Biphasic hydroformylation in ionic liquids: interaction between phosphane ligands and imidazolium triflate, toward an asymmetric process†

Loïc Leclercq, Isabelle Suisse and Francine Agbossou-Niedercorn*

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Biphasic hydroformylation of dec-1-ene and styrene, at commercially competitive rates, can be successfully performed in imidazolium triflate ionic liquids; the ionic liquid network forms 'inclusion complexes' with the phosphane ligands used to modify the rhodium catalyst.

Biphasic homogeneous catalytic systems can be considered as the most efficient ecological reaction media to allow proper recovery and recycling of soluble catalysts.[1] Fluorous-biphasic, aqueous-biphasic, supercritical, and ionic liquids (ILs, which are salts that melt below 100 °C)[2] media have been developed for that purpose. Currently, only an aqueous biphasic system is in industrial use for the hydroformylation of propene and 1-butene catalysed by a rhodium complex of the sodium salt of trisulfonated triphenylphosphine (TPPTS). Due to the low solubility of higher alkenes in water, the process is limited to light olefins. Several solutions have been reported to enhance the solubility of higher olefins in an aqueous medium *viz.* the use of co-solvents,[3] of modified cyclodextrins,[4] and of surfactants.[5] Unfortunately, the selectivity towards the linear aldehyde product decreased even though the rates were higher. In addition, the formation of stable emulsions and leaching of the catalyst were sometimes observed.[3,5]

Organic–IL systems can constitute interesting alternatives to aqueous biphasic media. Indeed, rhodium catalysed hydroformylation has been performed in organic–IL systems and the catalytic results are dependent upon the combination of cations, anions, and phosphorus ligands. For example, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] has been applied in the hydroformylation of light olefins catalysed by a rhodium complex of triphenylphosphine (TPP) or TPPTS which is retained in the IL phase.[6] For higher olefins, the phase distribution of the components of the catalytic system and the phase in which the catalytic reaction is occurring are central issues for successful processes.[7] Also, the exact solvation patterns of solutes, including the catalytic species, still need to be assessed in neat ILs or in the key domain of the interface, even if recent molecular simulations provide some information.[8]

As part of our studies on catalytic reactions in ILs, we report here on the influence of various imidazolium triflate salts on the rate and selectivity of rhodium catalysed hydroformylation of dec-1-ene and styrene under biphasic conditions (Fig. 1). We show that, with a careful choice of the substituents on the imidazolium cation, quite relevant activities can be attained as well as some enantioselectivity. We also show how the interactions existing between the IL and the solutes influence the overall properties of the catalytic system.

As mentioned by many authors, purity of the ILs is essential for a catalytic process in order to avoid undesirable modifications of the active species.[9] Thus, we have used triflate based ILs either commercially available or prepared according to our reported procedure which avoids a route *via* intermediate imidazolium chlorides.[10] As a control experiment, we carried out the hydroformylation of dec-1-ene in the presence of $Rh(CO)_2$(acac) in [BMIM][TfO]‡ without a phosphane ligand (unmodified catalyst). A high activity (1315 h^{-1}) was observed along with a low regioselectivity (*n*/*iso* = 0.5). These values are typical of ligand free rhodium catalysed hydroformylations[11] and close to the results reported by Mehnert.[9] We next performed the hydroformylation of dec-1-ene in different ILs.‡ The rhodium catalysts were prepared from $Rh(CO)_2$(acac) and three phosphorus ligands (TPP, TPPMS, TPPTS) (Table 1). The initial turnover frequencies (TOF_0) were generally high. Interestingly, the TOF_0 measured for catalysts obtained from $Rh(CO)_2$(acac) and TPP increased linearly with the length of the alkyl substituent on the imidazolium cation (entries 1, 3, 5, 8, and 10). This can be related to the decrease of the overall organisation of the ILs with the increase of the imidazolium alkyl length. The resulting reduction of hydrogen bonding and enhancement of the tensioactivity[12] within the ILs are beneficial to the efficiency of the catalytic system. Concomitantly, the solubility of the alkene and CO/H_2 rises with the increase of the length of the alkyl side chain on the imidazolium cation.[13] The impact of the ionic liquid on the rate of the hydroformylation strongly suggests that the reaction is occurring in the ionic liquid phase.

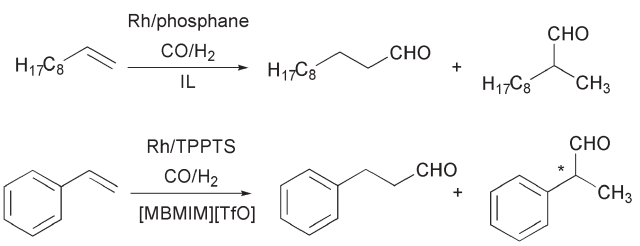

Fig. 1 Hydroformylation of dec-1-ene and styrene in IL-biphasic systems.

Université des Sciences et Technologies de Lille 1, CNRS Unité de Catalyse et de Chimie du Solide UMR 8181, ENSC(CHIMIE), BT C7, BP 90108, 59652, Villeneuve d'Ascq Cedex, France.
E-mail: francine.agbossou@ensc-lille.fr; Fax: +33 3 20 47 05 99; Tel: +33 3 20 43 49 27

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Table 1 Hydroformylation of dec-1-ene in imidazolium triflate ionic liquids[a]

Entry	Cation	Phosphane	Conv. (%)[b]	Sel. (%)[b]	*n*/*iso*[b]	TOF_0 (h^{-1})[c]
1	[EMIM]	TPP	58	85	2.8	400
2	[EMIM]	TPPTS	62	82	2.1	760
3	[BMIM]	TPP	88	89	2.8	530
4	[BMIM]	TPPTS	89	89	2.2	960
5	[MBMIM]	TPP	97	87	2.7	700
6	[MBMIM]	TPPMS	98	90	2.4	925
7	[MBMIM]	TPPTS	99	88	1.8	1300
8	[HMIM]	TPP	100	90	2.7	910
9	[HMIM]	TPPTS	97	86	1.4	1045
10	[OMIM]	TPP	99	72	2.7	1260
11	[OMIM]	TPPTS	98	66	1.2	1225

[a] Reaction conditions: $Rh(CO)_2(acac)$ = 0.02 mmol, ligand = 0.105 mmol; IL = 4 mL, *n*-undecane = 2.03 mmol, dec-1-ene = 20.60 mmol, CO/H_2 (1 : 1) = 50 bar, 80 °C, 1500 rpm. [b] GC (Chrompack CP-9200®, CPSil-5CB (25 m × 0.12 mm)) after 6 h. [c] Initial turnover frequency (mole of alkene converted per mole of rhodium per h).

We next replaced the TPP phosphane by the sulfonated derivatives TPPMS and TPPTS. The TOF_0 increased but the *n*/*iso* ratio diminished significantly (entries 5–7). The *n*/*iso* ratio and the reaction rate tend to shift to the values of the control experiment mentioned above, typically observed for unmodified rhodium catalysts.[11] The equilibrium existing in the reaction medium generating the active species selective for either the linear or the branched aldehyde product is influenced by the interactions between the IL and the phosphine ligand. In other words, the stronger the interactions between the IL and the phosphane, the less 'mobile' the phosphane in the IL medium. This slowed motion probably limits the formation of the $HRh(CO)L_2$ species selective for the linear product formation. The role that an ionic liquid can play in the formation of active species in transition-metal catalysed hydrogenations has been stressed.[14] It is clear here that the hydroformylation results are dependent on both the mobile phase and the phosphine on the catalyst. It can be suggested that in the presence of sulfonated phosphines, the active catalytic species is essentially in the ionic liquid phase, whereas in the presence of TPP the hydroformylation can take place in the ionic liquid phase and in the organic phase.[15]

The imidazolium salt can be considered as a molecular receptor through hydrogen bonding and π-stacking interactions with the phosphane ligands. It's easy to deduce that, in the case of neutral TPP, the properties of the catalyst are preserved with respect to those obtained in a pure organic medium. In contrast, the catalytic properties displayed in the presence of the ionic phosphanes TPPMS and TPPTS can be altered in the ILs. To confirm these supramolecular interactions, we performed an NMR study.

First, we carried out ^{31}P NMR titration experiments on phosphane ligands in 1-(2-methylbutyl)-3-methylimidazolium triflate ([MBMIM][TfO]) (Fig. 2). The ^{31}P NMR spectra were recorded in $[D_8]THF$ solutions containing identical concentrations of TPP or TPPMS while varying the concentration of the IL [MBMIM][TfO].[16] We could deduce a 1 : 1 complex between [MBMIM][TfO] and the two phosphanes. We propose that, for the sulfonated phosphane, the IL is principally an anion receptor through $C–H\cdots X^-$ hydrogen bonding and, for the neutral TPP, other supramolecular links like π-stacking interactions take place.

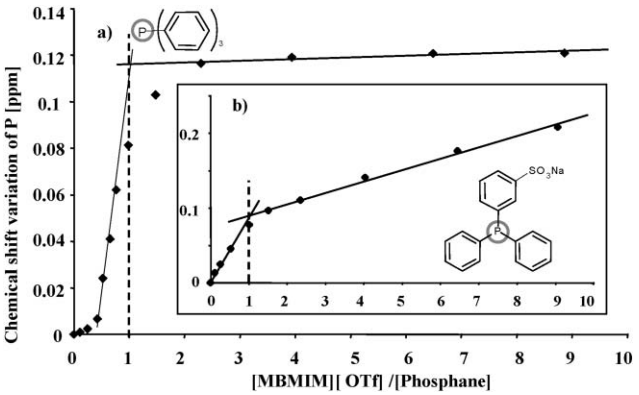

Fig. 2 ^{31}P NMR titration profile for addition of [MBMIM][TfO] to phosphanes in $[D_8]THF$ at 300 K.

To substantiate our assumptions, 2D NMR experiments have been performed with the aim of detecting spatial interactions between the sulfonated ligand TPPMS and the pure [MBMIM][TfO]. T-ROESY data, which are anticipated to be helpful for our purpose,[17] have been acquired on a coaxial tube containing a mixture of TPPMS and [MBMIM][TfO] (16% m/m) placed in an NMR tube charged with D_2O. The existence of cross-peaks between the sulfonated and unsubstituted aromatic protons of the ligand and the protons located on the imidazolium ring fully proves the interactions and gives information on the arrangement between the solute and the IL (Fig. 3). The weak cross-peaks observed between the [MBMIM] protons H(2), H(4), H(5), $N–CH_3$, H(9), and H(10) of the imidazolium cation and those of the sulfonated phenyl residue of the TPPMS suggest that the TPPMS exchanges the sodium for an imidazolium cation in the mixture. On the other side, the non-sulfonated phenyl residue interacts strongly with H(4), H(5), $N–CH_3$, H(6), H(9), and H(10). This NMR pattern establishes the existence of π-stacking interactions between the two aromatic rings (imidazolium and

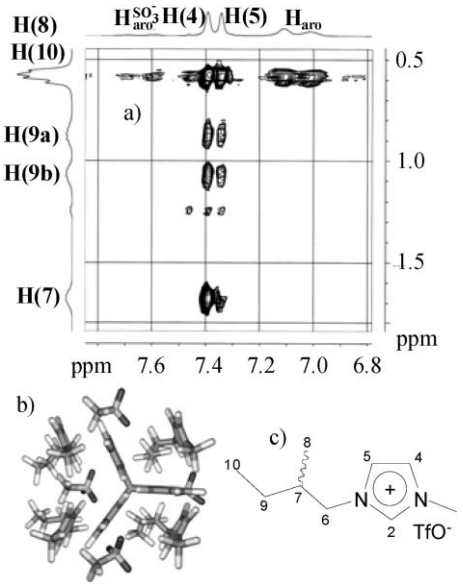

Fig. 3 Partial contour plot of T-ROESY spectrum of mixture containing TPPMS and MBMIM 16% (m/m), 300 K, external lock: D_2O. The structure deduced for the MBMIM–TPPMS complex is also presented.

Table 2 Rh–TPPTS catalysed hydroformylation of styrene in [MBMIM][TfO][a]

Entry	Chirality	T (°C)	Conv. (%)[b]	Sel. (%)[b]	n/iso[b]	TOF_0 (h^{-1})[c]	ee (%)[d]
1	±	80	98	96	0.2	1610	*rac*
2	*S*	80	97	98	0.2	1560	4
3	*S*	50	98	97	0.1	1095	6
4	*S*	45	98	98	0.1	655	12

[a] Reaction conditions: $Rh(CO)_2(acac)$ = 0.02 mmol, ligand = 0.105 mmol; [MBMIM][TfO] = 4 mL, *n*-undecane = 2.03 mmol, styrene = 20.60 mmol, CO/H_2 (1 : 1) = 50 bar, 80 °C, 1500 rpm. [b] GC (Chrompack CP-9200®, CPSil-5CB (25 m × 0.12 mm)) after 6 h. [c] Initial turnover frequency (mole of alkene converted per mole of rhodium per h). [d] GC (Chrompack CP-9300®, Chirasil-Dex (25 m × 0.32 mm) (*R*) enantiomer).

phenyl). Wipff has also deduced from simulations that the cations $[BMIM]^+$ are π-stacked with the phenyl moieties of TPPMS ligands and form hydrogen bonds with the sulfonate groups.[8] For small dilutions of the pure mixture (up to 25% m/m in $[D_8]$THF), similar cross-peaks remain between the unsubstituted phenyl group of TPPMS and the MBMIM cation. Nevertheless, the contacts with the sulfonated phenyl group are lost. For higher dilutions (over 50% m/m in $[D_8]$THF), all contacts are lost; only anion exchange remains.

Finally, we wondered whether a chiral ionic liquid (CIL)[18] would induce stereoselectivity in the hydroformylation of styrene. The results are reported in Table 2.

Interestingly, a reaction carried out in the optically pure IL (*S*)-[MBMIM][TfO] proceeded with some enantioselectivity (4% ee) (entry 2). Thus, the strong interactions, *i.e.* hydrogen bonding and π-stacking existing between the TPPTS anion and the chiral imidazolium cation, are creating a chiral environment around the rhodium active centre immobilised in the IL. The latter is thus able to transmit chiral information. However, the solvation of the other solutes of the catalytic mixture by chiral imidazolium cations can probably also play a role in the transmission of the chiral information.

Interaction of the metal centre with the IL might provide altered catalytic species.[19] The results of the control experiment carried out in the IL and in the absence of any external ligand (see above) suggest we can rule out the participation of, for example, imidazolylidene-rhodium species in the catalytic process. We could increase the enantioselectivity up to 12% ee while decreasing the temperature from 80 to 45 °C (entries 2–4). Although it is a challenging task to induce enantioselectivity during a hydroformylation reaction, here, a quite 'simple' chiral IL is inducing selectivity in the hydroformylation of styrene. The imidazolium salt can be considered a chiral molecular receptor through hydrogen bonding and π-stacking interactions for the achiral catalyst.

Recycling experiments of the Rh–TPPMS catalyst in [MBMIM][TfO] were performed by decantation of products. After washing with hexane and drying, the mixture containing the rhodium complex was charged with dec-1-ene and H_2/CO and placed in identical reaction conditions. The activity and selectivity of the catalyst were the same after five consecutive recyclings. This is indicative of the stability of the catalyst in the IL medium and of its recycling potential.

In conclusion, we have demonstrated that imidazolium triflate salts can be used in an IL-biphasic hydroformylation process of higher olefins. The reaction proceeds at commercially competitive rates with good separation ability. The decrease observed in the linear to branched aldehydes ratio for dec-1-ene and the drop in activity is due to 'inclusion complexes' formation between imidazolium cations and ionic phosphane ligands. Such complexes were also responsible for the asymmetric induction observed during styrene hydroformylation. The combination of an achiral organometallic catalyst with a chiral IL acting as both the reaction medium and the chiral inducer is a way to induce stereoselectivity during a catalytic process.[18d] The IL is interacting with species present during catalysis providing elements valuable for further developments. These results support the idea that the supramolecular assistance by the imidazolium salts is a phenomenon of general importance even if complex. This approach seems particularly suitable when ionic species intervene in the catalytic process. Due to the current interest in the development of the preparation of chiral ILs, fruitful developments are expected for asymmetric catalytic applications.

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Notes and references

‡ Cations: [EMIM] 1-ethyl-, [BMIM] 1-butyl-, [MBMIM] 1-(2-methylbutyl)-, [HMIM] 1-hexyl-, [OMIM] 1-octyl-3-methyl-imidazolium.

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