Aqueous-biphasic hydroformylation of higher alkenes promoted by alkylimidazolium salts

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Aqueous-biphasic hydroformylation of higher alkenes (>C_5) can be greatly accelerated by addition of 1-octyl-3-methylimidazolium bromide without affecting the phase separation and with good catalyst retention in the aqueous phase.

While homogeneous catalysis allows reactions to proceed at high rates and selectivities under mild conditions, only rather few industrial applications have been realised. The main reason is the inherent difficulty of separating and recycling the dissolved (expensive) catalyst from the products and starting materials in an efficient and simple manner. Several approaches have been developed to tackle this problem.[1] Anchoring the catalyst on a solid support allows the catalyst to be separated by filtration or by using a fixed catalyst bed and continuous operation. Nevertheless, such methodology often leads to some drop in catalyst activity and leaching of the metal slowly takes place over prolonged operation. Multiphasic systems, where the catalyst is dissolved in one phase while the products form a different phase under the separation conditions, have been extensively studied.[2] Systems such as fluorous-biphasic, ionic liquids, $scCO_2$, as well as the combination of the last two, show very promising results but their cost has so far restricted their commercial application. An aqueous-biphasic system is industrially applied for the hydroformylation of propene and butene at 800 000 tonne per annum scale using a rhodium catalyst in combination with the sodium salt of trisulfonated triphenylphosphine (TPPTS) as ligand (RuhrChemie/Rhône-Poulenc process). Nevertheless, due to the poor solubility in water of higher alkenes, the rates of reaction are far too low to use such an approach for the commercial production of higher aldehydes (Fig. 1).†

Numerous studies have aimed at extending the scope of the aqueous-biphasic hydroformylation to more hydrophobic substrates. The use of co-solvents such as lower alcohols results in higher reaction rates but the linear selectivity drops, side reactions such as acetal formation occur and leaching of the co-solvent into the product phase complicates the product separation.[3] Using inverse phase-transfer catalysts such as modified cyclodextrins or calixarenes leads to moderate rate improvements but is accompanied by a linear selectivity drop.[4] Cationic surfactants, especially cetyltrimethylammonium bromide (CTAB), greatly enhance the rate of hydroformylation of higher alkenes. According to Li *et al.*, the rate enhancement is due not only to the solubilisation of the substrate within micelles but also to a high micro-concentration of the catalyst caused by electrostatic interaction between the positively charged head groups of the surfactant and the negatively charged sulfonate groups of the ligand.[5] The major drawback of surfactant addition is the formation of stable emulsions which render the phase separation difficult or even impossible. Such emulsions seem to be formed within the optimal operating conditions, high stirring rate and high conversion.[6] Moreover, the presence of water trapped in the product phase leads to catalyst leaching. New ligand design, aiming at rendering the catalyst tensioactive or to impart thermoregulated ability, has also been proposed.[7]

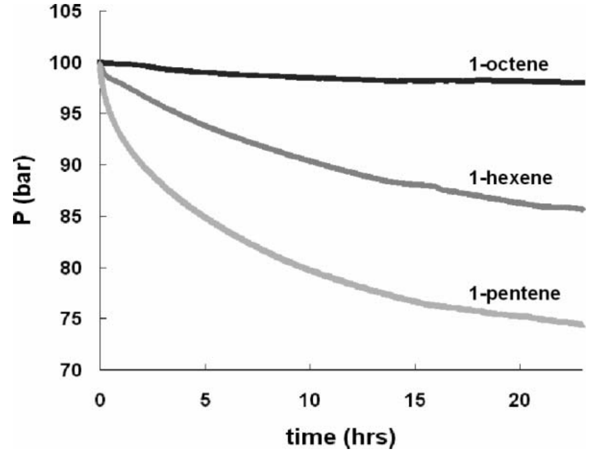
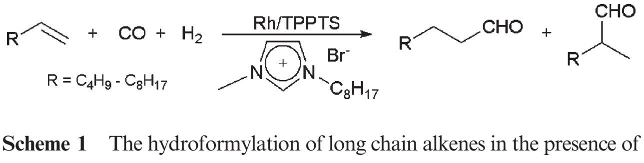


Fig. 1 Effect of chain length of the substrate on gas uptake from a ballast vessel in aqueous-biphasic hydroformylation.† The gas uptake for 1-decene is too slow to measure.

Here we describe the use of alkylmethylimidazolium salts as additives for the aqueous-biphasic hydroformylation of higher alkenes (>C_5, Scheme 1). We demonstrate that such additives, with careful choice of their side chain, allow substrates such as octene to undergo aqueous-biphasic hydroformylation with industrially relevant rates without impairing the phase separation and with good catalyst retention within the aqueous layer.

In the course of our investigations into mass-transfer improvements in aqueous-biphasic hydroformylation reactions, we studied



Scheme 1 The hydroformylation of long chain alkenes in the presence of OctMimBr under aqueous-biphasic conditions.

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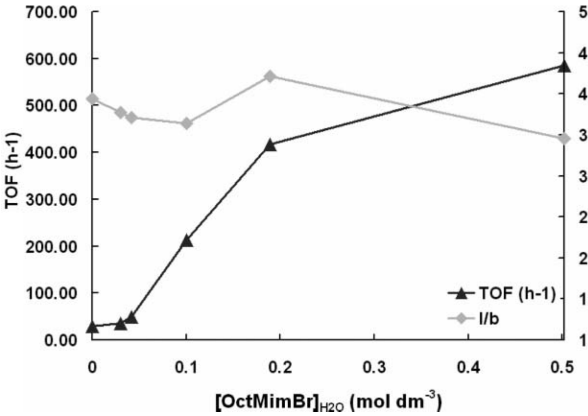

Fig. 2 Effect of the concentration of OctMimBr on the average TOF and the linear/branched ratio for the hydroformylation of 1-octene.

the effects of adding water soluble imidazolium salts to the biphasic system. As screening experiments, we carried out the aqueous-biphasic hydroformylation of 1-octene in the presence of various amounts of 1-octyl-3-methylimidazolium bromide, OctMimBr, catalysed by Rh–TPPTS in a closed batch reactor (100 °C; 20 bar; CO : H_2 = 1 : 1; 2 h, $[Rh]_{H2O}$ = 1.25 mM; P/Rh = 10; H_2O: 8 cm^3; 1-octene: 2 cm^3) (Fig. 2).‡

In the presence of 0.1 mol dm^{-3} of OctMimBr, the average turnover frequency increased from 10.5 (mol product) (mol catalyst)$^{-1}$ h^{-1} to 213 h^{-1}, while the linear selectivity remained virtually unchanged. More interestingly, by the time the autoclave was opened, *ca.* 10 minutes after the reaction was stopped, the phases were perfectly separated and the organic layer did not show any coloration. Further increases in the amount of OctMimBr present in the water phase further accelerated the reaction while maintaining an almost constant linear selectivity. Again the phase separation was found to be excellent. No OctMimBr was detected in the organic phase using ^{1}H-NMR spectroscopy.

We then compared the hydroformylation of different substrates with and without 1-octyl-3-methylimidazolium bromide as an additive (Table 1).

For all of the studied alkenes, the initial turnover frequency is greatly increased when OctMimBr (0.5 mol dm^{-3}) is added to the system. 1-Hexene and 1-octene are hydroformylated with commercially competitive rates (initial TOF > 1000 h^{-1}). Even 1-decene can be converted at a relatively high rate (initial TOF = 340 h^{-1}). The linear selectivity seems to drop slightly, but this may be due to the higher conversion reached. At low conversion, the more reactive terminal alkene is converted, leading mainly to linear aldehydes. At high conversion, internal alkenes formed by competitive isomerisation of the terminal alkene start to be converted leading to branched aldehydes, including 2-ethylheptanal. Interestingly, for 1-hexene and 1-octene the initial parts of the gas uptake curves obtained in the presence of OctMimBr are linear, suggesting that the reactions are zero order with respect to the substrate at the beginning of the reaction and are no longer limited by the rate of mass transfer of alkene or catalyst across the water–organic interface. For 1-decene, an exponential decay of the ballast vessel pressure as a function of time, typical of a first-order dependence in substrate, which could arise from kinetic control or as a result of a dependence upon the liquid mass transfer across the interface, is observed throughout the reaction.

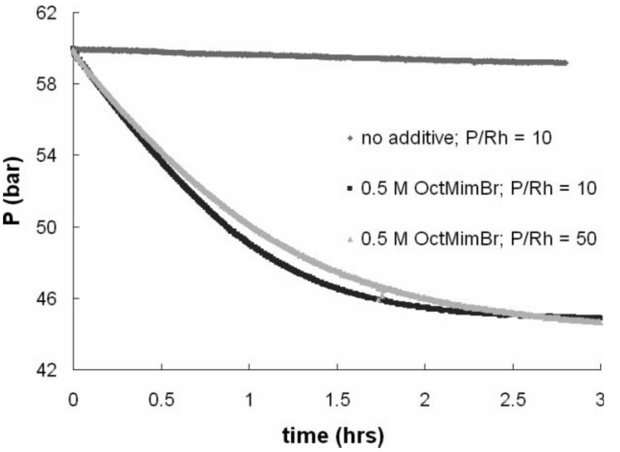

Fig. 3 Effect of the presence of OctMimBr and different P/Rh ratios on the gas uptake from a ballast vessel during the aqueous-biphasic hydroformylation of 1-octene.

In the presence of OctMimBr (100 °C; 20 bar; CO : H_2 = 1 : 1; 3 h, $[Rh]_{H2O}$ = 1.25 mM; H_2O: 8 cm^3; 1-octene: 2 cm^3), a fivefold increase in the excess of ligand does not greatly change the initial reaction rate (Fig. 3). The initial rates in the presence of a 10- and 50-fold excess of ligand are 3.1×10^{-4} and 2.5×10^{-4} mol dm^{-3} s^{-1} respectively. However, the first-order rate constants (measured from the exponential portion of the curve) differ more significantly, 5.3×10^{-4} s^{-1} in the presence of a 10-fold excess of phosphine and 3.2×10^{-4} s^{-1} with a 50-fold excess. Increasing the phosphine concentration hinders the ligand

Table 1 Hydroformylation of different alkenes in the presence or absence of OctMimBr[a]

Entry	Alkene	[OctMimBr]/mol dm^{-3}	Aldehydes (%)	Isomerised alkenes (%)	l/b	TOF$_0$/h^{-1} [b]
1	1-Hexene	0	37.8	3.85	4.5	317
2	1-Hexene	0.5	90.2	8.95	2.8	1561
3	1-Octene	0	1.9	1.4	4.9	10.5
4	1-Octene	0.5	91.5	5.7	2.9	1105
5	1-Octene[c,d]	0.5	91.9	2.9	3.2	912
6	1-Octene[c,e]	0.5	58.7	2.7	3.3	884
7	1-Decene	0	1.3	30.3[f]	3.1	nd[g]
8	1-Decene	0.5	62.8	18.1[f]	2.5	340

[a] Reaction conditions: T = 100 °C, P = 20 bar (CO : H_2 = 1 : 1), 3 h; $[Rh]_{H2O}$ = 1.25 mM, P/Rh = 10; H_2O: 8 cm^3; alkene: 2 cm^3, hydrogenation is <0.5%. [b] Initial turnover frequency (mole of alkene converted per mole of rhodium per h); calculated from the tangent at the origin of the gas uptake curve obtained. [c] P/Rh = 50. [d] Octane = 1.9%. [e] Reaction time = 1.1 h, no 2-ethylheptanal observed. [f] Includes 12% isomerised decenes present in the original sample. [g] The reaction is too slow for the gas uptake to be measured.

Table 2 Hydroformylation of 1-octene in presence of different 1-alkyl-3-methylimidazolium bromides[a]

Entry	Additive[b]	TOF_0/h^{-1}	Phase separation
1	HexMimBr	47.2	<10 min[c]
2	DecMimBr	1239.3	Stable emulsion

[a] Reaction conditions: T = 100 °C; P = 20 bar (CO : H_2 = 1 : 1); 3 h; $[Rh]_{H_2O}$ = 1.25 mM; P/Rh = 50; [additive] = 0.5 M; H_2O: 8 cm^3; alkene: 2 cm^3. [b] HexMimBr = 1-hexyl-3-methylimidazolium bromide; DecMimBr = 1-decyl-3-methylimidazolium bromide. [c] The phases were fully separated by the time the autoclave was opened, *ca.* 10 min after the reaction was stopped.

dissociation necessary for the formation of the 4-coordinated active rhodium species, $[RhH(CO)(TPPTS)_2]$, giving a drop in rate. The initial insensitivity of the reaction rate toward the excess ligand suggests that the reaction rate is not limited by simple kinetics.

The rhodium leaching into the organic phase has been determined using ICP-MS for the reactions carried out in presence of OctMimBr. With a 10-fold excess of ligand, the leaching of the metal was high, 126.2 ppm, but with a 50-fold excess the leaching dropped to 0.49 ppm. The phase separation at the end of the reaction was clean and fast, especially when a P/Rh ratio of 50 was used. Strangely, the linear to branched ratio was not greatly affected by the excess ligand, 2.84 with a 10-fold excess of phosphine and 3.19 with a 50-fold excess.

There are two possible explanations for the increased rate when adding OctMimBr to these aqueous-biphasic systems. The additive could have surface active properties and form micelles in which the substrate is solubilised. In this case, the positively charged imidazolium moiety could attract the negatively charged ligand, creating a high concentration of catalyst around the substrate. Alternatively, the OctMimBr could act as a phase transfer agent, exchanging the imidazolium with the sodium cations of the TPPTS making the catalyst soluble in the organic phase. The reverse exchange would bring the catalyst back into the aqueous phase.

To distinguish between these two mechanisms, we determined the critical micelle concentration of OctMimBr in water from conductivity measurements. We found that, at room temperature, OctMimBr starts to aggregate to form micelles above 2.16×10^{-2} mol dm^{-3}. This corresponds approximately to the concentration of OctMimBr at which we start to observe a rate improvement. We then conducted the hydroformylation of 1-octene in the presence of imidazolium salts with alkyl chains of different lengths (Table 2).

It appears that the shorter chain alkylimidazolium bromide, HexMimBr, has only a limited effect on the reaction. On the other hand, the longer chain additive, DecMimBr, greatly increases the rate of the reaction but leads to stable emulsions. Therefore, we propose that the rate improvement observed with OctMimBr is due to its surfactant properties. Nevertheless, the emulsions formed under the reaction conditions are not stable and the phases are fully separated by the time the autoclave is opened, *ca.* 10 min after the reaction was stopped. If a genuine phase-transfer mechanism were operating, significant rate improvement would have been expected when HexMimBr was used as the additive. Moreover, it would significantly promote rhodium leaching. With both additives, the rhodium leaching in the organic phase was less than 0.5 ppm.

In summary, we have demonstrated that 1-octyl-3-methylimidazolium bromide can be used successfully as an additive for the aqueous-biphasic hydroformylation of higher alkenes. The reaction proceeds at commercially competitive rates without greatly impairing the catalyst retention and with rapid phase separation.

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Notes and references

† A stock solution was prepared as follows: weighed amounts of $[Rh(acac)(CO)_2]$ and TPPTS were dissolved in a known volume of water containing 1-alkyl-3-methylimidazolium bromide at the desired concentration. CO–H_2 was then bubbled through the resulting yellow solution at 60 °C for 1 h. The solution obtained was stored under CO–H_2.

Typical procedure for reaction in an open reactor: an autoclave, fitted with a mechanical stirrer, thermocouple pocket, pressure transducer and attached to a ballast vessel *via* a catalyst injector and mass flow controller, was degassed by pressurising three times with CO–H_2 and releasing the pressure. The stock catalyst solution (8 cm^3, 1.25×10^{-5} mol Rh and the appropriate amount of TPPTS in water) was transferred into the autoclave and degassed by pressurising three times with CO–H_2 and releasing the pressure. The autoclave was pressurised with CO–H_2 (1 : 1, 15 bar) and heated to 100 °C (stirrer speed = 1000 rpm). Meanwhile, the substrate injector was charged with 1-octene (2 cm^3). Once the reactor had reached 100 °C, the substrate was injected using an overpressure of CO–H_2 and the pressure was brought to 20 bar. CO–H_2 was then fed from the ballast vessel so as to maintain the pressure in the autoclave at 20 bar and the pressure in the ballast vessel was monitored electronically. At the end of the reaction, the autoclave was cooled and depressurised and the contents analysed using GC for the organic products. The results presented are the average of at least 3 runs under each set of conditions.

‡ Typical procedure for a closed reactor: an autoclave, fitted with a mechanical stirrer, thermocouple pocket, pressure transducer, gas inlet and injection port, was degassed by alternate vacuum–N_2. The stock catalyst solution (8 cm^3, 1.25×10^{-5} mol Rh) and the substrate (2 cm^3) were transferred into the autoclave. The autoclave was purged three times with pressurised CO–H_2. The autoclave was pressurised with CO–H_2 (1 : 1, 20 bar) and heated, with stirring, to 100 °C. At the end of the reaction, the autoclave was cooled, depressurised and the contents analysed using GC for the organic products. The results presented are the average of at least 3 runs under each set of conditions.

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