

Cloud Points of Water-soluble Polyether Phosphites and Their Application in the Biphasic Hydroformylation of Higher Olefins

LIU, Xiao-Zhong(刘晓忠) WANG, Yan-Hua(王艳华) KONG, Fan-Zhi(孔凡志) JIN, Zi-Lin*(金子林)
State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning 116012, China

Water-soluble polyether phosphites alkyl polyethylene glycol *o*-phenylene phosphite (APGPPs) were easily prepared via alcoholysis of phosphorus chloride with polyoxyethylene alkyl ether. With appropriate HLB (hydrophile-lypophile balance), the phosphites possess clear cloud points below 100 °C. Addition of some inorganic salts decreases cloud points of the phosphites. When the phosphites have long polyether chain binding to short-chain alkyl group, their cloud points could be extrapolated from figure of dependence of cloud points on addition of inorganic salts. Utilizing octylpolyglycol-phenylene-phosphite (OPGPP) (APGPP, R: Octyl)/Rh complex formed *in situ* as catalyst, over 90% conversion of 1-decene was obtained, avoiding the limitation of water insolubility of substrates. Preliminary results indicated that micellar catalysis and thermoregulated phase-transfer catalysis (TRPTC) coexist in the reaction system. Below cloud point, micellar catalysis induced by polyether phosphites may be existed. When temperature is increased to above cloud point of the phosphites, this reaction works mainly in TRPTC. The catalysts could be easily separated by simple decantation, but followed by considerable loss in activity after three successive reaction runs. Preliminary results indicated hydrolysis of OPGPP happened during the reaction, which may explain for the bad loss in activity. The catalyst was reused up to seven times without clear decrease in activity when OPGPP/Rh ratio was increased to 50.

Keywords hydroformylation, higher olefins, micellar catalysis, thermoregulated phase-transfer catalysis

Introduction

Hydroformylation of olefins is a very important industrial process, which is catalyzed homogeneously by complexes of transition metal like cobalt, ruthenium and rhodium. More than 90% of the process for hydroformylation of higher olefins so far in industry are still using traditional cobalt catalyst, which suffer from strict conditions and environmental problems. Inspired by commercial process of biphasic hydroformylation of propylene employing water soluble HRh(CO)-(TPPTS)₃ (TPPTS, trisodium salt of trisulfonated triphenylphosphine) as catalyst, worldwide research efforts in this field are concentrated on aqueous/organic biphasic catalytic system and related water-soluble ligands. The major drawback in homogeneously catalyzed hydroformylation processes for

higher olefins—catalyst/product separation, may be overcome by employing the biphasic catalysis.¹ But low activity was usually observed in aqueous/organic system which facilitates the product/catalyst separation in the hydroformylation of higher olefins because of mass-transfer limitations resulted from very slight water-solubility of such long-chain olefins. Recently addition of surfactant or a co-solvent to the commercially employed RCH/RP system suitable for lower weight olefins,^{2,3} and supported aqueous-phase catalysis,^{4,5} has proved to promote profound improvement in activity. However, so far catalytic system to achieve sufficient high conversion and to bring a complete catalyst separation by decantation or simple phase separation as well has yet been a challenge in industrial application. Our group has developed a novel concept of thermoregulated phase-transfer catalysis (TRPTC),⁶⁻⁹ which provides a perspective future in a path to aqueous/organic biphasic hydroformylation of water immiscible olefins.⁹ According to the principle of TRPTC, Rh complexes modified with polyalkyl glycol ether derived phosphines which give precise cloud point (Cp), could precipitate from the aqueous phase at a temperature higher than Cp of the phosphine and then transfer into organic phase to catalyze the reaction. After the reaction, the complexes return to the aqueous phase and are separated by simple phase separation from the product at a temperature below Cp and could be employed in the successive reaction runs.

The validity of this concept has been successfully demonstrated for hydrogenation, CO selective reduction of nitroarenes^{10,11} and hydroformylation reactions.⁶⁻⁹ Thermoregulated phase-transfer catalysts (TRPTCs) show higher activity as compared to those obtainable by using other biphasic catalysts. Therefore employment of TRPTC was successfully taken in achieving high conversion of substrate in the aqueous/organic biphasic hydroformylation of higher olefins, avoiding the limitation of low solubility of substrate in water. This inspired us to get more insight into catalytic behavior of the TRPTC catalysts in the catalytic process and properties of the polyether substituted phosphines in aqueous solution.¹² Attempts to design and prepare new active hydroformylation catalysts possessing TRPTC function are encouraged as well. In

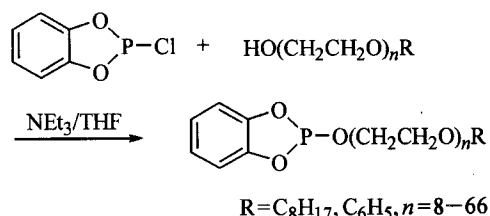
* E-mail: hpzuo@mail.dlptt.ln.cn

Received March 26, 2002; revised January 13, 2003; accepted January 20, 2003

Project supported by the National Natural Science Foundation of China (No. 29906001).

recent years, phosphites as modified ligands have received much attention because of their clear improvement in activity of the catalysts in the hydroformylation of higher olefins and less reactive internal olefins. Here a type of polyether phosphite (alkyl polyethylene glycol *o*-phenylene phosphite, APGPP) was synthesized by using alcoholysis of *o*-phenylenephosphorochloridite with polyoxyethylene alkyl ether (Scheme 1). In contrast to most phosphites in literature, the demonstrated phosphites with certain lipophilicity and right length of polyether chain were water soluble and possessed clear cloud points.¹³

Scheme 1



Results and discussion

Preparation of water-soluble phosphines

As generally accepted, water solubility of polyether nonionic phosphines depends on their length of polyether chains and structure of the hydrophobic group in the molecules, while effect of pH of aqueous solution on their solubility can be negligible. In literature, polyether phosphines were mainly prepared by two approaches. One is to through the reaction of functionalized polyether derivative with phosphorus chlorides or other phosphorus derivatives.¹⁴⁻¹⁶ This method was taken by most of the organic chemists and most of polyether phosphines were obtained in this way. In our group, most thermoregulated phase-transfer ligands were synthesized via catalyzed ethoxylation of phosphines containing active hydrogen groups. Water solubility of the phosphines is only dependent of length of polyether chain. Meanwhile, more or less of phosphine oxides were produced during the ethoxylation on high temperature, inducing discrimination of three valence phosphines from the phosphine oxides. Here alkyl polyethylene glycol phenylene phosphites (APGPPs) (R: Octyl, OPGPP) were prepared via the former approach. From Scheme 1, APGPPs are apt to be manufactured in contrast to industrially employed phosphites. Water solubility of the phosphites was obviously effected by the group of polyoxyethylene alkyl ether. Some specifications of the phosphites can be adjusted accordingly by changing alkyl group or length of polyether chain in the molecules.

Determination of cloud point of polyether phosphites

In our previous study, polyether substituted triaryl phosphines showed cloud points, which could be adjusted with

ethylene oxide addition during the ethoxylation of the phosphines.^{6,8} In comparison, APGPPs' cloud points are dependent on polyether chain length and structure of alkyl group as well. Their cloud points were determined to be below 100 °C with right polyether chain length as alkyl group is defined. While length of polyether chain surpasses 19 unit ethylene glycol, cloud points are above 100 °C, which is not easily determined by using traditional methods at atmospheric pressure.

Usually cloud points of nonionic surfactant are dependent on their structures. Addition of inorganic salts, alcohol *etc.* to the aqueous solution was reported to flutter their cloud points.^{17,19} Specifically, different inorganic salts have different dependence figure of addition amount on cloud points of the nonionic surfactants.¹⁹ Table 1 shows that addition of inorganic salts decreases cloud points of APGPPs. Theoretically, cloud points of APGPPs could decrease to be below 100 °C when enough inorganic salts is added to its aqueous solution. Figure of cloud points dependence on addition of inorganic salts was accordingly formed. From the reversing direction in the figures, real cloud point of the aqueous phosphine solution could be obtained by extrapolating the figure to the point without addition of salt. Apparently figure expression takes different figures from types of the addition salts. Here three inorganic salts were under consideration to deduce the cloud points of OPGPP with $n > 19$ ethylene glycol units, which are difficult to determine their cloud points under atmospheric solution. As a result, average values deduced by addition of different salts are taken as their cloud point. As shown in Figs. 1 and 2, OPGPP (A, $n = 13$; B, $n = 19$), polyether phosphonites (C, $n = 16$; D, $n = 28$) were investigated on this extrapolation of cloud points, respectively.

Table 1 Cloud points (C_p) of APGPPs' aqueous solution

R	n	C_p^a (°C)	C_p^b (°C)	HLB ^c	Water solubility
CH ₃	3	—	—	8.9	soluble
C ₆ H ₅	13	65	—	13.2	soluble
C ₈ H ₁₇	13	58	—	12.6	soluble
C ₈ H ₁₇	19	—	55	14.6	soluble
C ₈ H ₁₇	26	—	67	16.1	soluble
C ₈ H ₁₇	38	—	73	18.1	soluble
C ₈ H ₁₇	58	—	—	20.2	soluble
C ₁₂ H ₂₅	19	55	35	13.2	soluble

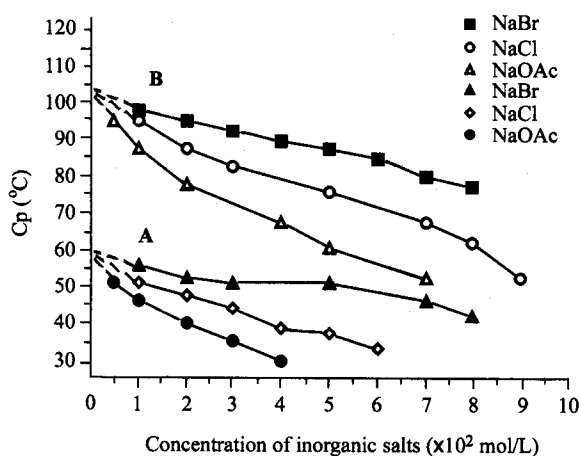
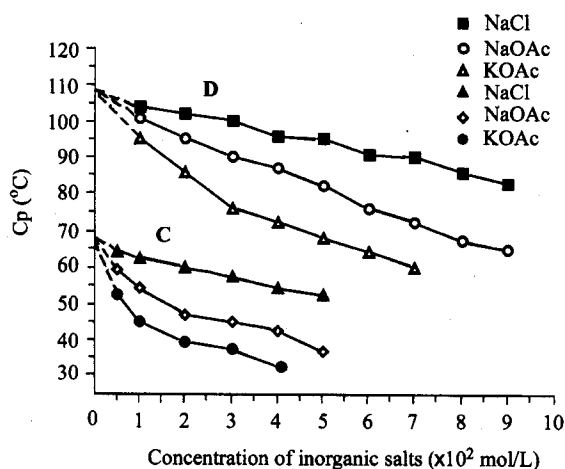
^a C_p , cloud point, w (3%) aqueous solution; ^b 90 mmol/kg NaCl + w (3%) APGPPs' aqueous solution; ^c HLB, hydrophile-lipophile balance: $7 + 11.7 \times \lg(M_w/M_o)$, M_w and M_o are molecular weight of hydrophilic and hydrophobic group respectively.¹⁸

From Fig. 1, phosphite A (OPGPP, $n = 13$) was deduced to have a cloud point of 60 °C, indicating only 2 °C gap from its experimental value (58 °C), while phosphite B (OPGPP, $n = 19$) was deduced to have its cloud point of 103 °C. In addition, cloud points of C (PhP[(OCH₂CH₂)₁₆-OPh]₂) and D (PhP[(OCH₂CH₂)₂₈OPh]₂) in Fig. 2, were determined to be 66 °C and 107 °C respectively according

Table 2 Hydroformylation of 1-decene catalyzed by TRPTC ligands/Rh catalysts

Entry	Ligand ^a	Reaction time (h)	1-Decene conversion (%)	Aldehyde yield (%)	Aldehyde selectivity ^b (%)	Aldehyde <i>n/iso</i> ^c	Average TOF ^d (h ⁻¹)
1	A	5	97.5	94.0	84.5	0.67	188.0
2	B	8	95.0	90.5	85.1	0.70	113.1
3	C	6	96.3	93.1	89.5	0.71	155.2
4	D	4	98.0	97.3	89.3	0.75	243.0
5	E	4	95.6	93.4	90.2	0.76	233.5
6	F	3	98.7	94.2	83.6	0.73	314.0
7	G	3	97.6	92.6	84.5	0.78	308.7
8	TPPTS	8	15.6	14.8	80.5	3.9	18.5

^a Ligand: A: Ph₂P-*p*-C₆H₄-(OCH₂CH₂)₁₈OH; B: P-*p*-C₆H₄-(OCH₂CH₂)₈OH|₃; C: PhP-*p*-C₆H₄-(OCH₂CH₂)₉OH|₂; D: Ph₂P(OCH₂CH₂)₁₆OC₈H₁₇; E: PhP[(OCH₂CH₂)₁₄OC₈H₁₇]₂; F: OPGPP (R = C₈H₁₇, *n* = 13); G: OPGPP (R = C₈H₁₇, *n* = 19). ^b Aldehyde selectivity = (1-undecanal + 2-methyl decanal)/total aldehydes. ^c *n/iso* = mol (normal aldehyde)/mol (*iso* aldehyde). ^d TOF = mol (aldehyde)/mol(Rh)/h. Reaction conditions: Rh(acac)(CO)₂ (2.78 × 10⁻⁵ mol), ligand (3.62 × 10⁻⁴ mol), P/Rh (mol) = 13, 1-decene (1.058 × 10⁻² mol), toluene (4.0 mL), H₂O (6.0 mL), standard internal (0.2 mL), syngas pressure 5.0 MPa, CO/H₂ = 1, reaction temperature 100 °C, reaction time 3 h.

**Fig. 1** Dependence on addition of inorganic salts to cloud points (Cp) of OPGPP.**Fig. 2** Dependence on addition of inorganic salts to cloud points (Cp) of PhP[(OCH₂CH₂)_nOPh]₂.

to the the extrapolating method. There is only 1.5 °C gap between the deduced value of C and its experimental value. From the figures, it was also observed that addition of KOAc, NaOAc, NaCl and NaBr would decrease cloud points of the polyether phosphites and polyether phosphonites, while decreased extents in the cloud points seemed to follow on a tendency as KOAc > NaOAc > NaCl > NaBr.

Therefore extrapolation of cloud points from dependence of cloud points on addition inorganic salts would provide some significant physical character for polyether derived nonionic phosphines with cloud points. In a further practice, application of phosphines may be made sensible in varying their cloud points by addition of inorganic salts to their aqueous solution.

Hydroformylation of olefins by OPGPP/Rh complexes

Comparison of different TRPTC ligands in the hydroformylation

In industrial practice, linear aldehydes from hydroformylation process have found more application in the production of detergent alcohols in the range of C(12)—C(18) or plasticizer alcohols in the range of C(8)—C(11). Some of the results for 1-decene hydroformylation are summarized in Table 2 for several representative TRPTC ligands. More than 80% of the hydroformylation products were determined to be *n*-undecanal and 2-methyl-decanal, which would find their potential application in perfume industry.

Owing to the limitation from mass-transfer, only 15.6% conversion of 1-decene was achieved with TPPTS/Rh as catalyst. Conversely high conversion of 1-decene is usually reached because TRPTC catalyst transfers to organic phase and the catalysis takes place in organic phase in terms of full homogeneous catalysis. So water solubility of substrate has no effect on the activity of the substrate. Different TRPTC catalysts may reach almost full conversion when reaction hours was enough. In comparison, almost full conversion of 1-decene was achieved in 3 h with OPGPP/Rh as catalyst.

Roles of thermoregulated phase-transfer catalysis (TRPTC) and micellar catalysis

When OPGPP ($n = 13$), corresponding to a cloud point of 58 °C, was used as ligand, there was a sudden increase in conversion at temperature from 50 °C to 60 °C (Table 3). The results could be elucidated from the TRPTC principle that when the temperature is higher than their cloud points, the catalyst could precipitate from aqueous solution and transfer to organic phase, causing the catalysis in full homogeneous catalysis in the organic phase. Interestingly considerable activity as 42 % conversion of 1-decene was yet achieved at 50 °C though this is below its cloud point. It may be the result of formation of micelles in this system owing to the existence of polyether phosphites. As was reported, aqueous amphiphilic phosphines solution led to formation of micelles as aggregates, in which water-immiscible reactants were encapsulated.^{20,21} It was proposed that the catalysis took place mainly in the micelles at this lower temperature.

Table 3 Effects of temperature on the hydroformylation

Entry	OPGPP n	Temp. (°C)	1-Decene conversion (%)	Aldehyde yield (%)	Aldehyde n/iso
9	13	40	25.0	25.0	2.5
10	13	50	42.0	42.0	2.1
11	13	60	84.7	84.7	1.36
12	13	70	88.7	88.7	1.33
13	13	80	99.3	97.3	0.91
14	13	90	99.8	90.0	0.72
15	19	80	98.5	97.8	0.92
16	28	80	98.6	97.5	0.91
17	38	80	99.2	98.0	0.92

Reaction conditions: 1-decene (1.0 mL), *n*-heptane (2.0 mL), H₂O (3.0 mL), ligand/Rh (mol) 13, Sub/Rh (mol) 1000, Syngas pressure 5.0 MPa, CO/H₂ = 1/1, reaction time 3 h.

It is reasonable that TRPTC will prevail in the catalysis when temperature is increased to above cloud points of the corresponding complexes. The conversion of substrates may be mainly the result of micellar catalysis induced by the polyether phosphines below cloud points.

Recovery of catalyst and the improvement in catalyst recovery

One main goal to meet in aqueous/organic biphasic catalysis has still been the catalyst separation and recovery. TRPTC has broken mass-transfer limitation due to substrate's insolubility in water, but catalyst separation and recovery have been yet a problem to be tackled as the first item. In the system (Fig. 3), it was observed that a considerable decrease in conversion appeared after consecutive four reaction runs. In the fifth run, conversion of 1-decene was determined to be only 45%. Significant loss in activity may be the result of hydrolysis of the polyether phosphines since phosphites are probably sensitive to water or alcohol. On the similar conditions of hydroformylation, aqueous OPGPP solution was

stirred for 72 h hence the solution gradually turned to brown, different from its original colorless solution. ³¹P NMR determination of the solution was observed at a range from $\delta - 1.37$ to $\delta 3.46$ indicating that OPGPPs have been undergone full hydrolysis. The resulted solution shares close chemical shift values with that from previous phosphites hydrolysis in the presence of strong acid or base.²²⁻²⁴ Hydrolysis of OPGPP may gradually go on through paths accordingly as shown in Scheme 2, and the hydrolysis may be carried on to the final step. Hence considerable loss in activity in the successive reaction runs may be mainly attributed to the hydrolysis of the OPGPP.

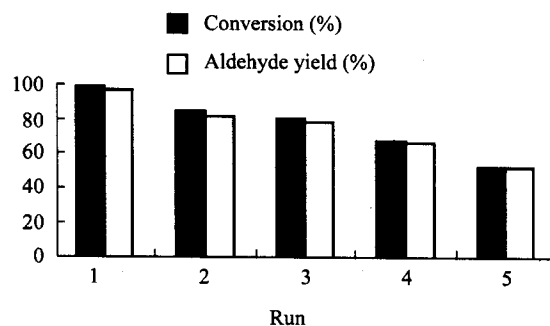
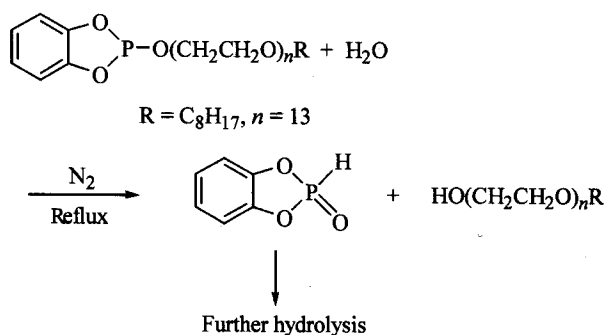


Fig. 3 Recycling of OPGPP ($n = 13$)/Rh catalyst in the hydroformylation of 1-decene. Reaction conditions are the same as Entry 13 shown in Table 3.

Scheme 2



It was also observed that catalyst separation and recovery in the successive runs were improved greatly by using higher phosphite/Rh ratio for the hydroformylation system (Table 4). It was made sensible that high excess of phosphites in the reaction may make up for the decomposed phosphites, retaining enough ligands to coordinate to the rhodium center.

Experimental

General methods

The preparation and purification of materials were performed under pre-purified nitrogen using standard Schlenk-type techniques. The following reagents were of analytically pure: PCl₃, distilled prior to use, phenol, catechol (from EtOH); Rh(acac)(CO)₂ (from Beijing Chemical Institute), 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene

(from Fluka); toluene, heptane, THF, ether were distilled from sodium; methylene chloride and Et₃N were distilled from CaH₂. Octanol was treated with sodium and distilled under pre-purified nitrogen. Industrial ethylene oxide was purified via gasification followed by liquefaction (colorless). TPPTS from Technische Hochschule Aachen, Germany; KOAc, NaOAc, NaCl, NaBr; water was redistilled prior to use under nitrogen.

Table 4 Recycling of OPGPP/Rh catalyst in a P/Rh ratio of 50

Reaction runs	Successive runs	Conversion (%)	Aldehyde yield (%)	<i>n</i> -Undecanal (%)	Aldehyde <i>n/iso</i>
18	1	98.8	98.8	48.9	0.95
19	2	97.6	93.4	49.2	0.97
20	3	97.1	94.2	50.7	1.03
21	4	96.8	95.1	50.1	0.99
22	5	99.4	93.4	52.3	1.10
23	6	93.3	80.2	60.8	1.55
24	7	94.3	83.2	58.6	1.23
25	8	94.2	85.6	56.2	1.20

Reaction conditions: 1-decene (2.0 mL), solvent (4.0 mL), H₂O (6.0 mL), temperature 80 °C, Sub/Rh (mol) 1000, P/Rh ratio 50, syngas 5.0 MPa, CO/H₂ = 1/1, reaction time 3 h.

Infrared spectra were recorded on a Perkin Elmer 2000 instrument. ¹H and ³¹P NMR were recorded at 300 MHz, 90 MHz respectively on a Varian VXR-300s spectrometer. Chemical shifts are referenced to residual deuterated solvent signals for ¹H NMR and external 85% H₃PO₄ (δ 0.00) for ³¹P NMR. Gas chromatography analysis was run on an SP-09 instrument (OV-101) (50-m capillary column, carrier gas: 0.2 MPa N₂, FID detector) equipped with a Shimadzu integrator. Dodecane was used as an internal standard. Mass spectra were measured on a Finnigan 312/SS 200 GC-Mass spectrometer.

Preparation of polyethoxyethylene alkyl ethers

C₈H₁₇(OCH₂CH₂)₁₃OH was taken as an example of R(OCH₂CH₂)_{*n*}OH. Octanol (5.0 g, 45 mmol) and anhydrous NaAc (0.08 g, 9 mmol) were added to a 100-mL glass autoclave. The autoclave was flushed three times with N₂ before setting the pressure at 0.2 MPa and heated in an oil bath, stirred with magnetic stirrer. When the temperature reached to 130 °C, desired amount of ethylene oxide was added dropwise into the autoclave, the pressure being maintained at 0.4 MPa. After addition, the reaction mixture was distilled in vacuum for another 2 h and then flushed with N₂ for three times. On cooling to room temperature, the product was obtained as a viscous liquid. The average length of polyoxyethylene ether chain was determined from its hydroxyl value, *n* = 13. MS-APCI (M + Na)⁺: 351.2, 393.4, 439.4, 483.4, 527.5, 569.5, 615.5, 659.7, 703.6, 746.7, 792.8, 836.8.

Synthesis of *o*-phenylenephosphorochloridite (PPC)²⁵

PCl₃ (94 g) was added in one portion to catechol (50 g) in which 1.0 mL of water had previously been added. There was a brisk evolution of hydrogen chloride and the mixture became solid. After an hour, another portion of phosphorus trichloride (39 g) was added and the mixture was heated with stirring, on the steam bath for 2.5 h. Distillation gave 74.5 g colorless fluid (b. p. 91 °C/18 mm). Hours later the fluid turned to colorless needle crystalline. Yield 94%, m. p. 30–30.5 °C, ³¹P NMR (CDCl₃, 90 MHz) δ: 174.5.

Preparation of alkylpolyethylene glycol phenylenephosphite

Dry R(OCH₂CH₂)_{*n*}OH (57.3 mmol, 1 equiv.) was dissolved in degassed dry THF and the solution was cooled in the range of –5 °C to 0 °C. Mixture of dry Et₃N (57.3 mmol, 1 equiv.), PPC (86 mmol) and THF (20 mL) was added to the cooled solution in 15–30 min with vigorous stirring. A white precipitate immediately formed in the drop adding. The mixture was stirring for another 6 h and kept overnight. THF was removed from the clear and colorless filtrate. To the viscous resultant 100 mL of dry ether was added in three portions and the solution was stirred for 2 h on below –15 °C before being filtered. The final filtrate was obtained as a colorless viscous fluid or pale wax. Conversion (85–90%) was determined by the total of Et₃N·HCl. Yield varies in the range from 40% to 80% on the polyether chain length. ³¹P NMR (CDCl₃, 90 MHz) δ: 127.64–129.23; ¹H NMR (CDCl₃) δ: 0–1.28 (m, 14.6H, C₇H₁₅), 3.4–3.96 (m, 62H, OCH₂), 6.8–7.2 (m, 4H, arom); FT-IR ν: 3454 (OH – PEG), 3050 (arom), 2950, 2880, 2958, 1640, 1590, 1500, 1470, 1387, 1324, 250, 1080, 970, 868, 775, 774, 697 cm⁻¹.

General procedure for hydroformylation of higher olefins

Hydroformylation experiments were performed in a 75 mL stainless steel autoclave equipped with magnetic stirrer. Hydroformylation catalysts were formed *in situ* from Rh(acac)(CO)₂ with ligands. The autoclave was charged with 1-decene, catalyst precursor, ligand, solvent, degassed water and internal standard. The system was flushed five times with CO of 1.0 MPa and checked for leaks. Then the autoclave was pressurized with CO/H₂ (1/1) to the desired pressure, and heated to the required temperature in a thermostatic oil bath. After 3 h, the samples were taken from the reaction products, dried over anhydrous MgSO₄, and analyzed by GC-MS.

Hydrolysis of octylpolyethylene glycol phenylenephosphite

OPGPP with *n* equal to 13 dissolved in degassed water and 3% aqueous OPGPP solution was accordingly obtained. The solution was stirred for some hour with a magnetic stirring in a thermostatic oil bath. The temperature was kept at 80 °C. The solution gradually turned to brown. ³¹P NMR deter-

mination of the solution was observed at a range from δ - 1.37 to δ 3.46.

Conclusion

It is shown that polyether phosphites APGPP could be easily prepared by alcoholysis of phosphorus chloride with polyoxyethylene alkyl ether. With appropriate hydrophile-lipophile balance (HLB), the phosphites possess clear cloud points below 100 °C. When the phosphites have long polyether chain binding to short-chain alkyl group, cloud points of the phosphites could be extrapolated from figure of dependence of cloud points on addition of inorganic salts. Utilizing OPGPP/Rh complex formed *in situ* as catalyst, 90% or more conversion of 1-decene was obtained, avoiding the limitation of substrate insolubility, which may be attributed to the results of micellar catalysis and TRPTC in the reaction system. When temperature is above the cloud point of the phosphines and complexes, this catalysis works mainly in TRPTC. Furthermore, the catalysts could be easily separated by simple decantation, but followed by considerable loss in activity in the successive reaction runs. Preliminary results indicated hydrolysis of OPGPP happened in the reaction, which explain for the bad loss in activity after four successive reaction runs. It was also proved that catalyst separation and recovery could be greatly improved with higher OPGPP/Rh ratio. The catalyst was reused up to seven times without clear decrease in activity with a ratio of OPGPP/Rh equal to 50. In view of the fact that search for water-soluble ligands and new potential biphasic catalytic systems are focal points of present academic and industrial work, the above polyether phosphine, OPGPP and its induced micellar catalysis and TRPTC in the aqueous biphasic hydroformylation inspired our further study on polyether phosphines and their application in biphasic catalysis.

References

- Bahrmann, H.; Bogdanovic, S. In *Aqueous-phase Organometallic Catalysis*, Eds.: Cornils, B.; Herrmann, W. A., Wiley-VCH, Weinheim, 1998, p. 306.
- Monteil, F.; Queau, R.; Kalck, P. *J. Organomet. Chem.* 1994, 480, 177.
- Purwanto, P.; Delmas, H. *Catal. Today* 1995, 24, 135.
- Arhancet, J. P.; Davis, M. E.; Merol, J. S. *J. Catal.* 1990, 121, 327.
- Guo, I.; Hanson, B. E.; Toth, I. *Chem. J. Chin. Univ.* 1993, 14, 863 (in Chinese).
- Jin, Z. L.; Zheng, X. L.; Fell, B. *J. Mol. Catal.* 1997, 11, 655.
- Zheng, X. L.; Jiang, J. Y.; Liu, X. Z.; Jin, Z. L. *Catal. Today* 1998, 44, 175.
- He, M. Y.; Min, E. Z. *Catal. Today* 2000, 63, 113.
- Cornils, B. *Angew. Chem., Int. Ed. Engl.* 1995, 34, 1575.
- Mei, J. T.; Jiang, J. Y.; Xiao, Q. M.; Li, Y. M.; Jin, Z. L. *Chem. J. Internet.* 2000, 1, 021002pe.
- Mei, J. T.; Wang, Y. H.; Miao, Q.; Jin, Z. L. *Chem. J. Chin. Univ.* 2000, 21, 381 (in Chinese).
- Jiang, J. Y.; Wang, Y. H.; Liu, C.; Han, F. S.; Jin, Z. L. *J. Mol. Catal. A: Chem.* 1999, 142, 339.
- Liu, X. Z.; Wang, Y. H.; Jiang, J. Y.; Jin, Z. L. *Chem. J. Internet.* 2000, 2, 7.
- Nuzzo, R. G.; Feither, D.; Whitesides, C. M. *J. Am. Chem. Soc.* 1979, 101, 3683.
- Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* 1993, 321, 524.
- Liu, X. Z.; Wang, Y. H.; Miao, Q.; Jin, Z. L. *Chin. J. Org. Chem.* 2001, 21, 191 (in Chinese).
- Mackay, R. A. In *Nonionic Surfactants: Physical Chemistry*, Ed.: Schick, M. J., Marcel Dekker, New York, 1987, p. 297.
- Shen, Z.; Wang, G. T. *Colloid and Surface Chemistry*, Chinese Chemical Press, Beijing, 1997, p. 360 (in Chinese).
- (a) Wu, J. P.; Gu, T. R. *Acta Phys.-Chim. Sinica* 1996, 12, 965 (in Chinese).
(b) Wu, J. P.; Gu, T. R. *Acta Chim. Sinica* 1995, 53, 958 (in Chinese).
- Oehme, G.; Grassert, I.; Paetzold, E.; Meisel, R.; Drexler, K.; Fuhrmann, H. *Coord. Chem. Rev.* 1999, 185-186, 585.
- Persigehl, P.; Jordan, R.; Nuyken, O. *Macromolecules* 2000, 33, 6977.
- Ramirez, F.; Bigler, A. J.; Smith, C. P. *Tetrahedron* 1968, 24, 5041.
- Walsh, E. N. *J. Chem. Soc.* 1959, 81, 3023.
- Khophyankina, M. S.; Karpukhin, D. N. *Neftekhimiya* 1965, 5, 49 (in Russian).
- Crofts, P. C.; Markes, J. H. H.; Rydon, H. N. *J. Chem. Soc.* 1958, 4250.