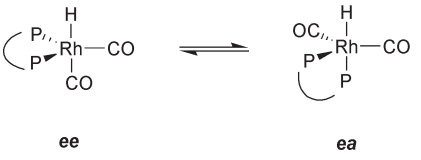
The rhodium-sulfoxantphos catalysed hydroformylation of 1-octene in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMI·PF_6) as a room temperature ionic liquid was monitored *in situ* by high pressure IR (HP-IR) and NMR (HP-NMR). Similar *ee* (bis-equatorial) and *ea* (equatorial-apical) (diphosphine)Rh$(CO)_2$H catalytic species, as observed in organic solvents, are formed in the BMI·PF_6 ionic liquid. The ratio of the *ee* and *ea* isomers is influenced by both the temperature and syngas pressure. An increase in hydrogen partial pressure has no effect on the activity of the system during the reaction performed in BMI:PF_6, while some hydroformylation systems using xanthene backbone ligands in conventional organic solvents can be sensitive to hydrogen partial pressure.

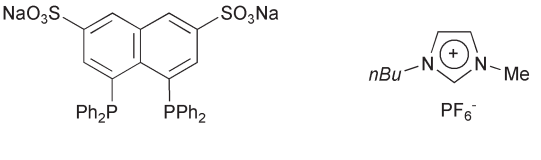
Room temperature imidazolium ionic liquids are one the most used and investigated classes of immobilising agents for organometallic catalysis.[1] Since the advent of the air-stable 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMI·PF_6) and its tetrafluoroborate (BMI·BF_4) analogue,[2] a plethora of homogeneous and biphasic transition metal catalytic reactions have been successfully performed in these liquids. In particular, the hydroformylation of olefins promoted by rhodium complexes immobilised in BMI·PF_6 ionic liquid[3] is emerging as an important alternative for the well-known aqueous biphasic catalysis.[4] Indeed, high catalytic activity, selectivity and complete retention of the catalyst in the ionic phase have been achieved in the hydroformylation of olefins by rhodium complexes, in particular those associated with modified xantphos ligands.[5,6] It is surprising, though, that little attention has been given to the determination of the species involved in hydroformylation reactions performed in these media. Moreover, it is well-known that the formation of (diphosphine)Rh$(CO)_2$H intermediate complexes under hydroformylation conditions can be monitored using HP-IR and HP-NMR spectroscopy in conventional organic solvents.[7,8,9] These techniques also allow the investigation of the dynamic *ee–ea* equilibrium established during the reaction (Scheme 1) that is associated with the *n*/*i* aldehyde selectivity.[8,10] Therefore, in order to gain some insights into the reaction mechanism and to verify the catalytic species involved in this reaction system, the 1-octene hydroformylation in BMI·PF_6 was followed by *in vivo* high pressure infrared and nuclear magnetic resonance spectroscopies.



Scheme 1

Unambiguous evidence for the existence of a dynamic equilibrium between the *ee* and *ea* complex isomers was provided by HP-NMR and HP-IR. The RhH$(CO)_2$(diphosphine) complexes, the catalyst resting state under hydroformylation conditions, were prepared *in vivo* from Rh(acac)$(CO)_2$ and the disodium salt of 2,7-bissulfonate-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene ligand (sulfoxantphos, **1**, Fig. 1) under syngas pressure. The complex formation in ionic liquids was studied using Rh(acac)$(CO)_2$ in the presence of 4 equiv. of sulfoxantphos dissolved in BMI·PF_6 under different pressures and ratios of H_2 and CO. The red-brown solution of the rhodium precursor with sulfoxantphos in BMI·PF_6 turns to light yellow in the presence of CO–H_2 at 40 °C. The appearance of four bands at 2032, 1985, 1967 and 1935 cm^{-1} in the IR spectrum of the reaction mixture is consistent with the formation of the RhH$(CO)_2$(sulfoxantphos) complex.

The wave numbers of these peaks are almost identical with those observed for the complex formed when 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) was used as the ligand in organic solvents.[8,9] Moreover, these four bands can be associated, as observed in conventional organic solvents (Table 1), with the *ee–ea* equilibrium (Scheme 1); the two bands at 2032 and 1967 cm^{-1} are related to the *ee* species and the other two bands, at 1985 and 1935 cm^{-1}, are related to the *ea* complex.[9] Under the conditions of 15 bar of syngas



Sulfoxantphos **1** BMI.PF_6

Fig. 1 Sulfoxantphos ligand and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (BMI·PF_6).

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Table 1 Comparison of IR data of $RhH(CO)_2$(diphosphine) in different solvents

Compound	"Solvent"	Isomer	ν_{CO}/cm^{-1}	Reference
$RhH(CO)_2$(Sulfoxantphos)	BMI·PF_6	*ee*	2032, 1967	This work
		ea	1985, 1935	
$RhH(CO)_2$(Xantphos)	Benzene	*ee*	2036, 1969	9
		ea	1991, 1941	
$RhH(CO)_2$(Thixantphos)	Cyclohexane	*ee*	2040, 1977	9
		ea	1999, 1953	

($CO/H_2 = 1$) HP-IR at different temperatures indicates that at 100 °C the *ee–ea* equilibrium reaches a constant value after 1 h. This result is in line with the *n*/*i* selectivity observed with the same catalytic system, where a higher *n*/*i* selectivity is obtained at higher temperatures.[5]

The effect of syngas pressure on complex formation was also investigated. The syngas pressure has a direct influence on the *ee–ea* equilibrium; when the pressure is increased the bands at 1985 and 1935 cm^{-1}, related to the *ea* complex also increase, suggesting that the increase of the syngas pressure should reduce the selectivity in aldehyde. This was indeed observed in the hydroformylation of 1-octene by this catalytic system.[5]

The above results clearly indicate that the formation of the *ee* and *ea* $RhH(CO)_2$(diphosphine) catalytic species can be monitored in BMI·PF_6 by HP-IR and the influence of the temperature and syngas pressure on the these complexes has a direct influence on the catalytic species formed under hydroformylation conditions.

The HP-NMR spectra were recorded in pure BMI·PF_6[11] and showed a characteristic doublet at 25–30 ppm with a rhodium–phosphorus coupling constant of around 145 Hz. It is known that the ^{31}P NMR spectrum of the compound $HRh(sulfoxantphos)(CO)_2$, prepared *in vivo* from a 1 : 1 mixture of $Rh(acac)(CO)_2$ and sulfoxantphos in DMSO-d_6 with 10 bar $CO–H_2$ (1 : 1), consists of a sharp doublet at 22.2 ppm ($J_{RhP} = 121$ Hz), indicating that the ligand is mainly coordinated to the rhodium in a *bis*-equatorial fashion.[12] Therefore, our results suggest that an *ee–ea* equilibrium is established when the Rh sulfoxantphos complexes are formed under hydroformylation conditions; moreover the high value of J_{RhP} could indicate that the ligand is coordinated to rhodium predominantly in the desired *ee* fashion. From previous work it is known that the complexes formed consist of a mixture of *ee* and *ea* isomers.[9,13] In HP-(^1H)NMR no hydride signals could be detected due to the intense signals of the solvent peaks, therefore the phosphorus–hydrogen coupling constants could not be estimated.

All ^{31}P NMR spectra recorded also showed the existence of signals at 0–10 ppm, which could be related to the formation of dimeric rhodium species. It is known that when the hydride of the catalytic precursor (sulfoxantphos)$Rh(CO)_2H$ dissolved in organic solvents is exposed to 1 bar of CO, it is completely transformed into the rhodium dimer [Rh(sulfoxantphos)-(CO)(μ-CO)]$_2$.[14] In our case this result can be related to the higher solubility of CO than hydrogen in BMI·PF_6,[15,16] the high ligand and rhodium concentrations or even to limitation of gas diffusion due to the lack of stirring during the NMR measurements.[17]

It is also worth mentioning that the *ee–ea* equilibrium does not undergo any modification during the hydroformylation reaction, since no changes in the absorbance or in the band positions were observed when the 1-octene hydroformylation, in the presence of the catalytic system prepared *in vivo* from $Rh(acac)(CO)_2$, diphosphine **1**, $CO–H_2$ (1 : 4, 20 bar) at 100 °C, was followed by HP-IR. Therefore, once the *ee–ea* equilibrium is attained any other Rh–carbonyl complex, product or substrate, present in the reaction media, does not influence it. This behaviour is the same as that reported in the homogeneous hydroformylation reaction performed in organic solvents using ligands based on the xanthene backbone.[8,9]

Moreover, it is known that in the hydroformylation of 1-octene in conventional solvents using ligands based on the xanthene backbone, as in the case of some phosphacyclic diphosphines, the system activity can be increased with an increase in hydrogen partial pressure,[8] but in our reaction system it was observed that hydrogen pressure has just a marginal influence on the catalytic activity in the pressure range investigated (Table 2). The catalytic activities observed in this study (homogeneous conditions) are higher than those obtained earlier[5] using the same catalytic system but in typical biphasic conditions where the reaction could be under mass-transfer limitations.

The slight increase in rate at higher pressures of H_2 can be explained by the limited solubility of hydrogen in the ionic liquid, which is much lower than that of carbon monoxide, as mentioned before.[15,16] Indeed, it has been estimated that CO is at least 13 times more soluble then hydrogen in BMI·PF_6 in the same pressure and temperature range.[15]

In summary we have shown that *in vivo* HP-IR and HP-NMR can be successfully used for monitoring the species involved in the hydroformylation of olefins in ionic liquids. Indeed, the HP-IR and HP-NMR studies revealed the presence of a Rh–sulfoxantphos catalytic complex and its dynamic *ee–ea* equilibrium in BMI·PF_6. This process is analogous to what was observed in conventional solvents and it is influenced by changes in temperature and syngas pressure of the system. An increase in hydrogen partial pressure has no effect on the activity of the system during the reaction performed in BMI·PF_6, while some hydroformylation systems using xanthene backbone ligands in conventional organic solvents can be sensitive to such changes in hydrogen partial pressure.

Experimental

Methods and materials

All preparations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were distilled and deoxygenated before use. 1-Octene was filtered over

Table 2 1-Octene hydroformylation reaction using sulfoxantphos at different hydrogen pressures[a]

Entry	P_{H2}/bar	P_{CO}/bar	% Conv.	TOF/h^{-1}	Chemoselect. (% Ald.)	Yield (% Ald.)	Regioselect. (% *n*-Ald.)	*R* (*n*/*i*)	Ref.
1	5.0	5.0	63	382[c]	63	39	88	7	This work
2	10.1	5.1	66	386[c]	55	36	86	6	This work
3	16.7	4.2	68	411[c]	53	36	86	6	This work
4[b]	10	10	20–30	453[d]	—	—	—	62	8
5[b]	50	10	20–30	676[d]	—	—	—	47	8

[a] Conditions: $T = 100$ °C (after 1 h complex stabilisation), reaction time = 1.5 h, L/Rh ratio = 4·1-octene/Rh ratio = 900, ionic liquid = BMI·PF_6 ($V = 10$ mL), [Rh] ~ 1.7×10^{-3} mol L^{-1}. [b] Phosphacyclic diphosphine was used as ligand, for more information see ref. 8. [c] Turnover frequencies were calculated as mol of 1-octene converted per mol of catalyst per hour. [d] Turnover frequency = (mol of aldehyde)·(mol of Rh)$^{-1}$·h^{-1}.

neutral activated alumina to remove peroxide impurities. The disodium salt of 2,7-bissulfonate-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (sulfoxantphos, ligand **1**) and the 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (BMI·PF_6) were synthesised as described in the literature.[12,18] The BMI·PF_6 employed was dried over 4 Å molecular sieves and contained less than 1.4 mg L^{-1} of chloride[19] and less than 0.1 wt % of water,[20] as determined by known methods. Note that the presence of water in the reaction mixture involving hydrogen and transition metal complexes causes decomposition of the ionic liquid with formation of phosphates and HF.[21]

All other reagents were commercial samples and were used as purchased. Gas chromatographic analyses were performed on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J & W Scientific, DB1 30 m column, film thickness 3.0 μm, carrier gas: He, FID detector, external standard: dibutyl ether). The mass spectra were obtained on a JEOL JMS-SX/SX102A. The NMR was performed on a Varian DRX 300. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. High-pressure IR spectra were measured using a 50 mL homemade stainless steel autoclave equipped with mechanical stirrer and ZnS windows.[22] Syngas ($CO–H_2$, 1 : 1, 99.9%), CO (99.9%) and H_2 (99.9%) were purchased from Air Liquide.

High pressure FT-IR (HP-IR) experiments

In a typical experiment a high pressure IR autoclave was filled with the previously prepared catalyst solution, 4 equiv. of ligand and 4.0 mg of $Rh(acac)(CO)_2$ in 15 mL of BMI·PF_6 The autoclave was purged three times with the desired gas mixture, pressurised with the amount of syngas or gas mixture needed for the experiment and heated to 100 °C. Catalyst formation was followed and was usually complete within 2 h.

Hydroformylation. For the hydroformylation reactions, after 1 h at 100 °C, 2.5 mL of 1-octene was introduced into the HP-IR autoclave and the spectra were collected. The products were analysed by gas chromatography and mass spectrometry.

High pressure NMR (HP-NMR) experiments

In a typical experiment the high pressure sapphire tube (ϕ = 10 mm) was filled with the previously prepared catalytic solution, 1 equiv. of ligand and 10 mg of $Rh(acac)(CO)_2$ in 3 mL of BMI·PF_6 The tube was purged three times with syngas and then pressurized with the amount of desired gas. Next, the tube was placed in the NMR spectrometer and the spectra were recorded.

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