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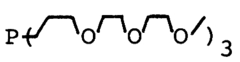
"Counter" Phase Transfer Catalysis by Water-soluble Phosphine Complexes. Catalytic Reduction of Allyl Chlorides and Acetates with Sodium Formate in Two-phase Systems

Tamon OKANO,* Yoshiyuki MORIYAMA, Hisatoshi KONISHI, and Jitsuo KIJI*
Department of Environmental Chemistry and Technology,
Faculty of Engineering, Tottori University, Tottori 680

In the reduction of allyl chlorides and acetates with sodium formate in a heptane-water two-phase system, water-soluble palladium complexes function as a novel type of catalyst which transports the substrate into the aqueous phase and causes it to react with sodium formate.

Although crown ethers and quarternary ammonium salts, which can transport the anions of lipophobic salts into an organic phase, have been extensively studied,1) little attention has been paid to the carrier compounds capable of transporting hydrophobic organic molecules into an aqueous phase.2) In order to achieve this counter, or inverse, transportation, both the ability to interact with organic molecules and enough affinity for water are indispensable to the carrier molecules. Transition metal complexes are satisfactory for the former requirement, but are hydrophobic. Although some water-soluble phosphine complexes have been reported,3) such a "counter" transportation phenomenon has not been found. From these viewpoints, we have examined whether the "counter" transportation is actualized by the transition metal complexes having water-soluble phosphine ligands.

Three water-soluble phosphines (L) shown below were used in this study. The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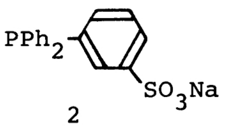

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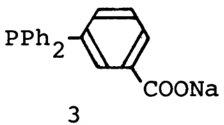

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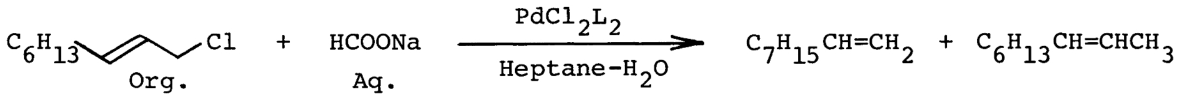
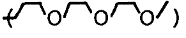
polyether phosphine, **1**, is liquid and was freely soluble in water at 30 °C.3a) The solid phosphines, **2** and **3**, were soluble to the extent of more than 20 g/100 ml of water at room temperature. The palladium complexes,4) PdCl$_2$L$_2$; **4** (L=**1**), **5** (L=**2**), and **6** (L=**3**), were also hydrophilic. The liquid complex, **4**, was freely soluble in water at 20 °C, but interestingly was also soluble in toluene, cyclohexane, and heptane. The distribution constants ($[\mathbf{4}]_{aq}/[\mathbf{4}]_{org}$) between the aqueous and the organic phases, which were determined by the UV spectra (λ_{max} 305 nm, ε 9.2 x 10^3), were 0.59 and >100 in toluene and cyclohexane, respectively. Though the exact solubilities and distribution constants of **5** and **6** could not be determined because of the instability of their aqueous solutions, a deep coloration of the aqueous solutions suggested that these complexes were highly soluble in water and that the distribution constants between toluene and water were very high.

Using the reduction of allyl chlorides and acetates with sodium formate as a model system, we investigated the "counter" phase transfer catalysis by the water-soluble palladium complexes. In this system, the allyl compounds exist in the organic phase and the reductant exists in the aqueous phase. If a non-polar solvent - water system is used, the hydrophobic substrate hardly comes into contact with the reductant. In fact, $PdCl_2[P(n\text{-}Bu)_3]_2$ (7) was inefficient for the reduction of (E)-1-chloro-2-nonene in a heptane-water solution. On the other hand,



Catalyst		Conversion/% a)	Yield/% of products a)	
$PdCl_2[P(n\text{-}Bu)_3]_2$	(7)	26	20	3
$PdCl_2[P$$)_2]_2$	(4)	100	82	17

Conditions; $PdCl_2L_2$(0.05 mmol):$C_9H_{17}Cl$:HCOONa = 1:100:200, heptane(8 ml), H_2O(2 ml), with vigorous stirring under reflux for 6 h. a) Based on used $C_9H_{17}Cl$.

the water-soluble complex , 4, was very active, and nonenes were obtained in a quantitative yield. An analogous phenomenon was observed in the reductions of cinnamyl chloride and acetate (Table 1). In the heptane-water system the reduction of cinnamyl chloride using 4 was fast and produced phenylpropenes in a high yield, but the catalytic activity of 7 was poor. In the reduction of cinnamyl acetate, which was faster than that of cinnamyl chloride, the difference of the

Table 1. Catalytic Two-phase Reduction of Cinnamyl Chloride and Acetate a)

Cinnamyl compound	Catalyst system c)	Ligand (L)	Organic phase	Time h	Conversion % d)	Yield/% of products d)	
						PhC_3H_5 e)	$PhCH=CHCH_2OOCH$
Chloride	A	$P(n\text{-}Bu)_3$	Heptane	7	59	22 (59)	30
Chloride	A	$P(n\text{-}Bu)_3$	Toluene	7	65	33 (64)	21
Acetate b)	A	$P(n\text{-}Bu)_3$	Heptane	1	16	15 (67)	1
Acetate	A	$P(n\text{-}Bu)_3$	Toluene	1	37	34 (71)	3
Chloride	A	1	Heptane	3	100	95 (27)	4
Chloride	A	1	Toluene	7	53	31 (35)	22
Acetate b)	A	1	Heptane	1	100	99 (34)	0
Acetate	A	1	Toluene	1	41	37 (73)	3
Chloride b)	B	1	Heptane	3	93	81 (28)	10
Chloride b)	B	1	Toluene	3	95	68 (71)	27
Chloride	A	2	Heptane	5	89	84 (45)	5
Chloride b)	B	2	Heptane	3	80	78 (55)	0
Chloride	A	3	Heptane	5	100	52 (53)	45
Chloride b)	B	3	Heptane	3	91	63 (56)	27

a) A mixture of substrate(5 mmol), catalyst(Pd;0.05 mg atom) and HCOONa(10 mmol) in organic solvent(5 ml) and H_2O(2 ml) was vigorously stirred at 100 °C. b) organic solvent(8 ml) was used. c) System A; $PdCl_2L_2$ and B; $[Pd(C_3H_5)Cl]_2$ + 6 L. d) Based on used substrate. e) Percentages of $PhCH_2CH=CH_2$ were in parentheses.

catalytic activity between **4** and **7** was great. The catalyst system B, composed of $[Pd(C_3H_5)Cl]_2$ and 6 L, also showed a tendency for the water-soluble phosphines to increase the catalytic activity.

Owing to the polyether chains, **1** and **4** possess the normal function[4a)] of transporting formate anion from an aqueous phase into an organic phase, but **2** and **3** do not have such a function. However, the water-soluble complexes with **2** and **3** also effective in this two-phase reduction. Therefore the high activity of **4** can not be attributed to the normal phase transfer function. It is also unlikely that a formate or hydride palladium species generated by the reaction of $PdCl_2L_2$ with sodium formate transfers into the heptane phase and then reacts with the allyl compounds just like a transition metal phase transfer catalyst, because the water-soluble complexes contrary to **7** were more active in heptane-water than in toluene-water. If the water-soluble complexes act as the transition metal phase transfer catalyst, the reaction rate is expected to be faster in toluene-water than in heptane-water. This deduction is based on the following reason: since the transition metal phase transfer reaction follows substantially the same mechanism as the normal phase transfer catalytic reaction which occurs in an organic phase, the higher solvency the organic phase has, the more the concentration of hydride or formate species increases, and so the reaction is accelerated. Such a solvent effect is general in the normal phase transfer catalysis.[1)]

Consequently it is reasonable that the water-soluble complexes function as the "counter" phase transfer catalyst. Namely, a palladium(0) species,[5)] which transfers from the aqueous phase, firstly reacts with allyl compounds in the organic phase to produce a π-allyl palladium species. This π-allyl complex, which is considered as a key intermediate,[5)] is transferred into the aqueous phase and then reacts with sodium formate to give the corresponding olefins. On the basis of this mechanism, the high activity in heptane-water is explainable by an increased concentration of the π-allyl species in the aqueous phase owing to its high distribution constant between heptane and water.

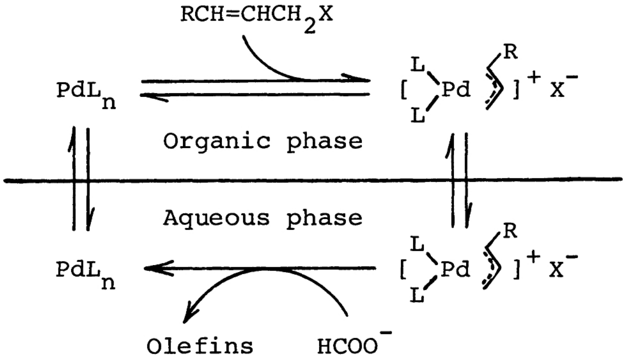


Fig. 1. Proposed mechanism for the reduction.

Further evidence for the "counter" phase transfer catalysis was obtained from the experiments to see the phase in which the reduction occurs. For this purpose, the reduction of allyl acetate to gaseous propene was carried out in the apparatus illustrated in Fig. 2. Ultrasonic waves were employed for the agitation for fear that the organic solvent should stray into part I of the aqueous layer. The propene gas, which was formed either in the organic layer or at the interface, was collected from outlet A. The propene from part O of the aqueous layer also emerged from outlet A, whereas only the propene from part I could be collected from outlet B. By assuming that part O is equivalent to part I in the propene formation per unit volume of the aqueous layer, both the amount of propene from the two parts of the aqueous layer and the propene volume from the organic phase and/or the interface could be calculated. The results are shown in Table 3. As expected, 98% of the propene was evolved from the aqueous layer in the heptane-water system using the water-soluble complex, **4**. On the other hand, the reductions with **7** in both solvent systems and with **4** in the toluene system produced the propene which exclusively came from the organic layer and/or the interface. The former result indicates that the allyl compound in the heptane phase was transported by the water-soluble complex and reduced to propene in the aqueous phase. This strongly supports the "counter" phase transfer mechanism, which is fundamentally different from the normal type of phase transfer catalysis.

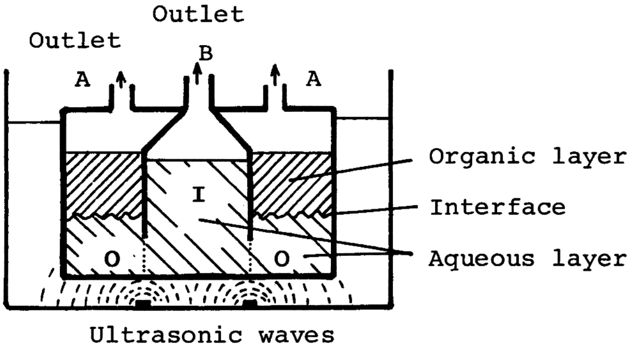
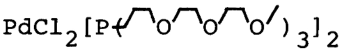


Fig. 2. Apparatus for the two-layer reduction.

Table 2. Reduction of Allyl Acetate to propene in Two-layer System [a)]

Catalyst		Organic layer	Yield/% of propene	Origin/% of propene [b)]	
				Aq.	Org. and Int.
$PdCl_2[P(n\text{-}Bu)_3]_2$	(**7**)	Heptane	38	12	88
		Toluene	31	15	85
	(**4**)	Heptane	55	98	2
		Toluene	41	23	77

a) Conditions; $PdCl_2L_2$(0.1 mmol):$C_3H_5OCOCH_3$:HCOONa = 1:200:400, organic solvent (4 ml), H_2O(7 ml), 80 °C, 0.5 h. b) Based on the yield of propene.

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