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High Rate and Highly Selective Vinyl Acetate Hydroformylation in Ionic Liquids as Solvent or Cosolvent

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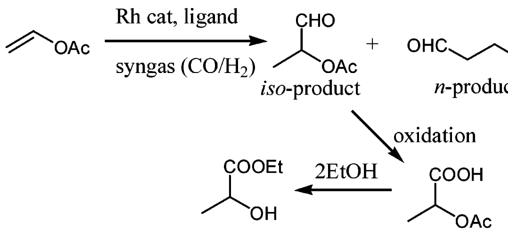
Summary: The hydroformylation of vinyl acetate to form 2-acetoxypropanal (an important intermediate in the synthesis of the environmentally friendly solvent ethyl lactate) catalyzed by $Rh(CO)_2(acac)$ *using phosphite or phosphine ligands was investigated in ionic liquids as reaction media (neat and as blends) or as additives to organic solvents. The ionic liquid had a significant effect on the selectivity of the hydroformylation of vinyl acetate, with very high TOFs being realized and selectivities of over 99% being obtained for the desired branched product at >95% selectivity for aldehyde products in reactions up to 0.3 mol scale. This effect could be obtained for relatively low volumes of the ionic liquid in an organic solvent, and combinations of benefits were observed by blending ionic liquids. It was also shown that the ionic liquid/catalyst could be recycled without loss of activity.*

1. Introduction

Room-temperature ionic liquids are widely used as solvents for immobilizing organometallic complexes. Their remarkable properties, such as negligible vapor pressure and variable physicochemical characteristics, and the possibility of tailoring of the ionic liquids (ILs) to the needs of the reaction have led to their application instead of conventional organic solvents. A wide range of transition metal-catalyzed reactions, including olefin hydroformylation, have been performed in ionic liquids.[1] The first hydroformylation reaction in ionic liquids using rhodium was performed by Chauvin et al.[2] They reported the biphasic hydroformylation of pentene in [1-butyl-3-methylimidazolium][hexafluorophosphate] ([bmim][PF_6]) using $Rh(CO)_2$(acac)/triarylphosphine as catalyst. Many other reports on the hydroformylation of olefins catalyzed by rhodium complexes in ionic liquids have since been reported.[3] A monophasic hydroformylation system of methylpent-3-enoate in [bmim][PF_6] was also reported,[4] in which the IL−catalyst solution could be recycled 10 times without significant loss of activity (recycling performed by product distillation and reuse of the remaining ionic liquid−catalyst solution). It was shown that the addition of the IL significantly increases the catalyst lifetime and overall productivity.

Scheme 1. Hydroformylation Route to Ethyl Lactate



Over the past number of years, ethyl lactate has been receiving increased attention as a high-performance, environmentally friendly, "green" solvent.[5] It is anticipated that ethyl lactate could possibly replace ozone-depleting CFCs, dichloromethane, and ethylene glycol ethers as the solvent of choice in the near future. The idea to produce lactic acid and lactates using the hydroformylation of vinyl acetate was first patented by Monsanto in 1975 using a triphenylphosphine-modified rhodium catalyst system,[6a] while other industrial players have also shown interest in this route.[6b] The process involves three steps, namely, hydroformylation, oxidation, and trans-esterification (Scheme 1).

In the present work, the viability of performing the hydroformylation of vinyl acetate (VA, a commodity chemical) in ionic liquids as solvent, as cosolvent, and, providing interesting results, as ionic liquid blends, using rhodium complexes with phosphine or phosphite ligands, was investigated. The study involved the hydroformylation of this substrate in a monophasic reaction mixture of VA and imidazolium- or ammonium-type ionic liquids with bis(trifluoromethylsulfonyl)imide ($N(SO_2CF_3)_2$, BTI) counteranions. $Rh(CO)_2$(acac) was used as the catalyst precursor, and phosphite or phosphine ligands were added. These systems compared favorably to reactions performed in conventional organic solvents, also allowing recycling of the catalyst. In this work, the *branched* product is the desired isomer and high rates of reaction and selectivities for this isomer are ultimate goals of this research. Given a potential industrial scenario or potential application in bench- to pilot-scale synthesis, even relatively small increases in yield, conversion, and/or selectivity are significant.

2. Results and Discussion

We initially investigated the hydroformylation reaction of vinyl acetate (up to 0.3 mol scale) using phosphite ligands (see Experimental Section). The influence of ionic liquids as either solvents (Table 1) or additives (Table 2) using $Rh(CO)_2$(acac) and tris(2,4-di-*tert*-butylphenyl)phosphite as ligand was inves-

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Table 1. Comparison of Ionic Liquids and Toluene for VA Hydroformylation[a]

entry	solvent	TOF ($\times 10^3$)[b]	*b*:*l*[c]	selectivity:[c] % CHO
1	toluene	3.5	96:4	92
2	[bmim][BTI]	4.5	96:4	94
3	[NOc$_3$Me][BTI]	1.2	>99:1	89
4	[NBnEt$_3$][BTI]	7.3	96:4	96
5	[C$_4$Py][BTI]	7.4	95:5	95

[a] Reaction conditions: 1 mM Rh(CO)$_2$(acac), 7 M VA, 1:3 Rh:L (L = tris(2,4-di-*tert*-butylphenyl)phosphite), 85 °C, 20 atm H$_2$/CO (1:1). [bmim]-[BTI] = [1-butyl-3-methylimidazolium][BTI], [NOc$_3$Me][BTI] = [methyltrioctylammonium][BTI], [NBnEt$_3$][BTI] = [benzyltriethylammonium]-[BTI], [C$_4$Py][BTI] = [*N*-butylpyridinium][BTI]. [b] Turnover frequency (TOF) is moles product formed per mole of catalyst per hour, based primarily on gas uptake, and calculated for the linear part of the CO consumption profile with lower than 5% deviation for repeat runs. [c] Isomer ratios and selectivity for aldehyde products were determined by GC-FID analysis, using standards.

Table 2. Use of [NOc$_3$Me][BTI] as an Additive with Diphenyl Ether as Solvent[a]

entry	solvent	TOF ($\times 10^3$)[b]	*b*:*l* [c]	selectivity:[c] % CHO
1	diphenyl ether	4.1	97:3	90
2	diphenyl ether/ [NOc$_3$Me][BTI] (31/2 mL)	1.9	98:2	89
3	diphenyl ether/ [NOc$_3$Me][BTI] (30/3 mL)	1.2	>99:1	89

[a] Reaction conditions: 1 mM Rh(CO)$_2$(acac), 2 M VA, 1:3 Rh:L (L = tris(2,4-di-*tert*-butylphenyl)phosphite), 85 °C, 20 atm H$_2$/CO (1:1). [NOc$_3$Me][BTI] = [methyltrioctylammonium][BTI] [b] Turnover frequency (TOF) is moles product formed per mole of catalyst per hour, based primarily on gas uptake, and calculated for the linear part of the CO consumption profile with lower than 5% deviation for repeat runs. [c] Isomer ratios and selectivity for aldehyde products were determined by GC-FID analysis, using standards.

Table 3. Combinations of Ionic Liquids (50/50 mixtures) on VA Hydroformylation[a]

entry	IL combinations	TOF ($\times 10^3$)[b]	*b*:*l* [c]	selectivity:[c] % CHO
1	[NBnEt$_3$][BTI]/[NOc$_3$Me][BTI]	2.9	>99:1	89
2	[bmim][BTI]/[NOc$_3$Me][BTI]	2.8	99:1	87

[a] Reaction conditions: 1 mM Rh(CO)$_2$(acac), 7 M VA, 1:3 Rh:L (L = tris(2,4-di-*tert*-butylphenyl)phosphite), 85 °C, 20 atm H$_2$/CO (1:1). [bmim]-[BTI] = [1-butyl-3-methylimidazolium][BTI], [NOc$_3$Me][BTI] = [methyltrioctylammonium][BTI], [NBnEt$_3$][BTI] = [benzyltriethylammonium]-[BTI]. [b] Turnover frequency (TOF) is moles product formed per mole of catalyst per hour, based primarily on gas uptake, and calculated for the linear part of the CO consumption profile with lower than 5% deviation for repeat runs. [c] Isomer ratios and selectivity for aldehyde products were determined by GC-FID analysis, using standards.

tigated (repeat reactions indicated reproducibility to within 5%). Comparative reactions were performed in toluene as conventional solvent. In all instances, selectivity to aldehydes is provided as an additional indicator of the performance of the catalyst. Reactions were performed until CO uptake was no longer observed (by digital pressure reading to a computer, leading to quantitative conversion, as also determined by GC-FID, which indicated the absence of VA substrate) or were stopped at 4 h (limited conversion of VA) for the slower reactions (see Experimental Section).

It is clear from Table 1 that, with the exception of [NOc$_3$Me][BTI] (NOct$_3$Me = methyltri-*n*-octylammonium), the reactions performed in the presence of ionic liquids afforded higher activity than the toluene reaction, giving excellent selectivities (both for the *branched* product and for aldehyde products) and very high turnover numbers. Interestingly enough, the former cases of faster reactions afforded generally lower selectivities (with the exclusion of the [bmim][BTI] reaction, which was superior in all respects to the reaction performed in toluene) than the slower reaction performed in [NOc$_3$Me][BTI], the latter reaction of which afforded a >99:1 selectivity for the *branched* product, at a still-high turnover frequency (TOF, moles product formed per mole of catalyst per hour measured for the linear part of the CO consumption profile) of 1.2 × 10^3. The *branched*:*linear* selectivity is dictated by the manner in which the [Rh−H] intermediate binds and adds to the VA, and it is the orientation of this binding that is presumably influenced by the nature of the IL solvent. Quite possibly, the cation of the IL is associated with the [Rh−H] species (solvation effects or ion pairing;[7] the solution behavior of ion pairs has been investigated using NMR NOE effects[7c]), and changes to the cation influence not only the rate but also the *branched*:*linear* selectivity. When using bulky phosphites such as the one employed here, the Rh metal accepts only one P ligand and the catalytically active HRh(CO)$_3$L complex so formed tends to be unstable.[8] Complexes of this nature have been shown to have an acylrhodium resting state in the catalytic cycle, and the reaction with dihydrogen is rate-limiting.[9] Since this is the case, the rate enhancements observed in this study probably arise from improved reaction of the coordinatively unsaturated 16-electron (16e) acylrhodium species [RC(O)RhL(CO)$_2$] with dihydrogen (hydrogen activation/hydrogenolysis step). Indeed, it is reasonable to postulate that even the RC(O)RhL(CO)$_2$ (16e) $\leftrightarrows$ RC(O)RhL(CO)$_3$ (18e) equilibrium may be influenced by the IL to favor the active 16e species. In the best case (entry 3), the selectivity in the presence of the IL is substantially superior to that in the presence of a conventional solvent. In other instances, selectivities were similar to those in toluene at substantially higher rates of reaction (TOF). In order to test catalyst stability and possible recycling of the catalyst-containing IL in a repetition of entry 2 using [bmim][BTI] (bmim = 1-butyl-3-methylimidazolium) as the IL, the reaction was performed as described in the table, the product was removed by short-path distillation (80 mmHg, 85 °C), and two further reactions were carried out with the IL residue, again after distillation of the product after each run. Similar rates and selectivities were observed in all runs (run 1: TOF 4.5 × 10^3, *b*:*l* 96:4; run 2: TOF 4.3 × 10^3, *b*:*l* 94:6; run 3: TOF 4.3 × 10^3, *b*:*l* 96:4), clearly indicating catalyst stability and recylability.

Wishing to capture the exceptionally high *b*:*l* selectivity obtained with [NOc$_3$Me][BTI] as solvent and intending to ameliorate its somewhat retarding effect on the rate of the reaction, we investigated its use as an additive to an organic solvent (Table 2) and also in IL blends (Table 3). Table 2 shows that decreasing amounts of the specified IL led to faster reactions with concomitant decreases in *b*:*l* selectivity, confirming that the outcome of the reaction is linked to the levels of the IL (specifically the NOc$_3$Me cation since the anion BTI was the same in all instances: Table 1) present. This study showed that even relatively small amounts of IL present in an organic solvent may impart substantial benefits to the outcome of the reaction. This is in accordance with our similar observations with ILs as additives in the context of the homogeneous metathesis reaction.[10]

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Table 4. Influence of Phosphine Ligands on VA Hydroformylation in ILs and Toluene[a]

entry	solvent	ligand	TOF ($\times 10^3$)[b]	*b*:*l*[c]	selectivity:[c] % CHO
1	[bmim][BTI]	**1**	0		
2	toluene	**1**	6.5	80:20	77
3	[bmim][BTI]	**2**	0.5	>99:1	63
4	toluene	**2**	0.6	99:1	62
5	[bmim][BTI]	**3**	1.6	98:2	79
6	toluene	**3**	2.9	98:2	87
7	[bmim][BTI]	**4**	13.6	94:6	89
8	toluene	**4**	15.2	86:14	89

[a] Reaction conditions: 0.25 mM $Rh(CO)_2(acac)$, 3 M VA, 1:15 Rh:L, 100 °C, 70 atm H_2/CO (1:1). [bmim][BTI] = [1-butyl-3-methylimidazolium][BTI]. [b] Turnover frequency (TOF) is moles product formed per mole of catalyst per hour, based primarily on gas uptake, and calculated for the linear part of the CO consumption profile with lower than 5% deviation for repeat runs. [c] Isomer ratios and selectivity for aldehyde products were determined by GC-FID analysis, using standards.

Combinations of ionic liquids were investigated with the view to enhancing selectivity for the *branched* product, specifically for ionic liquids producing lower selectivities (as demonstrated in Table 1), while improving the rate of the reaction. Accordingly, [NOc_3Me][BTI] (which afforded higher selectivities but at lower reaction rates (Table 1)) was added to [$NBnEt_3$][BTI] ($NBnEt_3$ = benzyltriethylammonium) and [bmim][BTI], respectively (which showed poorer selectivities but at higher reaction rates (Table 1)), to generate 50/50 mixtures. The effect of the combination of ILs on hydroformylation selectivity and activity is shown in Table 3.

In both instances of mixed ILs, the rates of the reactions were significantly higher than the comparable reaction of pure [NOc_3Me][BTI] (TOF $>2.8 \times 10^3$, up from a TOF of 1.2×10^3: Table 1, entry 3), while retaining all or much of the selectivity advantage that this IL engenders. This work neatly demonstrates that it is possible to blend the ILs mentioned here to secure a combination of the benefits (enhanced selectivity at higher reaction rates) afforded by each of the ILs individually.

We contemplated the possibility that the very high selectivities observed for our reactions, upon their completion, may arise by virtue of the linear 3-acetoxypropanal product decomposing to form acetic acid and acrolein, which is a known decomposition pathway.[11] Therefore, analyses were performed during the course of the reactions, at regular intervals, to see if a steady state of the linear aldehyde product could be observed or indeed if a buildup of acetic acid or acrolein could be observed. These products would be markers of a decomposition pathway, but none of these compounds were observed, indicating that no decomposition was taking place and that the analyses were truly indicative of the nature of the products being formed. In instances where lower selectivities were observed, the byproducts were found to be small amounts of ethyl acetate (hydrogenation product of VA, as the major byproduct) and very low levels of acetic acid (via Rh-catalyzed VA decomposition) and propanal (probably from acrolein hydrogenation). It is unlikely that these byproducts influenced the rates of the reactions, since varying rates were observed in several instances at similar product selectivities (see also Table 4).

Next, phosphine ligands (Figure 1) were investigated for the rhodium-catalyzed hydroformylation of VA in ionic liquids. Here, the reactions are more sluggish than those performed with phosphite ligands, as anticipated since the phosphite ligands are known to provide improved rates of reaction,[12] and were consequently carried out under more forcing conditions. The reaction conditions employed (temperature, pressure, Rh:L ratio of 1:15, etc.; see footnote "a" to Table 4) were determined in early experiments in this study to provide optimum TOF and selectivity to aldehyde: higher ligand concentrations, for example, improved the *b*:*l* ratio but at the cost of rate and selectivity.

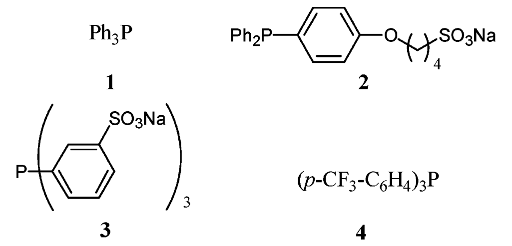

Figure 1. Ligands used for VA hydroformylation.

The phosphine ligands **1**−**4** were used in the hydroformylation of VA in the [bmim][BTI] ionic liquid, and the reactions were compared with those performed in toluene as solvent (Table 4).

As shown in entry 1, no activity at all was registered for triphenylphosphine **1** in the IL. In contrast, the rates in toluene were quite high and were accompanied with moderate selectivity. The reasons for the lack of activity in the IL are not known, but may relate to a lack of solubility of the ligand in that solvent. With ligand **2**, catalytic activity was relatively low for both the IL and toluene runs, but very high *b*:*l* ratios were obtained for both solvents. The low reactivity probably relates to the conjugated O atom increasing the electron density on the P atom, which is known to be deleterious to the rate of the Rh-catalyzed hydroformylation reaction.[13] The reaction performed in the IL (entry 3, Table 4) produced only *branched* product with no trace at all of the *linear* product being detected. Ligand **3** resulted in good activities and high *b*:*l* ratios for both reactions. However, no advantage was seen for this reaction when using the IL as solvent in favor of toluene. Ligand **4** gave very high activities in both the IL and toluene cases (TOF of 13.6×10^3 and 15.2×10^3, respectively, entries 7 and 8, Table 4). The *b*:*l* ratio obtained in the IL was much higher that that in toluene (94:6 vs 86:14). The high rate reflects the electron-deficient nature of the ligand, which is known to enhance the rate of the hydroformylation reaction.[14] The influence of the electronic nature of the ligand on the selectivity of the reaction for the aldehyde products probably lies in the influence of the electrophilicity of the ensuing Rh species and its consequent interaction with CO. Accordingly, the two equilibria $HRhL(CO)_2$ (16e) $\leftrightarrows$ $HRhL(CO)_3$ (18e) and $RC(O)RhL(CO)_2$ (16e) $\leftrightarrows$ $RC(O)RhL(CO)_3$ (18e) would be influenced by the electron-donating/withdrawing effect of the ligand: a more electron-donating ligand increases electron density on Rh, improving its ability to π-back-donate and slowing the CO dissociation (shown to be dissociative and zero-order in CO, but first order in Rh−CO complex concentration).[15] In contrast, the more electron-deficient the ligand, the faster the dissociation will be. Since the more electron-rich ligands will favor the

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saturated 18e species in both equilibria, slowing the catalytic cycle as a result, side reactions (such as hydrogenation) ensue and lead to a lower degree of selectivity for aldehydes (Table 4, entries 2−5).

3. Conclusion

In conclusion, substantially higher *b*:*l* ratios of the product aldehydes were obtainable when performing the hydroformylation reaction of VA in several ILs than analogous reactions in organic solvents. Selectivities of up to >99:1 (i.e., the *n*-isomer could not be detected) were obtained for the desired *branched* product, and high to extremely high rates of reaction were observed. Of probable substantial benefit to other applications is that this study has shown that Ils may be blended, either with an organic solvent in relatively small proportions or with another IL, to afford a reaction that allows an excellent compromise between rate enhancement and selectivity enhancement. The reactions were carried out in up to 0.3 mol scale and were found to be suitable to very low catalyst loadings. Unless very fast reactions are desirable (with phosphine ligand 4), the best selectivities at high rates of reaction are obtained with phosphites, which are therefore the ligands of choice for this reaction. There was no sign of catalyst decomposition in any of the experiments performed. Indeed recycling using the distillation method[4] of product and catalyst recovery has been shown to be applicable to and useful for our system, with three consecutive runs providing similar results.

4. Experimental Section

4.1. General Procedures. All experiments were performed using standard Schlenk techniques under an atmosphere of argon. A monophasic reaction mixture was obtained in all cases when VA was used with ionic liquids. The water content of the ionic liquids was determined by Karl Fischer titration and was normally in the range of <1000 ppm. Halide impurities can be qualitatively determined by addition of silver nitrate to an aqueous solution. Halides were quantitatively determined by the wet-chemical Volhard method[16] and were generally in the region of <1000 ppm. Commercially sourced vinyl acetate was used as received. Diphenyl ether and toluene were degassed with argon prior to use. Ionic liquids were synthesized according to literature procedures.[17] $Rh(CO)_2(acac)$ and ligands [tris(2,4-di-*tert*-butylphenyl)phosphite], **1**, and **3** were used as received from a commercial source. The samples were analyzed by GC-FID using nitrogen as carrier gas, and the reaction products were identified by GC-MS and against authentic samples. A 50 m PONA column of 0.2 mm internal diameter and 0.5 μm film thickness with a temperature limit of 320 °C was utilized. Temperature program: 50 °C, hold 5 min, ramp at 10 °C/min to 180 °C, hold 5 min. Injector temperature: 280 °C. Detector temperature: 300 °C.

4.2. General Hydroformylation Procedure. The rhodium precatalyst $Rh(CO)_2(acac)$ (0.0103 g, 0.0399 mmol) and tris(2,4-di-*tert*-butylphenyl)phosphite (0.0625 g, 0.120 mmol, 1:3 Rh:L) or phosphine ligand were weighed out and dissolved in 26 mL of vinyl acetate (VA:catalyst ratio of 7070:1 [0.014% catalyst], 7 M in VA; this particular reaction represents Table 1, entry 2). The mixture was transferred to a 100 mL stainless steel Parr reactor, and the ionic liquid (14 mL) to be used was transferred by syringe into the reactor (total volume ≤40% of the total reactor volume). The reaction mixture was degassed with nitrogen and the reactor pressure-tested for leaks (pressurizing to 40 atm N_2, then releasing pressure). A ballast vessel was pressurized to the required pressure with syngas (1:1 CO/H_2 mixture; see table footnotes for pressure details). The reactor was heated to the required reaction temperature while stirring at 1250 rpm. The reactor was then pressurized with syngas to the required pressure from a direct line feed and the supply immediately changed to the ballast vessel setup. The drop in pressure in the ballast vessel was used (digital readings to a computer monitoring system, accuracy ±1%), together with the analytical results, to determine TOF and syngas consumption. The reactions were run until no uptake of syngas could be detected, limited to no more than 4 h. GC-FID analytical data indicated that quantitative conversions of substrate were obtained for all of the faster reactions (TOF $>2.0 \times 10^3$), also showing the presence of unreacted starting material in the case of slower reactions. These data compared well with the expected amount of residual VA using TOF-based calculations. In the slower reactions, gas uptake was still being observed at the time when the reaction was stopped, indicating persistent catalyst activity.

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