

# Thermoregulated phase transfer ligands and catalysis

## VII. Cloud point of nonionic surface-active phosphine ligands and their thermoregulated phase transfer property

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### Abstract

A series of nonionic surface-active phosphine ligands with the general formula,  $[\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n]_m\text{PPh}_{3-m}$  ( $m=1,2$ ), (AEOPP) has been synthesized. Cloud points of the phosphine ligands are measured and effects of changing hydrophilic and lipophilic groups on the cloud point of the phosphine ligand are examined. Experiment shows that AEOPP has distinct cloud point when  $n$  is greater than 7, R group larger than butyl and EO/Cj ratio greater than 0.5 (where  $\text{EO} = n \times m$ , Cj represents the total number of carbon atoms of both R and phenyl group). The rhodium complex of AEOPP shows thermoregulated phase transfer property in water/organic two-phase system. The complex exhibits good catalytic activity in the hydroformylation of 1-dodecene in water/organic two-phase medium and the conversion of the 1-dodecene and the yield of the aldehyde are 98% and 96%, respectively. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The successful industrial application of Rh/TPPTS in the hydroformylation of propylene in water/organic two-phase media is an outstanding achievement for the separation and recovery of homogeneous catalysts [1–3]. However, this technology termed RCH/RP process is not suitable for the hydroformylation higher olefins because the water solubility of the substrate is too low. In order to solve this problem, Jin et al. [4,5] used the catalytic system based on a nonionic surface active phosphine PEO-TPP with rhodium and proposed a concept of thermoregulated phase transfer catalysis (TRPTC). Promising results have been achieved in the hydroformylation of  $\text{C}_6\text{--C}_{12}$  olefins in aqueous/organic two-phase media by using this catalyst.

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Harris et al. [6] have prepared a high-molecular weight water-soluble phosphine

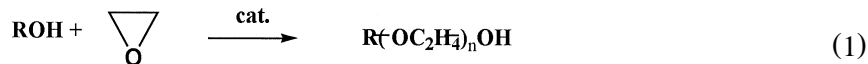


through the functionalization of poly(ethylene glycols) (PEG). There is no R group substitutes for the end hydroxyl hydrogen atom in the molecular structure of that phosphine. So that type of ligand does not show surface-active property. Bergbreiter et al. [7] have reported a phosphine ligand with cloud point comprising block copolymers of ethylene oxide and propylene oxide.

It is well-known that nonionic surfactants with polyoxyethylene chain as the hydrophilic group acquire their water solubility through the formation of hydrogen bonds between oxygen atoms and water molecules. These surfactants thus possess a property termed inverse temperature-dependent water solubility, i.e., they are soluble in water at low temperature but separate from it at a certain higher temperature (the cloud point) on account of the disruption of the hydrogen bonds. We have designed and synthesized a series of phosphine ligands of the general formula  $(\text{RO}-(\text{C}_2\text{H}_4\text{O})_n)_m\text{PPh}_{3-m}$  ( $m = 1, 2$ ) (AEOPP) by using a series of polyoxyethylene alkyl ethers having different Rs ( $\text{R} = \text{C}_4, \text{C}_5, \text{C}_8, \text{C}_{12}, \text{C}_{18}$  straight chain alkyls) and different numbers of polymerized ethylene oxide unit  $n$  ( $n = 7, 8, 10, 13, 16$ ) to react with dichlorophenylphosphine or chlorodiphenylphosphine. The feature of the ligands is that the terminal hydroxyl hydrogen atom of polyoxyethylene ether is replaced by an R group and the length of polyoxyethylene chain is shortened in each molecule. This makes the hydrophilic and lipophilic groups properly matched. Therefore, this type of ligands possesses the property of a nonionic surfactant-cloud point. The thermoregulated phase transfer catalysis property of the complex of this type of phosphine with rhodium and its catalytic effect on the hydroformylation of 1-dodecene in aqueous/organic two-phase media were investigated.

## 2. Experimental

### 2.1. Preparation of polyoxyethylene alkyl ethers



$\text{C}_{12}\text{H}_{25}(\text{OC}_2\text{H}_4)_8\text{OH}$  was taken as an example of  $\text{R}(\text{OC}_2\text{H}_4)_n\text{OH}$ . Amounts of 12.5 g (0.0667 mol) of  $\text{C}_{12}\text{H}_{25}\text{OH}$  and 0.1 g (0.0012 mol) of NaAc were added to a 100-ml glass autoclave, which was then flushed three times with  $\text{N}_2$  and heated in an oil bath. The contents were stirred with a magnetic stirrer. When the temperature reached  $140^\circ\text{C}$ , ethylene oxide was added drop-wise into the autoclave, the pressure being maintained at 0.4 MPa. After 23.0 g (0.543 mol) of ethylene oxide have been added, the autoclave was again flushed with  $\text{N}_2$  for three times. On cooling to room temperature, 36.0 g of the product were obtained. The average length of polyoxyethylene ether chain was determined from its hydroxyl value,  $n = 8$ .

## 2.2. Preparation of $[R(OC_2H_4)_n]_mPPh_{3-m}$



$[C_{12}H_{25}(OC_2H_4)_8]_2PPh$  was taken as an example of  $[R(OC_2H_4)_n]_mPPh_{3-m}$ : 14.0 g (0.026 mol) of  $C_{12}H_{25}(OC_2H_4)_8OH$  in 10 ml toluene were stirred with a magnetic stirrer and heated to refluxing temperature, then 3.6 g (0.020) of  $PhPCl_2$  in 5 ml toluene were added drop-wise in 30 min. Reaction was continued while refluxing for 3 h. Then toluene was distilled under vacuum. Anhydrous ethyl ether amounting to 50 ml was added to the reaction mixture and the crude product was crystallized at  $-18^\circ C$ . White needle product in the amount of 6.7 g was obtained. The yield was 45.0%. Infrared (IR) spectra:  $\nu$  ( $cm^{-1}$ ) max: 2960 ( $-CH_3$ ), 2924, 2856, 1440, 1466 ( $-CH_2-$ ), 1116 (C–O–C), 751, 696 (mono-substituted benzene).  $^1H$ -NMR (nuclear magnetic resonance) ( $\delta$ ): 0.92 (6H,  $-CH_3$ ), 1.31 (40H,  $(-CH_2-)$ 10), 3.50 (68H,  $-CH_2O-$ ), 7.35 (5H, Ph).

## 2.3. Hydrogenation of sodium cinnamate

The hydrogenation was carried out in a 100-ml two-necked flask fitted with a reflux condenser and a thermometer. A water-sealed hydrogen dispenser was connected on the top of the condenser.  $RhCl_3 \cdot 3H_2O$ , AEOPP and water were added to the reactor under an atmosphere of  $N_2$ . The system was thoroughly purged with  $H_2$ , and checked for leaks. Then the reactor was heated to the reaction temperature and an aqueous solution of sodium cinnamate was injected into the reaction mixture. The uptake of  $H_2$  was monitored until all necessary experimental data were collected.

## 2.4. General procedure for hydroformylation

The hydroformylation reactions were carried out in a 75-ml stainless-steel autoclave immersed in a thermostatic oil bath equipped with a magnetic stirrer. Into the autoclave, 0.01 mmol Rh compound, 0.12 mmol AEOPP, 3.0 ml of  $H_2O$  and 2.0 ml organic solvent were added. To this mixture were added 1-dodecene and decane (internal standard). The reactor was sealed, flushed five times with CO at 10 atm and checked for leaks. Then the autoclave was pressurized with CO/ $H_2$  (1/1), and placed in the oil bath which had been preheated to  $100^\circ C$ . After the appropriate reaction time, the reactor was cooled to room temperature and depressurized. The organic phase was dried over  $MgSO_4$  and analyzed by gas chromatography immediately. Gas chromatographic analyses were run on a SP-09 instrument (OV-101, 50 m capillary column, carrier gas: 2.0 atm  $N_2$ , FID detector) equipped with a Shimadzu C-R3A integrator. The products were identified by GC/MS and compared with the standard spectra.

## 3. Result and discussion

### 3.1. Research on the cloud point of AEOPP

Effects of changing hydrophilic and lipophilic groups on the cloud point and water solubility of the phosphine ligands AEOPP are shown in Table 1.

Table 1

Effect of changing hydrophilic and lipophilic groups on the cloud point ( $C_p$ ) and water solubility of AEO-PP

R	$n$	$m$	$C_p^a$ (°C)	$C_p^b$ (°C)	Water solubility <sup>c</sup>	EO <sup>d</sup> /C $j^e$
C <sub>4</sub>	7	2	–	–	vs	1
C <sub>5</sub>	8	2	–	50.0	vs	1
C <sub>5</sub>	10	2		56.5	vs	1.25
C <sub>5</sub>	13	2		62.0	vs	1.625
C <sub>5</sub>	16	2		66.0	vs	1.875
C <sub>12</sub>	8	2	39.5	30.0	s	0.53
C <sub>12</sub>	10	2	59.0	49.0	vs	0.67
C <sub>12</sub>	13	2	66.0	57.0	vs	0.75
C <sub>12</sub>	16	2	70.5	68.0	vs	1
C <sub>18</sub>	8	2			ss	0.38
C <sub>18</sub>	10	2	33.0		ss	0.48
C <sub>18</sub>	13	2	46.0		s	0.62
C <sub>18</sub>	16	2	52.0		vs	0.76
C <sub>12</sub>	16	1		39.5	vs	0.67
C <sub>8</sub>	16	1		43.0	vs	0.80
C <sub>5</sub>	16	1		48.0	vs	0.94
C <sub>5</sub>	13	1		40.0	vs	0.76
C <sub>5</sub>	10	1		31.0	s	0.6

<sup>a</sup>Determined in 0.5% (w/w) water solution.<sup>b</sup>Determined in 2% (w/w) water solution.<sup>c</sup>Water solubility at room temperature.<sup>d</sup>EO = 2*n*.<sup>e</sup>Total number of carbon atoms of R and benzene.

Table 1 shows that AEOPP with  $n$  larger than 7 and EO/C $j$  greater than 0.5 possess good water solubility, and only when the R group is larger than butyl do the phosphine ligands have distinct cloud points. The cloud point of AEOPP increases with the increase of  $n$  and decreases with the increase of the number of carbon atoms in R group if the concentrations of the solution are the same.

### 3.2. The examination of thermoregulated phase transfer property of AEOPP

According to the principle of cloud point of the nonionic surfactant, it is reasonable to predict that AEOPP possesses a property which we termed as ‘thermoregulated phase transfer’ (in aqueous/organic two-phase system) or ‘thermoregulated phase separation’ (in aqueous system). This prediction has been proved through catalytic hydrogenation of sodium cinnamate in an aqueous system. The reaction was catalyzed by using a complex catalyst prepared in situ from RhCl<sub>3</sub> · 3H<sub>2</sub>O and AEOPP under normal pressure. Two ligands with different cloud points were selected, and their catalytic activities were observed at different temperatures (according to the amount of H<sub>2</sub> consumed). The results are shown in Fig. 1.

The curves in Fig. 1 show that when the reaction temperature is below the cloud point of the catalysts used, hydrogenation occurs. When it is above the cloud points of the catalysts used, the reactions decelerate or stop, and anti-Arrhenius phenomenon is observed. When the temperature is lowered to that below the cloud point, the reaction resumes. The explanation could be that the complex catalyst dissolves in water when the temperature is below the cloud point but separates from water when the temperature is above the cloud point.

Analogous phenomenon was first reported by Bergbreiter et al. [7,8] in case of phosphorus-bonded block copolymers of ethylene oxide and propylene oxide as ligands. Obviously, the existence of such an unusual temperature-dependent property provides a fundamental support for the concept of the

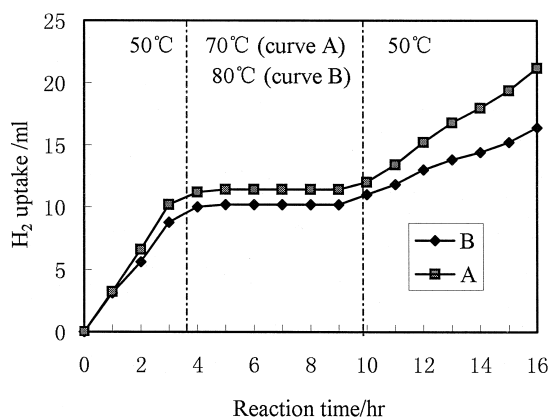


Fig. 1. Hydrogenation of sodium cinnamate in aqueous system under normal pressure using  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{AEO-PP}$  as catalyst. (A) Cloud point of reactive solution is  $64^\circ\text{C}$ ; concentration of Rh:  $1.83 \times 10^{-4}$  M, P/Rh = 13 (molar ratio). (B) Cloud point of reactive solution is  $72^\circ\text{C}$ ; concentration of Rh:  $9.86 \times 10^{-5}$  M, P/Rh = 13 (molar ratio).

TRPTC. If an extra organic phase containing a water-immiscible substrate was added into the reaction system, the catalyst being precipitated from the aqueous phase on heating above its cloud point would transfer into the organic phase and then the reaction would take place in the organic phase.

### 3.3. Hydroformylation of 1-dodecene by Rh/AEOPP

It is very attractive to extend the method of aqueous/organic two-phase catalysis to the reaction of substrates with very low water-solubility [9]. Based on the inverse temperature-dependent water-solubility of AEOPP, we have developed a new concept of two-phase catalysis—thermoregulated phase-transfer catalysis (TRPTC) [4,5]. The general principle of the TRPTC is outlined in Fig. 2. A basic feature of the TRPTC is that the catalyst can transfer into the organic phase to catalyze a reaction at a temperature higher than its cloud point. Thus, the water solubility of the organic substrate is no longer a control factor of the reaction rate.

Two-phase hydroformylation of higher olefins was chosen as a model reaction to investigate the tentative idea of the TRPTC. A major drawback associated with such a reaction lies in the limited water-solubility of higher olefins, which prevents the reaction from attaining viable catalytic rates [10].

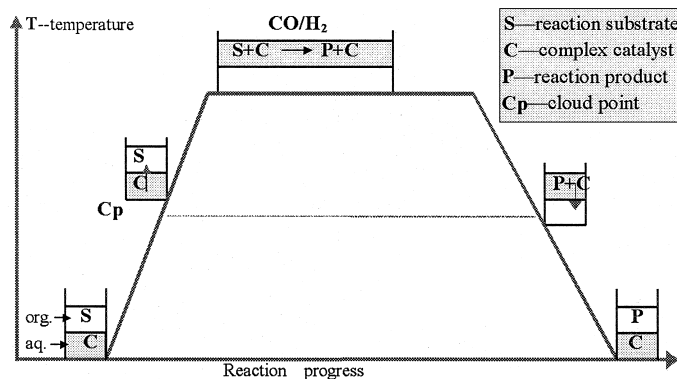


Fig. 2. General principle of thermoregulated phase-transfer catalysis.

Table 2  
Two-phase hydroformylation of 1-dodecene by different catalysts<sup>a</sup>

Precursor	Water-soluble ligands	Substitute/Rh (molecular ratio)	Conversion <sup>b</sup> (%)	RCHO yield (%)	<i>n</i> /Iso	TOF <sup>c</sup> (h <sup>-1</sup> )
RhCl <sub>3</sub>	Ph <sub>2</sub> P[(OC <sub>2</sub> H <sub>4</sub> ) <sub>16</sub> OC <sub>8</sub> H <sub>17</sub> ]	500	94.4	86.7	0.45	86
RhCl <sub>3</sub>	PhP[(OC <sub>2</sub> H <sub>4</sub> ) <sub>14</sub> OC <sub>8</sub> H <sub>17</sub> ] <sub>2</sub>	500	97.0	91.3	0.48	91
RhCl <sub>3</sub>	PhP[(OC <sub>2</sub> H <sub>4</sub> ) <sub>10</sub> OC <sub>12</sub> H <sub>25</sub> ] <sub>2</sub>	1000	98.3	96.0	0.60	192
Rh(CO) <sub>2</sub> (acac)	Ph <sub>2</sub> P[(OC <sub>2</sub> H <sub>4</sub> ) <sub>16</sub> OC <sub>5</sub> H <sub>11</sub> ]	1000 <sup>d</sup>	93.6	87.4	0.5	175
Rh(CO) <sub>2</sub> (acac)	P[ <i>m</i> -C <sub>6</sub> H <sub>4</sub> -SO <sub>3</sub> Na] <sub>3</sub> (TPPTS)	1000 <sup>d</sup>	15.3	13.9	3.5	28

<sup>a</sup>Reaction conditions: metal 0.01 mmol; P/Rh = 12; substitute (1-dodecene) 10 mmol; solution (toluene) 2.0 ml; H<sub>2</sub>O 3.0 ml; decane 0.3 ml, *P* = 5.0 MPa (CO/H<sub>2</sub> = 1/1), *T* = 100°C, time: 5.0 h.

<sup>b</sup>Based on the original amount of dodecene added.

<sup>c</sup>TOF = mol(aldehyde)/mol(metal)/h.

<sup>d</sup>Heptane was used instead of toluene.

Table 2 shows the results hydroformylation of 1-dodecene catalyzed by Rh/AEOPP complex in aqueous/organic two-phase media. It can be seen that the highest conversion of the olefin and the yield of the aldehyde are 98% and 96%, respectively. As a comparison, the Rh/TPPTS can only afford a conversion of 15.3%.

The satisfactory catalytic reactivity of Rh/AEOPP complexes indicates that the reaction occurs in organic phase. The result provides further proof for the thermoregulated phase transfer function of AEOPP in aqueous/organic two-phase system. At temperature lower than the Cp, AEOPP-modified rhodium catalyst would remain in the aqueous phase because the partitioning of the catalyst between water and nonpolar aprotic solvents strongly favors the former. On heating to a temperature higher than Cp, however, the catalyst loses its hydrated shell and then transfers into the organic phase where 1-dodecene is transformed into aldehydes. As soon as the reaction is complete and the system is cooled to a temperature lower than Cp, the catalyst regains its hydrated shell and returns to the aqueous phase to be separated from the products.

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