

Water Soluble Phosphine Complexes for Biphasic Catalysis

Keith A. Marek

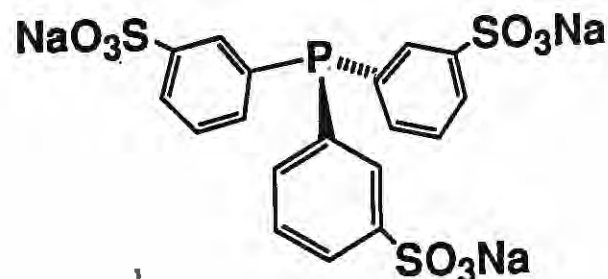
Literature Seminar

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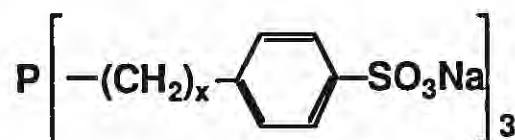
Homogeneous catalytic systems are attractive due to their mild operating conditions and high selectivities.¹ However, separation of the organic products from the active catalyst remains a problem. The concept of biphasic catalysis, in which the catalyst is contained in an aqueous layer, has been used to address this problem. Since the products are insoluble in water, they can be easily removed using a simple decantation step. Thus, biphasic systems combine the ease of separation, which is an inherent property in heterogeneous systems, with the high selectivities and mild conditions associated with homogeneous systems.²

The aqueous biphasic concept became a reality in 1984 with the implementation of the Ruhrchemie/Rhone-Poulenc process. A recent article published by the founders of this process describes the events leading up to this development.³ In this process, a water soluble analog of Wilkinson's hydroformylation catalyst, $\text{HRh}(\text{CO})(\text{TPPTS})_3$ (TPPTS = tris(3-sulphonatophenyl)phosphine, pictured below), is used to hydroformylate propene to *n*-butanal. Currently, this process produces *n*-butanal in excess of 300,000 tons/year.³

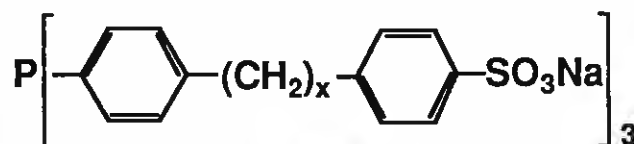
Hydroformylation in two phase systems is quite facile when the substrate is a lower molecular weight olefin. However, difficulty arises when using the Rh/TPPTS system with higher olefins. Substrates such as 1-hexene and 1-octene, for example, are virtually insoluble in water, and as a result, low activities are observed in hydroformylation reactions using the biphasic system. Solubility of these olefins can be improved by use of cosolvents,⁴ ligands with surface active properties,^{5,6} and supported aqueous phase catalysts.⁷⁻¹⁰



Recently, Hanson and coworkers^{6,11} developed two series of phosphine ligands, shown below, which seem to exhibit surfactant properties.

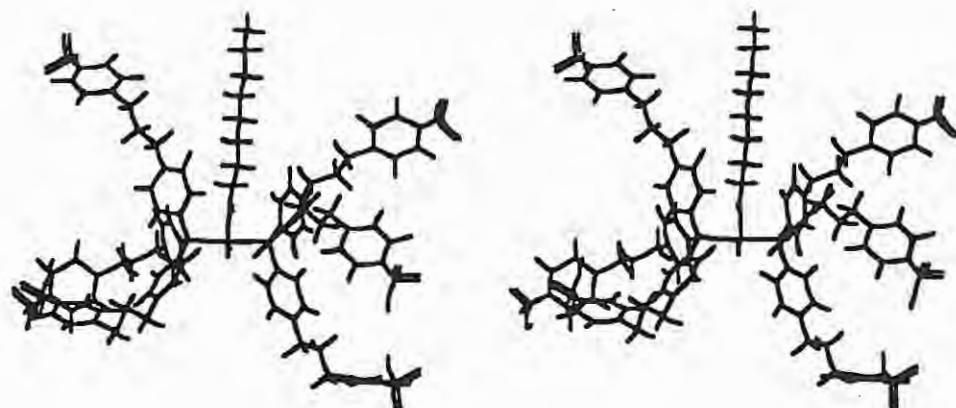


$x = 1, 2, 3, 6$



$x = 3, 6$

The tris(ω -phenylalkyl)phosphines exhibit higher activities with increasing chain length (x).⁵ In the $x = 6$ case, a great improvement in activity over the TPPTS system is observed. However, selectivities are considerably lower with these ligands compared to TPPTS. Using the $\text{Rh}/\text{P}[\text{Ph}(\text{CH}_2)_x\text{PhSO}_3\text{Na}]_3$ system, the selectivities are greatly improved, and linear/branched ratios of 9.5:1 have been obtained at relatively moderate ligand concentrations.⁶ These activities and selectivities have been attributed to the aggregation abilities of the ligand, which allow the substrates to be transported into the aqueous phase more readily. Pictured below is a proposed reaction intermediate which shows these aggregation abilities with a 1-octene substrate.

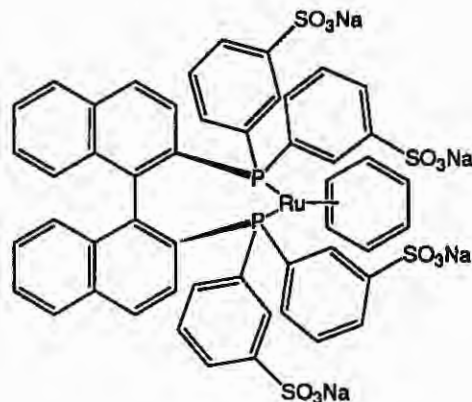


This structure, $\text{trans-Rh}^{\text{I}}\{\text{P}[\text{Ph}(\text{CH}_2)_3\text{PhSO}_3\text{Na}]\}_2[\text{CO}(\text{CH}_2)_7\text{CH}_3]$, is supported by light scattering experiments.

Salt concentration also seems to have an effect on biphasic catalysis. A series of studies^{12,13} was undertaken to determine the extent of this effect. Increased ionic strength in the conventional systems is observed to produce lower activities, due to decreased solubility of substrate in aqueous media. In the case of the surface active ligands, increased ionic strength promotes aggregation of the ligands, and a higher activity is observed. This seems to be the case with the monovalent cations Li^+ , Na^+ , and Cs^+ . When a trivalent cation, Al^{3+} , is used as a spectator ion, a decrease in the selectivity of the Rh/TPPTS system is observed due to coordination of the sulfate groups on TPPTS to the cation.¹⁴

Supported aqueous phase (SAP) catalysts are another answer to the solubility problems of the substrate.^{7,8} In these systems, the hydrophilic catalyst is present in a thin film of water which is adsorbed onto a support, such as SiO_2 . These catalysts have been found to be active in the hydroformylation of several olefinic substrates. It has also been found that the water content of the supported phase plays a crucial role in the activity of these catalysts. Control of the water content in these particles has yet to be realized in continuous flow settings, due to some leaching of the water into the organic phase.¹⁰ It is for this reason that these catalysts have not yet been incorporated into commercial processes.

Supported aqueous phase catalysts may find use in the synthesis of fine chemicals.^{2b} This is supported by the work of Davis and coworkers who recently utilized a supported aqueous phase catalyst in the synthesis of the anti-inflammatory agent naproxen.^{15,16} The Ru-based catalyst precursor, first synthesized in an earlier paper¹⁷ incorporates a sulfonated BINAP ligand. Comparisons of this supported aqueous phase method have been made with analogous homogeneous and biphasic systems.



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