

## Introducing TPPTS and related ligands for industrial biphasic processes <sup>☆</sup>

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Received 19 June 1995

### Abstract

This paper describes the beginnings and development of biphasic homogeneous catalysis. With water-soluble triphenylphosphine trisulfonate as the ligand, Rh catalyzed hydroformylation as part of the Ruhrchemie/Rhône-Poulenc process has become the first commercially viable technique using aqueous catalyst solutions.

**Keywords:** Homogeneous catalysis; Aqueous catalyst; Immobilization

### 1. Introduction and initial considerations

Theoretically the history of biphasic homogeneous catalysis starts with Manassen's prophecy

“..... the use of two immiscible liquid phases, one containing the catalyst and the other containing the substrate, must be considered. The two phases can be separated by conventional means and high degrees of dispersion can be obtained through emulsification” [1].

Roughly at the same time and in parallel to work done by J6o [2] and others [3,11d] one of us (EK at Rhône-Poulenc) started practical work on biphasic catalysis with organometallic catalysts, developing the biphasic principle and today's well-known standard ligand triphenylphosphine trisulfonate (TPPTS).

This work has to be considered against a background which Parshall described as follows: “There was some use of transition-metal carbonyls in catalytic reactions of CO, but soluble catalysts played only a minor role in industry” and “... the discovery that had the greatest impact in technology was recognition of the catalytic merit of rhodium complexes” [4], thus indicating that

only a few homogeneously catalyzed processes were commercialized before the early 1970s and only some of them used precious metals as the catalyst base. Examples were

- (1) the palladium–copper catalytic system used in the major process of oxidation of ethylene to acetaldehyde (Wacker-Hoechst process) [5],
- (2) the production of 1,4-hexadiene by codimerization of ethylene and butadiene catalyzed by rhodium trichloride. The scale of the production was not mentioned and the catalyst cycle was not published [6],
- (3) Monsanto's processes to yield acetic acid via methanol carbonylation [7] or a chiral L-DOPA precursor via hydrogenation of substituted cinnamic acids [8].

In the field of homogeneous catalysis, the late 1960s and early 1970s saw the discovery and utilization of catalytic systems involving metals associated with P-compounds and their use in oxo syntheses [9]. After the discovery of zero valent metal complexes in 1957 by Quin and in 1958 by Malatesta/Cariello [10] the Wilkinson school of thought opened up a new field of rhodium chemistry by applying the remarkable catalytic properties of triphenylphosphine- (TPP) substituted Rh carbonyls [HRh(CO)(TPP)<sub>3</sub>] in the hydrogenation and hydroformylation of olefins [11a–c,13]. The important Wilkinson complex stimulated a rapid expansion in the

<sup>☆</sup> Dedicated to Professor Henri Brunner on the occasion of his 60th birthday.

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chemistry of the lower oxidation state complexes. Thus the progress made in the area of homogeneous catalysis includes:

- the low-pressure, highly selective hydroformylation of lower olefins (mostly ethylene and propylene, yielding propionaldehyde or *n*-/*iso*-butyraldehyde, respectively) on a lab scale since 1967 using TPP-modified Rh-carbonyls with excess TPP [12]. This process was commercialized by Union Carbide, Celanese, and BASF [13,14].
- the oligomerization, functionalization and telomerization of dienes (1967–69): Butadiene and isoprene offered a lot of possibilities particularly with catalysts based on palladium, platinum, rhodium, nickel, or cobalt. The telomerization of butadiene with water to octadienols catalysed by Palladium-TPP under a carbon dioxide atmosphere should be mentioned here [15].
- The hydrocyanation of olefins and dienes (1969): a system containing zero nickel and arylphosphite catalysts permitted the synthesis of adiponitrile (an intermediate in nylon production) by butadiene hydrocyanation in several steps with a advantageous overall yield [16].
- The hydrogenation, isomerization and dimerization of olefins and miscellaneous reactions in fine chemistry.

In 1970, the discovery of these new organo-soluble catalysts based on rhodium, palladium or platinum was generally considered unfeasible for industrial processes because of the prohibitive price of the metals involved. However, the high activity and productivity of these catalysts (several catalytic cycles per minute) made possible production levels of 100,000 tonnes per year with only a few dozen kilos of precious metals needed as inventory by each plant. Thus the amount of precious metal involved represents only a minor part of the investment and the manufacturing costs, i.e. the price of the metal was not an important factor in the production unit cost, provided that its usage occurred without any loss.

In 1972 this hypothesis was confirmed by Monsanto. Commercialization of the important process of generating acetic acid by methanol carbonylation was more economical than the older, cobalt-catalyzed process due to its exceptional selectivity [17]. So the question arose as to whether precious metals could be used in chemical reactions other than exotic conversions, and if the handling of “commercial” quantities would be feasible. The other point in question was the technique to be used to separate the products from the expensive catalysts, i.e. to solve the imminent problem of homogeneous catalysis.

Noting the extraordinary developments of homogeneous catalysis by ligand modification with suitable phosphorus compounds—especially with triphenylphos-

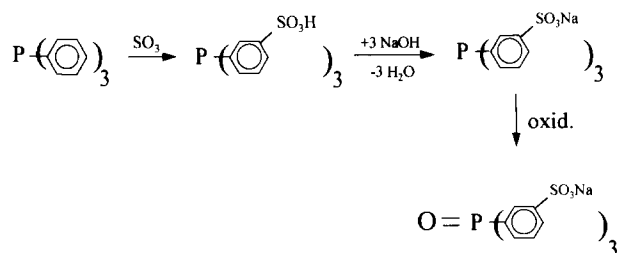
phine—it seemed useful to develop new catalyst recovery systems. One possible solution to the separation problem was distillation, however this caused thermal stress on the products to be separated and, more importantly on the residual catalyst. The other method of separation was decantation. This procedure was already known in connection with dimethylsulfoxide/organic products or other process proposals. However the use of the systems discussed was too complex for commercial and technical solutions. In the oxo technique in particular a biphasic process for the homogeneously catalyzed work-up of formic acid esters by cracking with aqueous sodium formate solutions as catalyst was run since 1967 [34] by one of us (BC at Ruhrchemie). According to Manassen’s proposal, decantation of catalyst and product meant that homogeneous catalysts dissolved in a liquid other than the organic phase to be separated. Water in particular would allow acceptable partition coefficients.

Was the progress recently achieved in homogeneous catalysis with precious metals possible in water? How could the catalyst be rendered soluble in water and, more importantly, non-extractable?

The principle of a technically feasible two-phase catalysis with water in parallel to Manassen’s [1] theoretical considerations was conceived in 1973. The metal complex catalyst solubilized in water by a hydrophilic ligand converts the starting material into the reaction products, which can be separated from the catalyst by phase decantation. During the hydroformylation of propylene it is important that the butanal (in which water is slightly soluble [3% at 20°C]) does not extract the hydrophilic complex from the water-soluble catalytic system. Before any experiments it was obvious that:

- the best hydrophilic substitute for the proven TPP as a ligand for a water-soluble complex catalyst would be the sodium salt of an appropriate TPP sulfonate, which is thermally very stable.
- According to experiences of Wilkinson and J6o, monosulfonated triphenylphosphine (with a carbon/sulfonate ratio of 18) would be slightly foamy, extractable and thus too organophilic (or hydrophobic) [2,11d].
- Therefore it proved essential to use the non-detergent, highly water-soluble (and thus hydrophilic) trisulfonated triphenylphosphine (C/sulfonate ratio of 6) which is not extractable by an organic medium and notably not extractable by water-saturated butanal [27].

The sodium salt of *m*-triphenylphosphino monosulfonate (TPPMS) was prepared in 1958 via the sulfonation of TPP [18]. In 1973 the first attempt to carry out a transition-metal-catalyzed reaction in an aqueous solution in the presence of hydroxy alkylphosphine was reported by Chatt [19]. These systems, however, did not



Scheme 1. Synthesis of TPPTS Herstellung.

catalyze the hydrogenation or the hydroformylation of olefins in water.

## 2. Basic work and investigations by Rhône-Poulenc

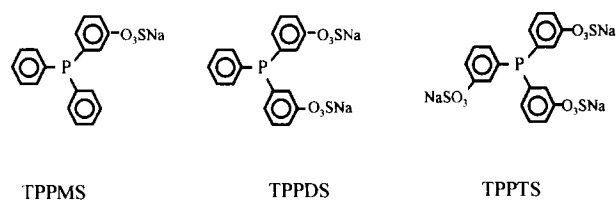
### 2.1. TPPTS synthesis

Following initial considerations in 1974 the preparation of TPPTS was carried out via the sulfonation of TPP with “oleum” (i.e. concentrated sulfuric acid containing 20% by weight of  $\text{SO}_3$ ) at  $40^\circ\text{C}$  during one day. After hydrolysis and neutralization by NaOH, an aqueous solution of sodium sulfate and a mixture of different P-compounds -consisting mainly of triphenylphosphine trisulfonate (TPPTS) and the corresponding P-oxide (“TPPOTS”) as key chemical species- were obtained [20–22] (Scheme 1).

Crude TPPTS fractions contained TPPTS and TPPOTS in ratios of roughly 55 : 45%. The separation of TPPTS from the other compounds was based on the fact that TPPTS is more soluble in water than sodium sulfate (approx.  $1100 \text{ g l}^{-1}$  for TPPTS [23]) and that  $\text{Na}_2\text{SO}_4$  is much less soluble than TPPTS in aqueous methanol. On the other hand TPPOTS is slightly more soluble than TPPTS in methanol/water mixtures. A further purification of TPPTS proceeded via repeated precipitation from those water/methanol mixtures, so purities of 95% TPPTS were possible. Today's processes give TPPTS/TPPOTS ratios of 94 : 6 under appropriate conditions and even in the crude material [54e]. Under suitable conditions even the less preferable mono- and the disulfonated species (TPPMS and TPPDS) can be formed in addition to TPPTS (Scheme 2)

### 2.2. Lab-scale catalysis in water under biphasic conditions

From 1974 onwards the scope of different reactions using biphasic catalyst systems preferably with precious metals, was tested in lab-scale experiments. Among these were butadiene hydrodimerization, hydrogenation of acrylonitrile or cyclohexene, hydroformylation of propylene, and some other conversions to fine chemicals. Even during this initial stage of experimental work it was shown that only a small fraction of the precious



Scheme 2. TPPMS, TPPDS and TPPTS as ligands.

metals (less than 0.1 ppm Rh in the case of hydrogenation or hydroformylation) is leached in the organic phase. At this stage the publication by J6o and Beck on the hydrogenation of pyruvic acid to lactic acid with aqueous solutions of Ru or Rh catalysts and monosulfonated TPP (TPPMS) [2] became known. To protect the results achieved so far Rhône-Poulenc decided to file different patent applications taking into consideration the state of the first laboratory results, the interest of Rhône-Poulenc (RP) in various product lines and the economic importance of the invention [27]. Thus a series of basic patents applications were filed to protect three different main fields of interest [20–22]. These include hydroformylation, hydrocyanation and diene conversions.

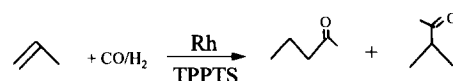
#### 2.2.1. Hydroformylation

Although RP was not an oxo producer the excellent lab results with the biphasic system as compared to conventional Co-based processes were regarded as an important opportunity. Taking the propylene hydroformylation to *n*-butyraldehyde with a TPPTS ligand modified Rh/TPPTS catalyst as an example, savings of up to 20% of propylene and of syngas could be envisaged [20] (Scheme 3).

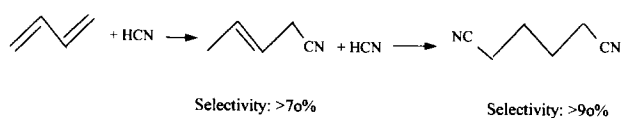
Because of the special properties of the biphasic catalysts and the low hydroformylation temperatures ( $80^\circ\text{C}$ ), the selectivities towards the desired linear *n*-isomer are high (*n/iso* ratio up to 96/4) and the formation of by-products (both propane and heavy ends with contents < 1%) is low. TPPTS proved to be the most suitable ligand as compared to TPPMS and TPPDS. Since the initial productivities at  $80^\circ\text{C}$  were too low higher temperatures of  $> 120^\circ\text{C}$  had to be used [25]. The stability of the aqueous catalyst system, the commercial design of a biphasic oxo unit and the influences of the different reaction variables — all under conditions of a continuous process — remained unknown.

#### 2.2.2. Hydrocyanation

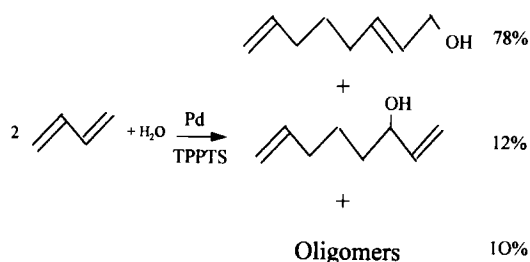
DuPont commercialized Drinkard's famous invention of the selective hydrocyanation of butadiene, catalyzed by  $\text{Ni}^0$ /triarylphosphite complexes [16]. Laboratory tests



Scheme 3. Hydroformylation of propene.



Scheme 4. Hydrocyanation of butadiene.



Scheme 5. Hydrodimerization of butadiene.

at RP demonstrated that the system consisting of  $\text{Ni}^{2+}$ , TPPTS and a reducing agent such as Zn or  $\text{NaBH}_4$  catalyzes the butadiene and 3-pentennitrile hydrocyanation and thus the formation of adiponitrile with high selectivities [21] (Scheme 4).

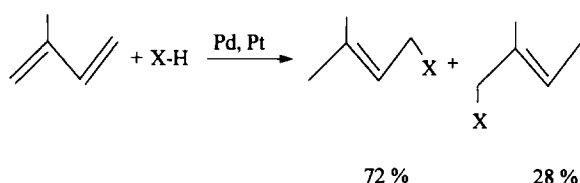
### 2.2.3. Diene conversions

The hydrodimerization of butadiene proved to be possible using a biphasic system with Pd as the central atom and TPPTS as the ligand. The telomerization of butadiene has been intensely investigated with compounds containing active hydrogen such as alcohols, amines, phenols, acids etc. [22] (Scheme 5).

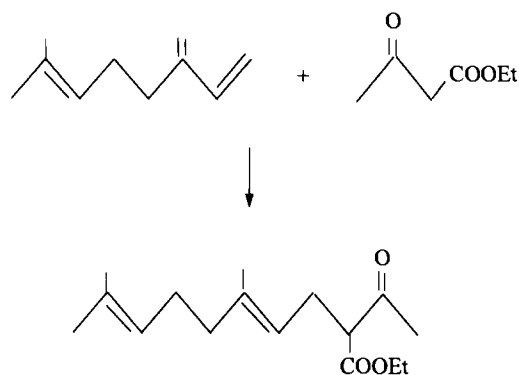
An improvement of the functionalization of isoprene with amines was made using Pd or Pt. In aqueous solutions these catalysts offer better selectivities than those normally expected in organic media [24] (Scheme 6).

### 2.3. Further investigations

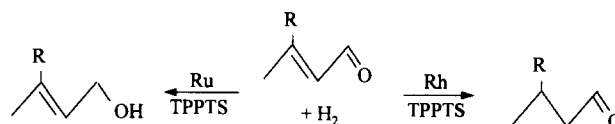
Continuing the research into the reactivity of dienes with biphasic catalytic systems, Morel and Mignani discovered the favourable effect of Rh-TPPTS on the functionalization of dienes in 4-position [26]. With other asymmetrical dienes such as myrcene and the addition of e.g. ethyl acetoacetate regioselectivities of 99% for the desired isoprenic compounds were achieved [28–31]. A couple of subsequent reaction steps converts geranylacetone to vitamin E. Today, this route represents another commercially viable application of biphasic catalysis with TPPTS (Scheme 7).



Scheme 6. X-H addition to dienes.



Scheme 7. Precursor of vitamin E synthesis.



Scheme 8. Partial hydrogenation of unsaturated aldehydes.

Besides diene reactions, selective hydrogenations and allylations attracted special interest. Alpha- and beta-unsaturated aldehydes are selectively hydrogenated with TPPTS-modified transition metal complex catalysts, either Ru or Rh [32a] (Scheme 8).

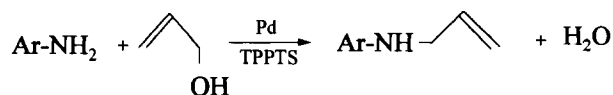
Palladium/TPPTS systems allow selective allylations of aromatic amines and phenols with allylic alcohol [32b]. The biphasic system limits the di-allylation of the amines: Later on various patents of RP protected different aspects of aqueous catalyses [33] (Scheme 9).

## 3. Investigations by Ruhrchemie AG

### 3.1. Application of TPPTS and other ligands

Following earlier contacts Ruhrchemie AG (RCH, now a part of Hoechst AG) and Rhône-Poulenc joined forces in 1982 to develop a continuous biphasic hydroformylation process for the production of n-butanal from propylene.

On the basis of the work documented in RP's patents and applications, RCH used its expertise with the biphasic catalytic cracking process [34] and its long experience in converting lab-scale syntheses to commercial processes. This was evident in many cases, e.g. Fischer-Tropsch synthesis, the Co-based oxo reaction (invented at RCH by Otto Roelen [35,36]), the UHMW



Scheme 9. Allylations of aromatic amines.

variant of Ziegler-type HDPE, the Texaco coal gasification etc.). Appropriate agreements defined the tasks for RP and RCH as the oxo producer, such as R & D, engineering, production, licensing, and marketing and distribution agreements. Between 1982 and 1984, in a period of less than 24 months, RCH developed and tested a completely new process for which no prototype was available. Using a scale-up factor of 1:10,000 the first production unit employing the “Ruhrchemie/Rhône-Poulenc oxo process” went on stream in July 1984 with an initial capacity of 100,000 tons per year (see section 3.2. [37]).

Because of Ruhrchemie’s commitment and status as an important oxo producer the development was thus primarily driven by product and commercial considerations. It was not until the 1990s that the further development became science-driven, including especially all the scientific research work currently being conducted at universities as a result of the successful realization of the RCH/RP process.

All the development tests included the full work-up of the reactants, side-streams and products, reflecting the characteristics of the biphasic system, the testing of reaction parameters, the dynamic responses of both the reactor and the catalytic system, product qualities, etc. [38].

The heart cut of the new process is the new catalyst  $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$  (Fig. 1).

Apart from the handling of the new catalyst system with a water-soluble species, a virtually new design of a hydroformylation process had to be prepared, involving

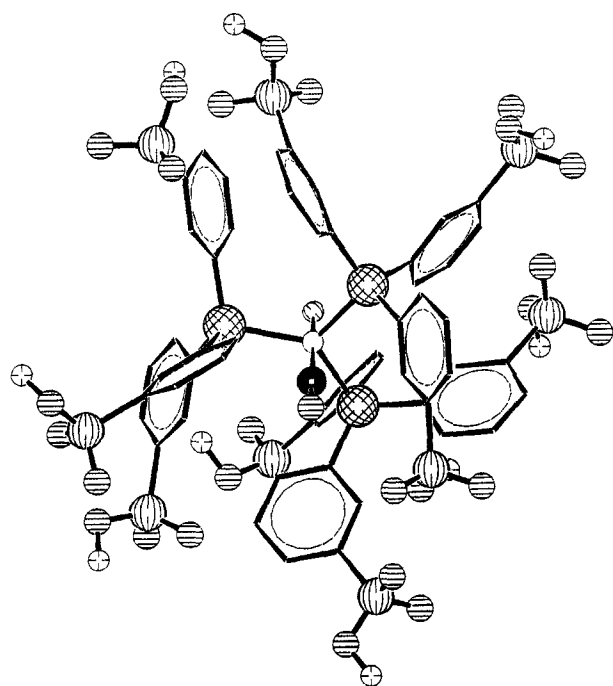


Fig. 1.  $[\text{Rh}(\text{CO})(\text{TPPTS})_3]$ , the water-soluble catalyst of the RCH/RP process.

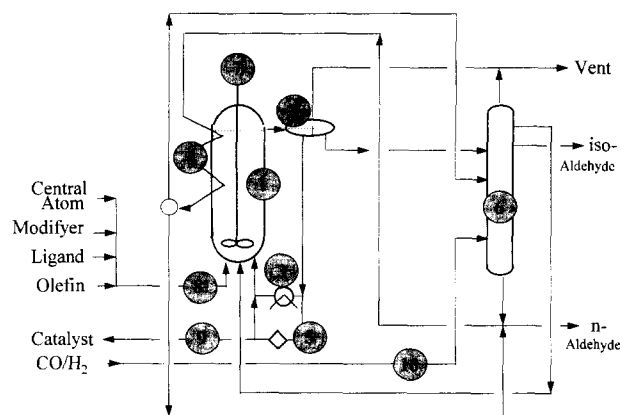


Fig. 2. General design of the biphasic hydroformylation process: focal points of R & D work as indicated. 1: Reactor; 2: Decantation; 3,4: Heat recovery and steam generation; 5: Rh recycle; 6: Distillation; 7: Control units; 8,10: Feed; 9: Catalyst.

a lot of detail work. Most of the solutions and numerous important variants have been patented. This detailed work focused on the special aspects of the process scheme as indicated in Fig. 2.

The sensitive areas of the process include the reactor and its environment (reactor, separation, control units, cooling devices, off-gases), olefin and syngas feed, preparation of the catalyst (including central atom, ligands, accompanying salts, and modifiers) and the catalyst recycle (including catalyst separation from different sources and catalyst recycles at different levels).

Some of the conditions of the new process were based on RP’s patents but had to be adjusted to the rougher operation conditions of a commercial plant, to different qualities and purities of commercial available reactants (olefins, syngas, catalyst precursors), to operation of 8760 hours per year, and to the fine-tuned relationships between e.g. temperatures, pressures/partial pressures, concentrations of various organic and inorganic components in different phases, mass and heat transfer and flow conditions etc. of a continuous process [39]. The economics of cooling and heat recovery and the utilization of unreacted substrates in off-gases or vents are of special importance [40]. In contrast to the literature [41] a combination of a low-pressure oxo step and a subsequent high-pressure stage proved to be more convenient than vice versa [40c]. Detailed work has focused on special reaction conditions and special measures (even within extreme limits) which base on the biphasic character of the conversion such as pH values, addition of  $\text{CO}_2$ , salt effects and ionic strengths, catalyst modifiers, or ultrasonic devices [42]. The measures mentioned allowed a considerably simplified process as compared with other oxo processes (basically consisting of a stirred tank reactor and a decanter), this being a consequence of the biphasic concept of Ruhrchemie/Rhône-Poulenc. These relationships ensure a smooth, stable operation yielding high selectivities to *n*-butanal.

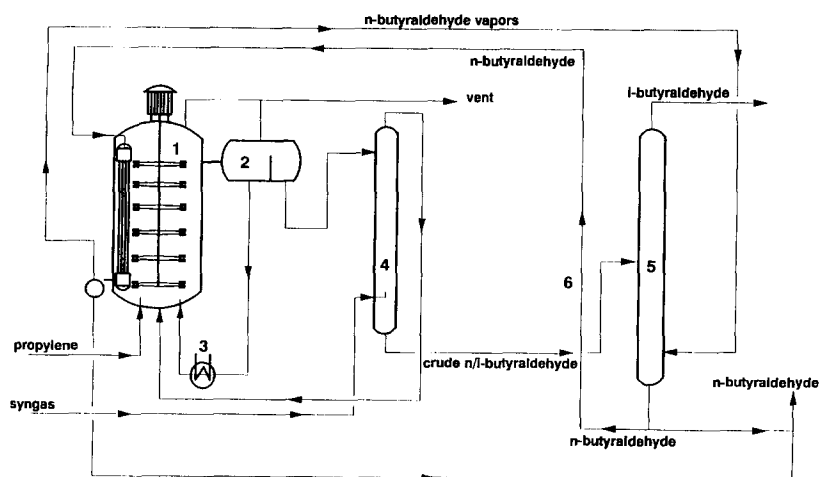


Fig. 3. Flow diagram of RCH/RP process (cf. [61]).

The specific load of the system may be altered very specifically by variation of temperature, pressure, partial pressures, and concentrations (catalyst, ligands, and salts).

In contrast to other low-pressure processes the purification of syngas is not critical [43]. Surprisingly, the presence carbon dioxide in the syngas acts as a selectivity improver [42c], a similar effect as has been described lateron by Rathke and Klinger [44]. The oxo units at Oberhausen have also been supplied with syngas from a TCGP (Texaco coal gasification plant) without any problems [45]. Although the RCH/RP process is more suitable for the conversion of lower olefins to the appropriate aldehydes (ethylene through pentenes) higher olefins may be converted using special precautions (cf. [46,50c]).

There is no prototype for the behavior and the lifetime of the biphasic catalytic system and the catalyst

recycle. Intense research work has been conducted to identify the optimal sets of operating conditions to ensure maximum efficiency and lifetime of the catalytic system. The advantages over other low-pressure processes are that the catalyst is on a "short circuit" around the reactor (ensuring fewer losses) and that because of mechanical separation of catalyst and product no thermal stress occurs. The catalyst may be regenerated within the reaction system using chemical or mechanical means [47]. The recycle via the work-up of the precious metal content as an ultimate solution is exceptional [48]. The losses of catalyst, a factor of major importance figure in precious metal-containing catalytic systems, are  $< 10^{-9}$  g Rh per kg *n*-butanal. Other methods of recovering Rh from oxo crudes [52,57a] or distillation residues [53] are also being investigated.

The catalyst  $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$  (see Fig. 1) is



Fig. 4. View of the RCH/RP process.

prepared from suitable precursors, which contain the central atom and the ligand. The catalyst can be pre-formed or may be prepared in situ [49]. The preparation of TPPTS is not as simple as it seems. Many misinterpretations concerning catalytic strength, behaviour, extractabilities, cluster or colloid formation etc. can be explained by unsuitable methods of ligand syntheses and purification [50]. For special purposes TPPTS may be modified [51]. These modifications of the original sulfonated phosphines result e.g. in different solubilities, re-immobilization etc. So very different levels of phase behavior and thus various degrees of immobilization may be adjusted.

The search for water-soluble ligands other than TPPTS is a focal point of present academic and industrial work. In cooperation with Prof. Herrmann of the Technical University of Munich and others the R & D department of Ruhrchemie has focused on special water-soluble phosphines [54], phosphites [55] and other catalysts [58] and their most suitable manufacture. The application of external or internal solubilizers may be recommended [56,57]. Appropriate complexes with other central atoms can be used for other syntheses [59].

Although commercial emphasis has been on propylene hydroformylation, other starting olefins include higher molecular substrates, e.g. [40d,46a–d,57b,60].

### 3.2. The RCH / RP process

As mentioned earlier the first commercial oxo plant using the Ruhrchemie/Rhône-Poulenc biphasic process went on stream in 1984 [37] and has been reviewed recently [61]. Water-soluble catalysts offer significant

Table 1  
Reaction conditions and results of RCH/RP's process (10 years' average)

		typical values	variance values
<i>iso</i> -butanal	[%]	4.5	4–8
<i>n</i> -butanal	[%]	94.5	95–91
<i>i</i> -butanol	[%]	< 0.1	< 0.1
<i>n</i> -butanol	[%]	0.5	0.5
Butyl formates	[%]	traces	traces
Heavy ends <sup>a</sup>	[%]	0.4	0.2–0.8
<i>n</i> : <i>iso</i> ratio		95:5	93–97:7–3
Selectivity towards C <sub>4</sub> products	[%]	> 99.5	> 99
Selectivity towards C <sub>4</sub> aldehydes	[%]	99	99
<i>parameters</i>			
Temperature	[°C]	120	110–130
Total pressure	[bars]	50	40–60
CO/H <sub>2</sub> ratio		1.01	0.98–1.03
Ratio water/org. phase		6	4–9
Energy efficiency <sup>b</sup>	[%]	100	100
Conversion	[%]	95	85–99
Propene quality	[% Propene]	95	85–99.9

<sup>a</sup> Mainly 2-ethyl-3-hydroxyhexanal-1.

<sup>b</sup> Besides losses of radiation.

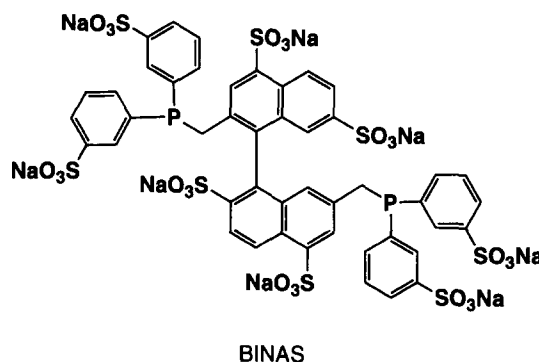
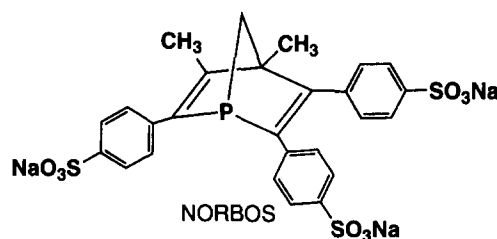
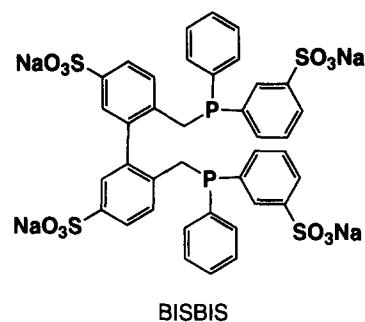


Fig. 5. Different new ligands [63].

advances in homogeneous catalysis: the “heterogenization” of the catalyst in a second, immiscible liquid phase (“liquid support”) immobilizes the catalyst phase, thus combining the advantages of heterogeneous catalysis (e.g. long lifetime, easy separation between product and catalyst) with those of the homogeneous mode, e.g. defined species of catalyst, gentle reaction conditions, high activity and selectivity.

The Ruhrchemie plant reacts propylene and syngas and yields *n*-butanal as desired product besides below 4% *iso*-butanal. The basic flow diagram of the 330,000 tonnes/yr. unit is shown in Fig. 3, a view in Fig. 4.

In comparison with other oxo processes the procedure is much simpler and many steps in the original process are superfluous. The actual catalyst [HRh(CO)(TPPTS)<sub>3</sub>] (Fig. 1) is simply made within the oxo

unit reacting suitable Rh salts with TPPTS of appropriate quality without any additional preformation step. The reaction system is self-adjusting; the on-stream-factor of the whole system is  $> 98\%$ . Typical reaction conditions and raw product compositions on an average of 10 years are compiled in Tab. 1.

Other details of the extremely environmentally sound process are discussed in [61]. The successful realization of the biphasic oxo process as the prototype of a homogeneous aqueous catalyst system will have different consequences as compiled in chapter 4.

#### 4. Outlook

The suitability of the homogeneous aqueous catalysts and thus the scope of application will be extended in commercial or pilot plant operation to other central atoms and reactions such as Heck reactions and other carbonylations (with Pd), hydrogenations (Pd, Pt, Rh, Ir), formation of water-soluble polymers (Pd), vinylations, metathesis conversions (Ru), etc. [56]. The hydroformylation itself will be extended to other starting olefins, the hydroformylation of which may need (be-

cause of limited miscibility of the olefins with water) special measures like sono-chemistry, preformations, other pH values or ionic strengths of the catalytic systems, amphiphilic or surface active ligands, solubilizers, modifiers, solvents, and co-solvents etc.

The development of ligands has not come to an end. The hydroformylation tests with different water-soluble ligands and complexes (cf. Fig. 5 with different new ligands [61b,63]) so far demonstrate that different requirements such as highest possible activity, highest  $n/i$  ratio, lowest required Rh concentration, or lowest excess of ligands may be achieved by different ligands, thus indicating bright prospects for future tailor-made oxo catalysts in biphasic operation. This is shown in Fig. 6 [61b].

A recent NATO workshop about aqueous homogeneous catalysis [62] summarized:

“A very important practical and environmental beneficial aspect of the use of a separate aqueous phase in catalytic reactions producing water-insoluble products is the potential for relatively easy and complete recovery of water-soluble catalysts. This could lead to the elimination of further steps for removal of traces of heavy metal from the product and to considerable savings.”

Reality shows this to be true.

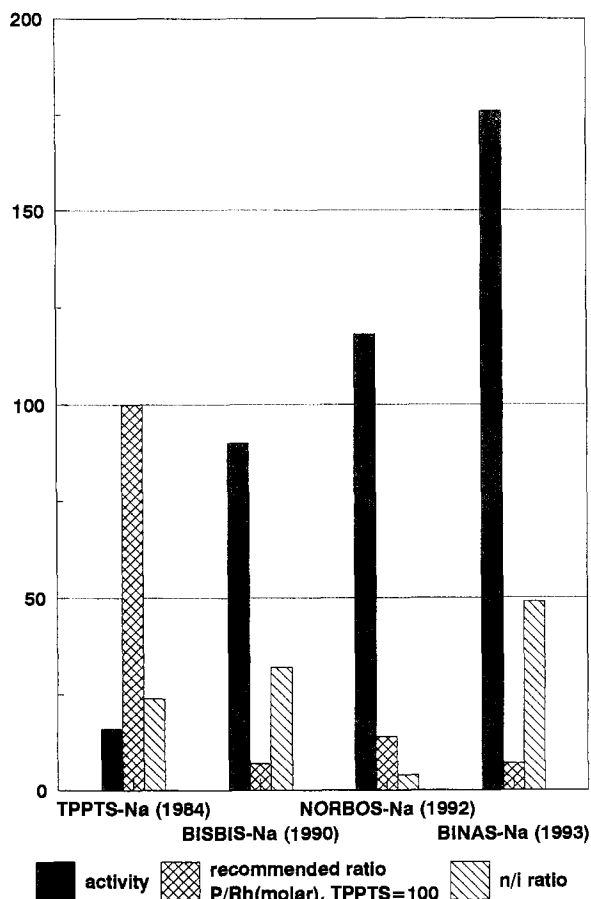


Fig. 6. How do oxo catalysts compare with each other?

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