

Rh-catalysed hydroformylation of higher olefins in IL

The hydroformylation of higher olefins was carried out in a 60 ml stainless steel autoclave with a magnetic stirrer. The desired amounts of catalyst precursor $[\text{Rh}(\text{CO})_2(\text{acac})]$, ligand, ionic liquid and olefin were introduced successively into the autoclave, which was purged with syngas (CO/H_2) several times. The reaction was carried out under the designed conditions for a desired time. After the reaction, the autoclave was quickly cooled to ambient temperature. The organic phase was separated by simple decantation and analysed by gas chromatography. The ionic liquid layer containing rhodium catalyst was reused in the successive runs.

Results and discussion

In order to gain a first insight into the influences of reaction parameters, the hydroformylation of 1-octene catalysed by water-soluble rhodium-phosphine complex Rh-BISBIS in $[\text{bmim}][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]$ was used as a model reaction under different reaction conditions.

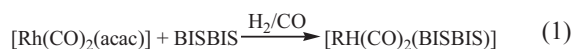
Effect of the molar ratio of phosphine/rhodium (P/Rh)

The P/Rh ratio is one of the important factors to affect the activity and regioselectivity of the hydroformylation.¹⁴ The influence of the P/Rh ratio was investigated on the 1-octene hydroformylation, and the results were summarised in Table 1.

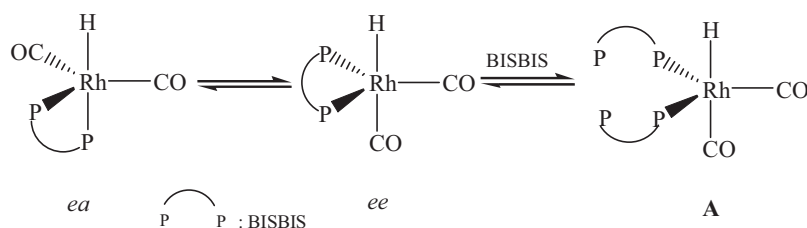
As shown in Table 1, the activity and chemoselectivity for aldehyde increased with P/Rh ratio from 4 to 12. But further increase of the P/Rh ratio was unfavourable for the reaction. The optimum activity and chemoselectivity for aldehyde were obtained at P/Rh = 12. The regioselectivity towards the linear aldehyde increased with increasing the P/Rh ratio, and a sudden jump in L/B ratio appeared at P/Rh = 10 (entry 3 in Table 1). The same trend was also observed in aqueous-organic biphasic systems.¹⁴

Similar to the mechanism of aqueous-organic biphasic hydroformylation, the mechanism of ionic liquid biphasic hydroformylation studied by Leeuwen²⁶ confirmed the presence of *ee* configuration and *ea* configuration of the active species $[\text{RhH}(\text{CO})_2(\text{diphosphine})]$ complexes, both of them are responsible for the production of aldehydes,²⁷ and there is an *ee*-*ea* equilibrium between *ee* configuration and *ea* configuration during the reaction (Scheme 2).

According to the above mechanism, there is a ligand exchange between acetylacetonate in $[\text{Rh}(\text{CO})_2(\text{acac})]$ and BISBIS under reaction conditions before the hydroformylation reaction (Eq. 1), and the mechanism also followed the generally accepted mechanism proposed by Wilkinson.²⁸



When the P/Rh ratio was low (entries 1–2 in Table 1), the concentration of BISBIS in the ionic liquid was too low to convert entirely $[\text{Rh}(\text{CO})_2(\text{acac})]$ into the active species $[\text{RhH}(\text{CO})_2(\text{BISBIS})]$ complexes.²⁶ The catalyst precursor $[\text{Rh}(\text{CO})_2(\text{acac})]$ was still the main active species and responsible for the low activity and regioselectivity.



Scheme 2 The *ee*-*ea* equilibrium of $[\text{RhH}(\text{CO})_2(\text{diphosphine})]$ active species.

Table 1 Effect of the BISBIS/Rh ratio on 1-octene hydroformylation

Entry	P/Rh	Conv./% ^a	S(ald.)/% ^b	L/B ^c	TOF/h ^{-1d}
1	4	28.4	42.9	7.3	156
2	6	64.7	62.1	9.3	513
3	10	68.8	81.8	15.1	719
4	12	89.6	92.2	15.5	1055
5	14	79.3	85.0	16.6	861
6 ^e	12	95.6	84.8	2.1	1035
7 ^f	12	90.8	85.4	15.3	990
8 ^h	12	85.7	76.7	17.9	940

Reaction conditions: $[\text{Rh}] = 5.0 \text{ mmol/l}$, 1-octene: 12.8 mmol, $[\text{bmim}][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]$: 1 ml, initial pressure: 3.0 MPa, 120°C, 2 h, stirring speed 1400 rpm.

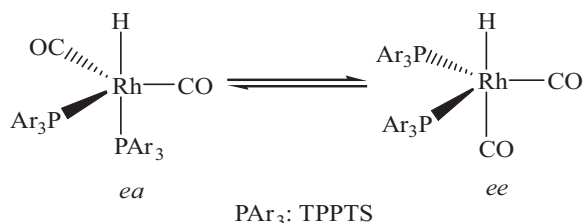
^aConversion: percent of converted 1-octene; ^bS (ald.): selectivity of aldehydes; ^cL/B: molecular ratio of linear aldehyde to branched aldehyde; ^dTOF: mole (aldehyde) per mol (rhodium) per hour; ^ethe ligand BISBIS was replaced by TPPTS; ^fcatalyst was replaced by $\text{RhCl}_2(\text{BISBIS})_2$; ^hcatalyst was replaced by $[\text{Rh}(\text{COD})\text{Cl}]_2$.

The concentration of $[\text{RhH}(\text{CO})_2(\text{BISBIS})]$ increased with the increase of P/Rh ratio, leading to high activity and regioselectivity towards the linear aldehyde. Since most hydroformylation catalysts exhibited a first order dependency in the concentration of this rhodium-hydride species,²⁹ when the P/Rh ratio was 12, the rhodium catalyst was completely converted into water-soluble active species $[\text{RhH}(\text{CO})_2(\text{BISBIS})]$, and therefore the highest reaction activity was observed. Further increasing the P/Rh ratio would be disadvantageous for the dissociation of BISBIS from the centre metal in catalytic recycle, which resulted in lower activity.

The data (entries 4, 7 and 8 in Table 1) illustrated that the nature of the rhodium catalyst precursor did not influence reaction rates and regioselectivities towards the linear aldehyde. Compared with the Rh-BISBIS complex, the Rh-TPPTS complex exhibited lower regioselectivity towards the linear aldehyde in the same conditions (entry 6 in Table 1). It further suggests that the ligand play an important role in the regioselectivity-determining step and the diphosphine BISBIS is advantageous for highly selective catalysts, which is due to their natural large P-Rh-P bite angle.³⁰ According to the results reported by Casey *et al.*³⁰ and van Leeuwen *et al.*,^{27,31,32} it is possible that the rhodium active species still keep the highly selective structure with *ee* configuration in the case of BISBIS, while the less selective structure with *ea* configuration could be the main active species in the case of TPPTS (as shown in Scheme 3).

Effect of the syngas pressure

The effect of total initial pressure on the hydroformylation of 1-octene is listed in Table 2. The results indicate that the pressure strongly influenced the regioselectivity towards the linear aldehyde. The regioselectivity towards the linear aldehyde gradually decreased with increasing pressure. Higher pressure caused the increase of syngas concentration



Scheme 3 The *ee*–*ea* equilibrium of $[\text{RhH}(\text{CO})_2(\text{TPPTS})_2]$ active species.

Table 2 Effect of pressure on 1-octene hydroformylation

Pressure/ MPa	Conversion	S(aldehyde) /%	L/B /%	TOF/h ⁻¹
1.5	90.8	85.6	28.6	992
2.0	89.8	86.9	25.4	996
2.5	85.6	87.3	23.6	954
3.0	89.6	92.2	15.5	1055

Reaction conditions are the same as in Table 1 except BISBIS/Rh = 6.

and the relative ratio of syngas/phosphine concentration in the ionic liquid. This variation could create a more unsuitable reaction microcircumstance producing linear aldehyde with a smaller L/B ratio. On the other hand, according to reported²⁶ results, there is an *ee*–*ea* equilibrium of active species in the catalytic system (Scheme 2), and the equilibrium between two complexes is strongly dependent on the syngas pressure; complex *ee* can readily be converted into complex *ea* at high syngas pressure. The complex *ea* is disadvantageous for producing linear aldehyde, which is in accordance with the observation at lower L/B ratio.

Effect of reaction temperature and stirring speed

The effect of temperature on the 1-octene hydroformylation follows two ways. Firstly, high temperature is favourable for the formation of the stable chelated species $[\text{RhH}(\text{CO})_2(\text{BISBIS})]$, leading to higher reaction activity and regioselectivity. Secondly, high temperature can shift the equilibrium of *ee* and *ea* species to *ea* (Scheme 2), which is favourable for the formation of branched aldehyde. It results in the decrease of the regioselectivity towards the linear aldehyde.

Table 3 Effect of the reaction temperature on 1-octene hydro-formylation

Entry	Temp/°C	Stirring speed/(rpm)	Conv./%	S(ald.)/%	L/B	TOF/h ⁻¹
1	110	1400	66.2	84.0	20.9	710
2	120	1400	90.8	85.6	28.6	992
3	130	1400	97.4	81.3	15.9	1011
4	120	1000	88.5	81.5	31.1	921
5	120	600	81.9	83.6	34.4	874

Reaction conditions are the same as in Table 1 except BISBIS/Rh = 6, 1.5 MPa.

Table 4 Effect of reaction medium on 1-octene hydroformylation

Reaction medium	Conversion/%	S(aldehyde)/%	L/B	TOF/h ⁻¹
[bmim][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] ^a	81.9	83.6	34.4	874
[omim][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] ^b	84.2	84.6	35.5	909
[dmim][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] ^c	81.6	85.0	43.1	886
[cmim][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] ^d	75.0	82.8	43.5	793
[bmim]BF ₄	82.0	16.5	8.2	61
[bmim]PF ₆	31.8	20.2	1.5	29

Reaction conditions: [Rh] = 0.5 mmol/l, 1-octene: 12.8 mmol, BISBIS/Rh = 6, 1.5 MPa, 120°C, 2 h, 600 rpm. ^a[bmim]: 1-*n*-butyl-3-methylimidazolium; ^b[omim]: 1-*n*-octyl-3-methylimidazolium; ^c[dmim]: 1-*n*-dodecyl-3-methylimidazolium; ^d[cmim]: 1-*n*-cetyl-3-methylimidazolium.

As shown in Table 3, the L/B ratio increased from 20.9 to 28.6 while the reaction temperature was raised from 110 to 120°C. The L/B ratio decreased from 28.6 to 15.9 while the reaction temperature elevated from 120 to 130°C, which is due to the increase of *ea* species. Furthermore, according to the literature¹⁶, at 130°C, $[\text{RhH}(\text{CO})_2(\text{BISBIS})]$ would become unstable towards reversible dissociation of a phosphorus atom in BISBIS and produce a monodentate trigonal bipyramidal complex **A** (Scheme 2). Both the formation of less selective species *ee* and complex **A** were responsible for the decrease in the regioselectivity.

Similarly, the regioselectivity also depended strongly on the stirring speed. As shown in Table 3 (entries 2, 4 and 5), the lower stirring speed was favourable for forming linear aldehyde, because low stirring speed was favourable for the formation of the active species *ee*. Meanwhile, the results listed in Table 3 also indicate that the reaction suffered from mass transfer limitations as the activity increased when the reaction mixture was vigorously stirred.

Effect of different ionic liquid

Several kinds of ionic liquids with different cations or anions were used as solvents in the hydroformylation using Rh-BISBIS as catalyst. The results summarised in Table 4 indicate the anion and cation of ionic liquid played important roles in the Rh-catalysed hydroformylation. The *n*-octyl-substituted imidazolium ionic liquid showed the better activity. The ionic liquids $[\text{Rmim}][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]$ with shorter or longer chain-length alkyl were disadvantageous for reaction rate. This suggests that there is a relationship between the lengths of the olefin chain and alkyl substituents in the ionic liquid. However, the regioselectivity towards the linear aldehyde increased when the chain-length of the alkyl substituent increased. The role of ionic liquids in the regioselectivity towards the linear aldehyde remains to be further clarified. But this phenomenon may be attributed to the influence of chain-length alkyl on the solubilities of water-soluble catalyst and 1-octene in ionic liquid media.³³

For comparison, the halogen-containing analogue $[\text{bmim}][\text{BF}_4]$ and $[\text{bmim}][\text{PF}_6]$ were used as media under the same conditions. The experimental results showed lower activity and regioselectivity towards the linear aldehyde while the hydrogenation and isomerisation of olefin became the main reactions. The results could be attributed to the lower solubility of water-soluble rhodium-phosphine complexes

Table 5 The hydroformylation of higher olefins in [bmim][*p*-CH₃C₆H₄SO₃]

Entry	Substrate	Conversion/%	S(aldehyde)/%	L/B	TOF/h ⁻¹	Rh leaching/wt% ^a
1	1-Hexene	94.5	75.7	40.4	1155	–
2	1-Octene	81.9	83.6	34.4	874	–
3	1-Decene	79.6	85.9	33.9	724	–
4	1-Decene ^b	47.2	82.3	22.1	351	0.063
5	Recycling 2	59.1	75.9	18.0	405	0.075
6	Recycling 3	48.2	69.7	18.2	303	0.062
7	Recycling 4	29.7	57.9	9.5	155	0.047
8	Recycling 5 ^b	39.8	75.2	19.9	270	–

Reaction conditions: olefin 2 ml, the others are the same as in Table 4. ^aPercentage of leached rhodium of initial intake; ^b0.01 mmol of additional ligand was added.

Table 6 1-Octene hydroformylation reaction using different catalytic systems

Ionic liquid	Ligand backbone	Conv./%	TOF/h ⁻¹	L/B	Ref.
[bmim]PF ₆	Xanthene	10.6–44.3	15–58	18.0–21.3	7
	Phenol	96	240	12.6	8
	2-Imidazolium	–	552	1.1	9
	Cobaltocenium	–	810	16.2	10
	Xantphos	77	32	13.1	11
	Xantphos	30	65	44	12
	Xantphos	63	382	7	26
[bmim][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃]	Biphenyl	81.9	874	34.4	This work

in [bmim]BF₄ or [bmim]PF₆. The phenomenon is in good agreement with the results reported in the literature.³⁴

Effect of chain-length of olefin

The hydroformylation of other olefins catalysed by water-soluble complex Rh-BISBIS in [bmim][*p*-CH₃C₆H₄SO₃] was investigated under the optimum reaction conditions. The results are summarised in Table 5.

Upon increasing the chain-length of olefin from 1-hexene to 1-dodecene, the reaction rates and L/B ratio decreased from 1155 h⁻¹ and 40.4 to 350 h⁻¹ and 22.1, respectively. This further confirms that the activities depend strongly on the solubility of olefin. In order to investigate the possibility of catalyst recycling, the organic products in reactions were carefully separated by decantation without special precautions, and the ionic liquid-containing complex Rh-BISBIS was reused directly in the next run after adding fresh olefin (entries 4–8 in Table 5). In successive catalytic reaction cycles carried out in identical reaction conditions, relatively stable reaction rate and regioselectivity were observed after three recycles. However, a significant decrease in the reaction rate and regioselectivity was observed in the fourth cycle (entry 7 in Table 5). However, the result showed the rhodium catalyst was nearly completely retained in the ionic liquid phase (<0.08% rhodium leaching detected by ICP-AES). It indicated the decrease of activity and regioselectivity in recycles was mainly due to the partial oxidation of ligand BISBIS during the separation of catalyst. A significant recovery in activity and regioselectivity was observed (entry 8 in Table 5) when 0.01 mmol of additional ligand was added in the fifth cycle. It further confirmed the lower activity and regioselectivity result from the phosphine oxidation rather than rhodium leaching into organic phase.

Overall, the activity and regioselectivity for the 1-octene hydroformylation experiments are by far superior to those reported in the literatures under comparable reaction conditions (Table 6).

Conclusions

The biphasic hydroformylation of higher olefins catalysed by Rh-BISBIS has been efficiently performed in ionic liquid

[Rmim][*p*-CH₃C₆H₄SO₃] (R = *n*-butyl, *n*-octyl, *n*-dodecyl, *n*-cetyl). The catalytic system offers good activity and high regioselectivity towards the linear aldehyde with a good retention of the catalyst in the ionic liquid phase, which is economical and environmentally friendly. The activity and regioselectivity towards linear aldehyde catalysed in ionic liquid [Rmim][*p*-CH₃C₆H₄SO₃] are higher than those in the halogen-containing analogues [bmim]BF₄ and [bmim]PF₆. The easy separation and recycling of the catalyst make the reaction system promising and attractive.

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