

## Reviews

# Industrial Aqueous Biphasic Catalysis: Status and Directions

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### Abstract:

The new technique for aqueous, homogeneous catalysis (phase separable homogeneous catalysis) has found its first industrial application in the production of *n*-butyraldehyde by hydroformylation of propylene. Its advantages are very convincing and will lead to the process principle also being used in other reactions. The status, directions, and possibilities of this new technique are indicated.

### Introduction

In aqueous, homogeneous two-phase catalysis, the active catalyst for the reaction is (and remains) dissolved in water, so that the reactants and reaction products, which are ideally organic and relatively nonpolar, can be separated off after the reaction is complete by simply separating the second phase from the catalyst solution, thus making it easy to recirculate the latter. This technique therefore makes it possible to utilize fully the inherent advantages of homogeneous catalysis. A major aspect of this new technology is the tailoring of organometallic complexes as catalysts, as is nowadays becoming increasingly important both for industrial applications and for new reactions and new products.<sup>1</sup> The fact that selectivity- and yield-reducing operations (such as thermal stresses caused by chemical catalyst removal or distillations) for separating product and catalyst are avoided makes it possible to use sensitive reactants and/or obtain sensitive reaction products of homogeneous catalysis. Furthermore, this spontaneous separation of catalyst and product is the most effective and the only successful method of immobilizing homogeneous catalysts and thus making them “heterogeneous”.

The idea and development of aqueous, homogeneous two-phase catalysis has followed a route which is completely unconventional for chemical processes. After the idea was first expressed by Manassen<sup>2</sup> (not Bailar,<sup>3</sup> as erroneously stated by Sheldon and Papadogianakis<sup>4</sup>), the concept was very quickly taken up in the work of the university researcher Joó<sup>5</sup> (Debrecen, Hungary) and the industrial researcher

Kuntz.<sup>6</sup> However, these studies remained curiosities and, particularly the far-sighted visions of Kuntz, aroused no interest in the academic community. The reason may have been that the idea of organometallic complex catalysts in the presence of water seemed contrary to the natural way of things, although even air-stable aquocarbonyl complexes of transition metals such as rhenium<sup>7</sup> have become known in the meantime. In addition, metal–C bonds are thermodynamically unstable relative to their hydrolysis products,<sup>8b</sup> although it was well-known that reaction rates could be increased by a factor of up to 10<sup>11</sup> by aqueous media.<sup>9</sup>

It was not until the work at Ruhrchemie AG (and thus in industry) that development led to the first large-scale utilization of the aqueous, homogeneous catalysis technique at the beginning of the 1980s, viz., in hydroformylation (the oxo process).<sup>10</sup> The generally used embodiment of two-phase catalysis, for example as practised in Shell's SHOP method,<sup>11</sup> was thus joined by *aqueous* two-phase catalysis. These (and some other industrial applications, see below) have led to the literature concerning these particularly attractive aqueous variants being dominated by publications from industry, particularly patent literature, for virtually a decade. Only in 1996 did the academic literature provocatively ask “Why water?”<sup>12</sup> This development sequence was quite unusual: idea from academia, initial experimental work by an industrial chemist (Kuntz, then at Rhône-Poulenc), first industrial use 14 years ago (by Ruhrchemie), and only then (for about the last eight years) more detailed scientific study.

- (1) Cornils, B.; Herrmann, W. A., Eds. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, Germany, 1996; 2 Vol.
- (2) Manassen, J. In *Catalysis Progress in Research*; Basolo, F., Burwell, R. L., Eds.; Plenum Press: London, 1973, p 177 f.
- (3) Bailar, J. C. *Catal. Rev.—Sci. Eng.* **1974**, *10* (1), 17.
- (4) Papadogianakis, G.; Sheldon, R. A. *New J. Chem.* **1996**, *20*, 175.
- (5) Joó, F.; Beck, T. *React. Kinet. Catal. Lett.* **1975**, *2*, 257.

- (6) Rhône-Poulenc (Kuntz, E. G.). FR 2.349.562, 2.366.237, and 2.733.516, 1976.
- (7) Alberto, R.; Egli, A.; Abram, V.; Hegetsweiler, K.; Gramlich, V.; Schubiger, P. A. *J. Chem. Soc., Dalton Trans.* **1994**, 2815. Alberto, R.; Schibli, R.; Egli, A.; Schubiger, P. A.; Herrmann, W. A.; Artus, G.; Abram, V.; Kade, T. A. *J. Organomet. Chem.* **1995**, *492*, 217.
- (8) (a) Cornils, B.; Herrmann, W. A. *Aqueous-Phase Organometallic Catalysis—Concepts and Applications*; Wiley-VCH: Weinheim, Germany, 1998. (b) W. A. Herrmann, in ref 8a, Chapter 2.2.
- (9) E.g.: Abraham, M. H.; Grellier, P. L.; Nasehzadeh, A.; Walker, R. A. C. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1717.
- (10) (a) Cornils, B.; Falbe, J. *4th Int. Symp. Homogeneous Catal., Proc. (Leningrad)* **1984**, 487. (b) Bach, H. W.; Gick, W.; Wiebus, E.; Cornils, B. *Int. Symp. High-Pressure Chem. Eng. (Erlangen, Germany)* **1984**, Preprints, 129. (c) Bach, H. W.; Gick, W.; Wiebus, E.; Cornils, B. *8th ICC (Berlin)* **1984**, Preprints Vol. V, 417; *Chem. Abstr.* **1987**, *106*, 198.051 [cited also Behr and Röper: Behr, A.; Röper, M. *Erdöl Kohle, Erdgas, Petrochem.* **1984**, *37* (11), 485]. (d) Bach, H. W.; Gick, W.; Wiebus, E.; Cornils, B. *1st IUPAC Symp. Org. Chem. (Jerusalem)* **1986**, Abstracts, p 295. (e) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177.
- (11) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1978**, *90*, 493. See Vogt, D., in ref 1, Vol. 1, p 245.
- (12) Lubineau, A. *Chem. Ind.* **1996**, February, 123 (not p 125, as printed).

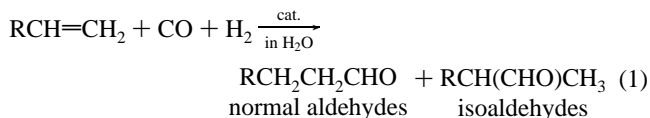


**Figure 1.** Large-scale oxo plant using water-soluble catalyst (Oberhausen/Germany).

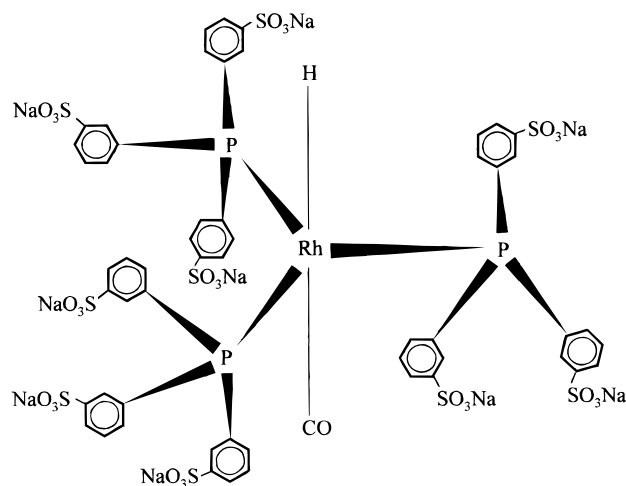
Joó and Kathó<sup>13</sup> politely referred to this time delay between academic and industrial research as an “induction period”, although it was more like a serious case of idea-transfer inhibition.

### Status of Industrial Aqueous-Phase Catalysis

**Hydroformylation.** Aqueous biphasic catalysis is used industrially for the hydroformylation of lower olefins (propylene to pentene) (eq 1). A total of about 600 000 t/annum



of preferably linear C<sub>4</sub> and C<sub>5</sub> aldehydes are being produced at two locations (Figure 1: Ruhrchemie/Oberhausen, Germany, and Yeochun, Korea). This corresponds to approximately 10% of the world capacity. The process is based on the ability to bring the homogeneous catalyst for the hydroformylation (a ligand-modified hydridorhodium carbonyl) into an aqueous catalyst phase and keep it there by appropriate modification of the ligands.<sup>14</sup> Previously, the



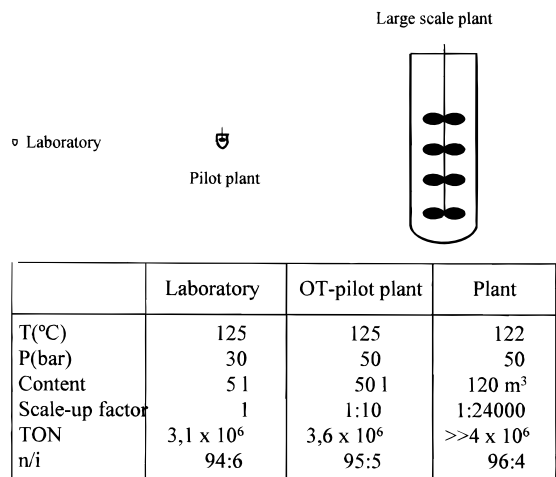
**Figure 2.** The active catalyst of Ruhrchemie/Rhône-Poulenc’s (RCH/RP’s) oxo process: trisulfonated triphenylphosphine (TPPTS) as ligand (schematic).

only industrially usable and inexpensive ligand<sup>15</sup> was TPPTS, viz., triply meta sulfonated triphenylphosphine (TPP) (Figure 2). The oxo catalyst formed after preactivation [HRh(CO)-{(m-SO<sub>3</sub>NaC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P}<sub>3</sub>] thus bears nine sulfonate substituents (i.e., three per P atom) and is accordingly readily soluble in water (approximately 1.1 kg/L).

(13) Joó, F.; Kathó, A. *J. Mol. Catal.* **1997**, *116*, 3.

(14) (a) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem.* **1993**, *105*, 1588; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (b) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219. (c) Cf. ref 1, Vol. 2, p 575.

(15) Cornils, B.; Wiebus, E. *CHEMTECH* **1995**, *25*, 33.



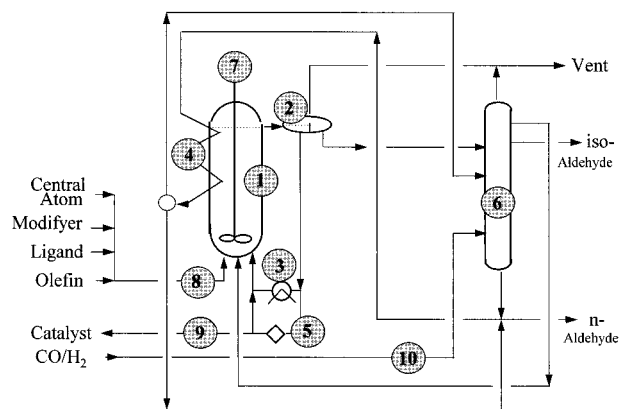
**Figure 3.** Scale-up of the process from a laboratory autoclave to the large-scale reactor.

The process is, as indicated above, relatively recent. It is based on the laboratory developments of Kuntz<sup>6</sup> which were, from 1982 to 1984, converted into a continuous process at the then Ruhrchemie AG<sup>10a</sup> within 2 years, which is short for process developments of this magnitude. The first 120 000 t/annum plant was started up in July 1984, which means that the development time of 2 years included the building time for this new plant, so that the actual process development was only about 1 year. It may be noted that the preliminary work of Rhône-Poulenc ended at the stage of batch autoclaves, and the problems of preparing the water-soluble ligand and also all questions relating to the continuous reaction procedure, the economics of the reactants and the reaction products, the energy balance, the environmental compatibility, the safety aspects, etc. were dealt with by Ruhrchemie.<sup>15-17</sup>

This tremendously concentrated development work was possible only because a team well-versed in all aspects of oxo development was able to take account of and master the unconventional risk of a scale-up factor of 1:24000 (batchwise laboratory development → production reactor) or 1:2400 (continuous pilot plant reactor → production reactor) (Figure 3).

The significant results were obtained in continuously operated laboratory autoclaves and then merely confirmed in the pilot plant reactor. The pilot plant step giving long-term simulation of all the system circuits under conditions very close to practice was therefore extraordinarily important. The short table of Figure 3 shows the extent to which the experimental results became more useful and more informative from step to step of the scale-up.

In the new oxo process, much was completely different from before, including (a) the catalyst, for the first time able to be supplied in water-soluble form, in satisfactory quality, and inexpensively; (b) the process procedure, viz., two-phase with phase separation in the process; (c) the reactor with special mixing of two phases; (d) the particular energy balance, as a result of which the process becomes a net steam



**Figure 4.** Detailed process development work focused on particular aspects: (1) reactor; (2) decanter (phase separator); (3, 4) heat recovery and steam generation; (5) recycle of aqueous catalyst solution; (6) distillation; (7) stirrer and control devices; (8, 10) feed; (9) catalyst regeneration/make-up.

supplier by utilizing the exothermic heat of reaction; and (e) the completely new, simple circulation of the aqueous catalyst solution.

Figure 4 shows the general design of the biphasic hydroformylation process and the focal points of the R & D work as indicated.<sup>10e</sup> Many alternative process concepts<sup>10e</sup> were tested during the development phase up to the continuously operated laboratory autoclave; however, only few were pursued further in the concept stage up to the pilot plant reactor. There remained, developed in long-term tests and protected by a matched patent strategy, the principle of the biphasic Ruhrchemie/Rhône-Poulenc oxo process which, as shown in Figure 4, is characterized by the following:

The reactor 1 is stirred (7) and supplied with the reactants through an appropriate feed system 8. The temperature is controlled by means of the effective cooling/heat recovery system 4. The heat of reaction taken from the oxo reactor (and thus from the exothermic hydroformylation reaction) via the internal cooler at the same time serves to heat the distillation column 6, whereby 4 becomes the reboiler of the column 6. The cooling medium is the reaction product *n*-butyraldehyde. As a consequence of the water solubility of the oxo catalyst and its insolubility in the organic phase comprising the reaction products, the oxo plant essentially becomes the stirred reactor together with downstream phase separator 2 and the stripping column 6. The major part of the catalyst solution remains in the reactor, and a smaller part is separated off in the phase separator and returns directly to the reactor. In the phase separator, the crude aldehyde formed by hydroformylation is freed of gases and separated into mutually insoluble phases. This decanter thus ensures the essential spontaneous phase separation. The part of the heat of reaction contained in the catalyst solution is recovered by means of a heat exchanger 3, and the catalyst solution, supplemented by an amount of water equivalent to that carried off with the crude aldehyde, is recirculated to the reactor. The crude aldehyde is freed of synthesis gas and any unreacted olefin, the other reactant, in the stripping column 6 by means of the reactants flowing countercurrently. It is also essential that this stripping be carried out in the

(16) Wiebus, E.; Cornils, B. *Chem.-Ing.-Tech.* **1994**, *66*, 916; *Hydrocarbon Process.* **1996**, March, 63.

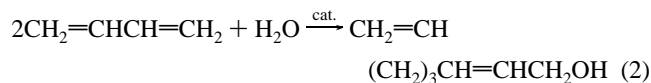
(17) Cornils, B.; Wiebus, E. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 211.

absence of the oxo catalyst and therefore no selectivity- and/or yield-reducing secondary reactions of the crude aldehyde occur.<sup>16,17</sup>

The new-generation oxo process thus becomes essentially a process with the following characteristics: (a) high selectivity, producing virtually exclusively aldehydes which are up to 98% linear; (b) simplicity in terms of apparatus and process operation; (c) net steam supplier, making excellent utilization of the heat of reaction by means of the "heat-transfer medium" *n*-butyraldehyde; (d) very simple recycling of the homogeneous oxo catalyst by immobilization using the "mobile support" water; (e) excellent economics owing to minimal losses of the catalyst metal rhodium, viz., 2 kg in the production of the first 2 000 000 t of *n*-butyraldehyde (i.e., losses in the ppb range); (f) low purity demands on the reactants; (g) excellent process potential from safety and environmental points of view; (h) interesting potential for tailoring the catalyst and thus the possibility of using olefins higher than C<sub>5</sub>.

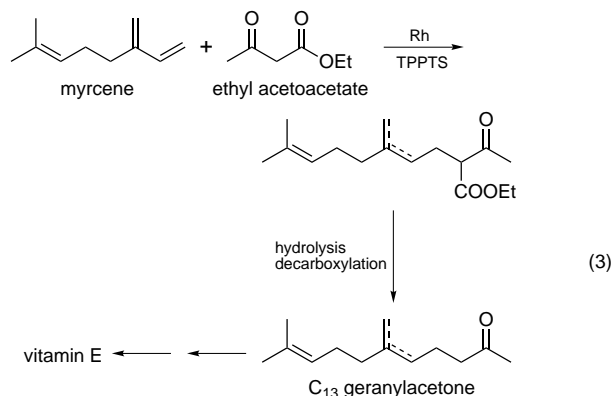
The results of this new procedure and its configuration in terms of equipment are excellent yields, selectivities to linear products (normal/iso ratios up to 98:2) and to aldehydes (99% aldehydes), and significantly lower production costs (10% lower).<sup>16</sup> For details of process operation and dependence on the process parameters see ref 16.

**Other Processes.** Aqueous, two-phase catalysis is utilized industrially in a number of other processes apart from hydroformylation. The hydrodimerization of butadiene and water, a telomerization variant (eq 2), is carried out at a capacity of 5000 t/annum by Kuraray Corp. in Japan. In

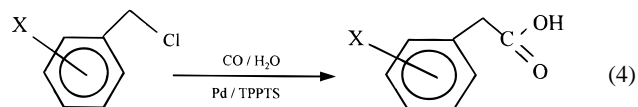


this process, an aqueous, two-phase procedure is first used to produce 2,7-octadien-1-ol, which can be easily hydrogenated to the desired 1-octanol (a sought-after plasticizer alcohol).<sup>18</sup> The catalyst used is palladium modified with the Li salt of TPPMS (the monosulfonated TPP) as a phosphonium compound. The octadienol can be dehydrogenated/hydrogenated internally to 7-octenal, and this may be *hydroformylated* to yield the dialdehyde nonadiol and then hydrogenated to nonadiol. An interesting feature is the use of CO<sub>2</sub> as coreactant, which stabilizes the phosphonium salt of the catalyst as a hydrocarbonate. Despite plenty of publicity, especially with regard to contradictory patent applications, the details of the Kuraray process and their significance are unclear.

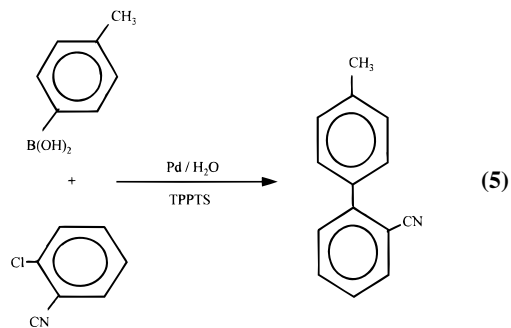
Rhône-Poulenc is operating two-phase, aqueous, catalytic C–C coupling processes (using TPPTS obtained from Ruhrchemie) for small-scale production of various vitamin precursors.<sup>19</sup> A new route to geranyl acetones starts from myrcene and ethyl acetonate (eq 3). Moreover, TPPTS-modified Ru catalysts have been proposed for the homogeneously catalyzed hydrogenation step for converting unsaturated into saturated ketones.



The homogeneous, aqueous two-phase catalysis has also acquired industrial significance for the production of the important intermediate phenylacetic acid (PAA). The previous process (benzyl chloride to benzyl cyanide and hydrolysis of the latter) suffered from the formation of large amounts of salt (1400 kg/kg of PAA).<sup>20</sup> The new carbonylation method (eq 4) reduces the amount of salt by 60% and makes use of the great cost difference between CN (approximately \$1.4/kg) and CO (<\$0.2/kg).



Finally, mention may be made of the Suzuki coupling of aryl halides and arylboronic acids. In earlier laboratory methods starting from expensive brominated or iodinated aromatics, only homogeneous Pd catalysts which had been modified with TPP or TPPMS could be used; the chlorine derivatives required very much more basic phosphines for the modification. Nowadays, cheaper chlorinated aromatics and catalysts based on Pd/TPPTS are used in an aqueous procedure on a commercial scale.<sup>21</sup>



The field is in flux; as a consequence of the increased scientific study of aqueous biphasic homogeneous catalysis; an increasing number of commercial applications may be expected in the future.<sup>8,13</sup>

### Directions for Further Development

In only about 13 years of commercial use of the comparatively recent technique of aqueous, two-phase ho-

(18) Yoshimura, N., in ref 1, p 351.

(19) Mercier, C.; Chabardes, P. *Pure Appl. Chem.* **1994**, *66* (7), 1509.

(20) Kohlpaintner, C. W.; Beller, M. *J. Mol. Catal.* **1997**, *116*, 259.

(21) Hoechst AG (Haber, S.; Kleinert, H. J.). DE-Appl. 195 27 118 and 195 35 528, 1997.

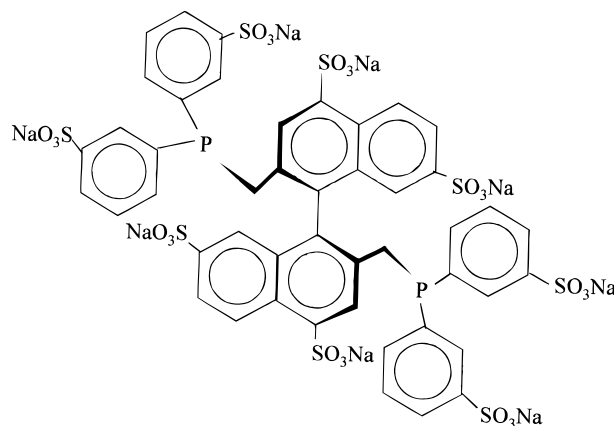
**Table 1. Properties of water as a liquid support of aqueous two-phase catalysis**

entry	
1	polar and easy to separate from unpolar solvents or products; polarity may influence (improve) reactivity
2	inflammable, incombustible
3	ubiquitous and with suitable quality available
4	odour- and colourless, making a contamination easily recognizable
5	formation of a hexagonal two-dimensional surface structure and a tetrahedral three-dimensional molecular network, which influence the mutual (in)solubility significantly; chaotropic compounds lower the order by H-bond breaking
6	high Hildebrand parameter as the unit of solubility of nonelectrolytes in organic solvents
7	a density of 1 g/cm <sup>3</sup> provides a sufficient difference from most organic substances
8	very high dielectric constant
9	high thermal conductivity, high specific heat capacity, and high evaporation enthalpy
10	low refraction index
11	high solubility of many gases, especially CO <sub>2</sub>
12	formation of hydrates and solvates
13	highly dispersible and high tendency of micelle formation; stabilization by additives
14	amphoteric behaviour in a Brønsted sense

mogeneous catalysis, over 4 000 000 t of building blocks have been produced. Nevertheless, their state of development and their degree of maturity are such that the following further developments may be expected.

**Other Solvents.** The technique of aqueous catalytic reactions has had such an impact on the field of more general two-phase reactions that scientists have now also proposed and tested other solutions. “Fluorous” systems<sup>22</sup> (FBS, perfluorinated solvents) and “nonaqueous ionic liquids”<sup>23</sup> (molten salts) meet the demand for rapid separation of catalyst and product phases and, owing to the thermoreversibility of their phase behavior, have advantages in the “homogeneous” reaction and the “heterogeneous” separation. However, it can be foreseen that the specially tailored ligands necessary for application of these technologies will be too expensive for normal applications. Compared to the inexpensive and ubiquitous solvent water with its unique combination of properties (cf. Table 1), these alternative solvents may well remain quite unimportant.

**Other Water-Soluble Ligands and Central Atoms.** TPPTS has up to now proven itself as a standard ligand for all aqueous two-phase systems. High water solubility (approximately 1.1 kg/L) and ready availability (sulfonation of TPP) are advantages which favor its industrial use. The high level of scientific interest has led to the development of a series of other ligands which are able to increase the activity of the Rh catalysts modified by means of them while retaining sufficient solubility in water. However, the fact that they enable the amount used to be decreased and the normal/iso ratio of the aldehyde mixtures produced to be increased<sup>24</sup> has not been sufficient to compensate for their high costs in everyday operation. The situation may be different for enantiomeric reactions.<sup>25</sup> A particularly promising candidate, BINAS-8 (cf. Figure 5),<sup>26</sup> has four sulfo groups per phosphorus atom despite being a diphosphine (compared to three in the case of TPPTS).

**Figure 5. BINAS-8 (Na salt) as ligand.**

Exotic ligands, for example, dextrans, supramolecular compounds, and templates, are attractive for academic applications in aqueous homogeneous reactions and can be expected to get a lot of publicity. However, there is no experience of their practical use so that questions of long-term stability, recycling, and dependence on parameter changes and also of toxicity, environmental behavior, costs, etc. remain unresolved. The cost of such ligands need not be prohibitive (as when the “expensive” rhodium is used as central atom in oxo catalysts) if virtually loss free recycling of the ligands as well as the central atoms can be guaranteed.

In the case of the chlorine-containing ligands or catalysts frequently used by academic researchers for reasons of convenience, attention has to be paid to materials problems (pit corrosion). They cannot be used industrially.

Ligand mixtures with tailored activities (for example TPP as “promoter ligand” and as additive to TPPTS<sup>27</sup>) are naturally attractive for scientific work and also enable particular effects to be achieved. However, for industrial use it must be ensured that *all* catalyst components can be recirculated simultaneously and in the same way with little expense, which can virtually never be ensured in the case of complicated mixtures. The same applies to the use of

(22) Exxon Res. and Eng. Co (Horváth, I. T.; Rábai, J.), US 5.463.082, 1995.

(23) Chauvin, Y.; Olivier, H. *CHEMTECH* **1995**, 25, 26.

(24) Herrmann, W. A.; Kohlpaintner, C. W.; Manetsberger, R. B.; Bahrmann, H. *J. Mol. Catal.* **1995**, 97, 65.

(25) Ding, H.; Hanson, B. E. *J. Mol. Catal. A: Chem.* **1995**, 98, 117.

(26) Herrmann, W. A.; Eckl, R. W. Unpublished work.

(27) Chaudhari, R. V.; Bhanage, B. M.; Deshpande, R. M.; Delmas, H. *Nature* **1995**, 373, 501.

soluble polymers (both as phase-separation agents and as ligands).<sup>28</sup>

Tests are being carried out to determine whether normal TPPTS with sulfo groups in the meta positions can be replaced by a “*p*-TPPTS” (with other solvent characteristics) prepared in another way. Regarding the matter of the TPPTS purity, it can only be pointed out that the cause of many of the micellar effects described in the literature lies in the purity.

Apart from rhodium, no other central atom (cobalt or central atom mixtures such as Pt/Sn) has so far been able to qualify for use in the industrial aqueous, biphasic oxo process. Should good results be obtained using central atom mixtures in experiments on multifunctional, aqueous homogeneous catalysis, the problem of simultaneous recycling of both components will have to be examined again. However, the prospects for industrial use of such mixtures are poor for the stated reasons.

**Other Technologies.** Theoretically, aqueous, two-phase homogeneous catalyses with their basic principle of phase separation can be achieved by combining various basic and auxiliary unit operations (such as extraction, extraction using solvent mixtures, reactive extraction, distillation, osmosis, reverse osmosis, phase transfer, absorption or adsorption, immobilization or partial immobilization, etc.).<sup>29</sup> Depending on the properties, or more precisely the property differences, of the reactants and the reaction products (solubility, polarity, boiling point), complex processes can be devised in this way.<sup>30</sup> However, it must be remembered that every additional process step and every additional material introduced into the process results in growing material losses and increased costs. For this reason, phase separation will remain the only viable option for industrial-scale applications.

The combination of aqueous homogeneous catalysis with elements of heterogeneous catalysis (“supported aqueous-phase catalysis”, SAPC<sup>31</sup>) also leads to a fundamentally different technology. This variant, which is particularly seductive for scientists (because it seems logical), has indeed produced good initial results in hydrogenation and hydroformylation, but industrial use will, as before, always founder on the problems inherent in the system (stability questions regarding the support as, in its time, in the SLPC variant of the oxo process, but particularly the leaching of the catalyst).

**Extension: To Other Feedstocks.** Especially in the case of hydroformylation, there is great interest in the use of olefins higher than pentene. The previous technology is restricted to the use of propylene and butylenes.<sup>32</sup> A reason which has been postulated for this is the decreasing solubility in water with increasing number of carbon atoms in the starting olefins and the products (Figure 6) and the associated

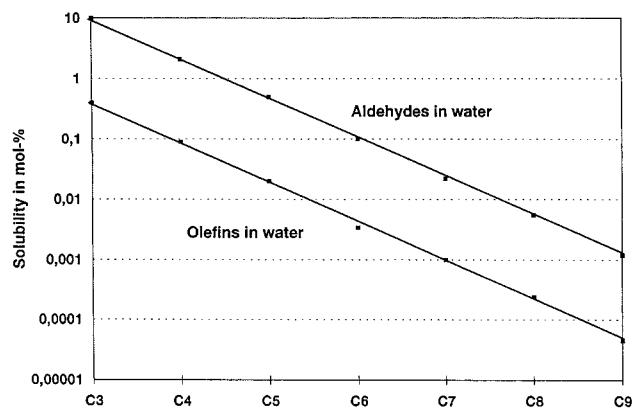
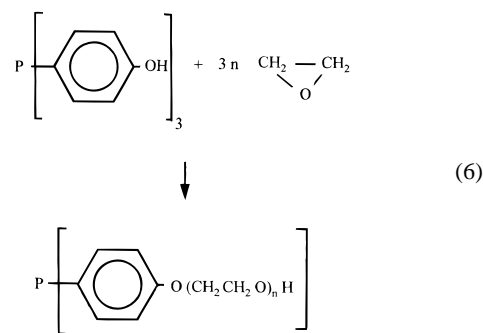


Figure 6. Solubility of olefins and aldehydes in water.

mass-transfer problems in the two-phase reaction.<sup>33</sup> Quite obviously, the problem is solved if the reaction is carried out in a homogeneous phase using thermoreversible catalysts and only the catalyst/product separation is carried out in the heterogeneous phase. This is the great advantage of the use of FBSs or ionic liquids.<sup>22,23</sup> However, for various reasons, both methods will not be used for the hydroformylation of higher olefins, which is under great cost pressure.

On the other hand, the possibility of achieving thermoreversibility, viz., reaction in a homogeneous phase at higher temperature and *two* phases at lower temperature, by means of appropriately tailored catalysts, specifically by means of tailored ligands, appears to have better prospects. Corresponding developments by Jin and Fell<sup>34</sup> based on ethoxylated phosphines (eq 6) give the first pointers to such a procedure. The great advantage of this method is that the



desired property, viz., the thermoreversibility of the phase behavior, is introduced by the ligand itself and not by means of auxiliaries or additives. The ability to circulate the catalyst is therefore ensured in principle, and the above warnings regarding additives and additional process steps do not apply. The above-mentioned limitations do, however, apply to solubilizing/thermoregulating additives such as poly(ethylene glycol).

Regarding combinations of thermoregulating reaction mixtures with the use of membrane processes, see ref 39.

(28) Bergbreiter, D. E. *CHEMTECH* **1987**, 686; presented at the 214th National Meeting of the American Chemical Society (Industrial Engineering Division), Las Vegas, NV, Sept 11, 1997.  
 (29) Behr, A.; Keim, W. *Erdöl, Erdgas, Kohle* **1987**, 103 (3), 126; *Fett. Wiss. Technol.* **1990**, 92, 375; *Henkel-Referate* **1995**, 31, 31.  
 (30) Haggin, J. *Chem. Eng. News* **1995**, April, 25. Abajotoglou, A. G. Presented at the 209 National Meeting of the American Chemical Society, Anaheim, CA, April 2–6, 1995.  
 (31) Davis, M. E. *CHEMTECH* **1992**, 498.  
 (32) Bahrman, H.; Frohning, C. D.; Heymanns, P.; Kalbfell, H.; Lappe, P.; Peters, D.; Wiebus, E. *J. Mol. Catal. A: Chem.* **1997**, 116, 35.

(33) Wachsen, O.; Himmler, K.; Cornils, B. Presented at the 214th National Meeting of the American Chemical Society (Industrial Engineering Division), Las Vegas, NV, Sept 11, 1997; *Catal. Today*, in press.  
 (34) Jin, Z.; Fell, B.; et al. *J. Mol. Catal.* **1997**, 116, 55; *J. Prakt. Chem./Chem.-Ztg.* **1996**, 338, 124.  
 (35) Cf. special issue of *J. Mol. Catal.* **1997**, 116, No. 1–2.

Although the membrane step does constitute an additional process element, its use could make it possible to regenerate the catalyst simultaneously and continuously and could thus be acceptable in terms of cost.

*To Other Reactions.* The academic world is working very intensively on extending the aqueous two-phase, homogeneously catalyzed method to reactions of other substrates. These include hydrogenations (which will have a hard time because of the dominance of heterogeneous hydrogenation processes), selective hydrogenations (in which tailor-made ligands are most likely to be able to show their full potential, which is also true for the interesting area of enantiomeric reactions), other carbonylations and C–C couplings (which can make direct use of the know-how developed for hydroformylation), hydrocyanations, the production of polymers (especially by ROMP reactions), oxidations, hydrations and aminations (preferably anti-Markovnikov), allylations, etc.<sup>8a,35</sup> In the case of hydroformylation, work is being carried out on variants of the earlier Aldox process (simultaneous hydroformylation, aldolization, and hydrogenation, for example, propylene → 2-ethylhexanol). This work leads into the field of the little-studied multifunctional (also multicomponent) homogeneous catalysis for which there are no models, especially not in the aqueous variant.

In all these developments, industrial implementation will depend very much on the additional expense of the tailored, water-soluble catalysts being compensated for by greater activity and selectivity (including enantiomeric selectivity) and by the simple process configuration which can be achieved by their use. Particularly in the case of catalyst and/or ligand mixtures, this is often questionable.

**Addition of Cosolvents and Additives.** The addition of such additives has frequently been tested in scientific laboratories, sometimes not without success. The patent literature also lists a whole series of additives (ref 10e). In industrial practice, however, detailed engineering and cost studies have resulted in none of these additives being adopted. The same applies to special technical solutions, for example, the use of ultrasonic reactors which have a solubilizing action.<sup>36</sup> The increased level of scientific work on supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and its overlap with the properties of media for FBSs<sup>37</sup> can, however, produce new and specific process variants in which the disadvantageous properties of perfluorinated compounds are no longer introduced by the solvents (e.g., scCO<sub>2</sub>), but only by the ligands present in catalytic amounts. In these developments, too, simultaneous catalyst regeneration with the aid of membrane separation is conceivable.

**Environmental Aspects.** The new oxo process is particularly environmentally friendly.<sup>17</sup> According to Sheldon,<sup>38</sup> the *E* factor of the Ruhrchemie/Rhône-Poulenc process is, depending on the way in which the by-product isobutyraldehyde is considered, between 0.04 and 0.1 and thus

falls into the product category of “oil chemicals”, that is, the synonym for production operations which owing to their size and importance are both economic and very environmentally conscious. Other oxo processes with their *E* factor of  $\gg 0.1$  correspond to the category of “bulk chemicals”. The environmental friendliness expressed by the favorable *E* factor of the new aqueous, biphasic process shows up in many places: the high selectivity of the chemical reaction (and thus low by-product formation), the low capital costs, the great reduction in amounts of waste gas and wastewater (in the case of water by a factor of 70) and the energy consumption (the oxo process is changed from a steam consumer to a net steam supplier, and the power consumption is more than halved), etc.<sup>17</sup>

Further advances can be expected from new developments. Thus, it would be possible to make the disposal of the gaseous (and highly pure) waste gas streams (residual propane content of the propylene feed) cost-effective and a source of electric power by connection to newly developed, compact membrane fuel cells. Potential synergisms would also occur in the operating temperature of the cells (intermediate-temperature cells at 120 °C using the residual exothermic heat of reaction from the oxo reaction), in the membrane costs by means of combined developments (e.g., for membrane separations of the catalysts<sup>39</sup>), and naturally also in the development of the “zero emission” automobile being carried out by the automotive industry. The combination of hydroformylation with fuel cells would further reduce the *E* factor.

Moreover, examination of the Sheldon *E* factors shows very vividly how much more logical and practical this concept is than Trost's<sup>40</sup> enigmatic “atom economy” which is concerned with examples which may well always be fitting but are esoteric and frequently of little relevance. The newer version of the atom economy does, justifiably, emphasize homogeneous catalysis, but the exotic examples with “the myriad of substances that are required to serve the needs of society” (!)<sup>40c</sup> are not better founded.

## General Assessment

Homogeneous catalysis was never the prototype of a “heat-and-beat” technology in chemistry. Given the opportunity of quickly and easily separating the homogeneous catalyst from the reaction products in an aqueous process, it will be even more interesting (and more feasible) to make use of all intrinsic features of homogeneous catalysis. This applies particularly to the possibility of tailoring the catalyst by varying the central atom, the ligand or the phase in which it is used. In this sense, homogeneously catalyzed aqueous syntheses will lead to an even more sophisticated field of chemistry under the most environmentally friendly conditions.

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