

Water Soluble Rhodium Catalysts

A HYDROFORMYLATION SYSTEM FOR THE MANUFACTURE OF ALDEHYDES FOR THE FINE CHEMICALS MARKET

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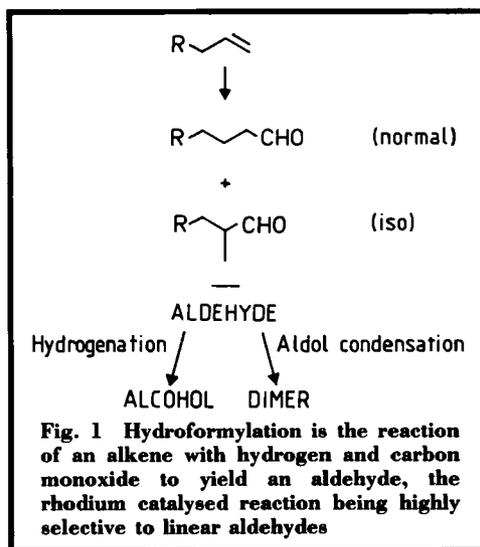
The rhodium catalysed hydroformylation reaction is one of the most widely used industrial applications of homogenous catalysis to employ platinum group metals. Potential limitations in the application of this technology to molecules which are heat sensitive or have high boiling points are the stability of the catalyst and the ability to separate the catalyst from the products. A means of circumventing these limitations is described. This involves locating the catalyst in an aqueous liquid phase, and it enables viable reaction rates to be achieved at moderate temperatures and pressures.

Hydroformylation is the reaction of an alkene, hydrogen and carbon monoxide to generate an aldehyde, as shown in Figure 1. While the reaction is energetically favourable it only proceeds in the presence of a catalyst. A number of different metal complexes have been investigated as potential catalysts, but the only ones with sufficient activity to be useful industrially are those of cobalt and rhodium. The relative activities of these metals are given in Table I.

The hydroformylation reaction was first reported by Roelen in 1938 during a study of Fischer Tropsch catalysts (1). Later it was realised that the active catalyst was a hydridocarbonylcobalt species, and in the period 1945 to 1951 a number of processes employing homogeneous cobalt catalysts were developed for the production of detergent and plasticiser alcohols.

It was demonstrated during the 1950s that rhodium compounds such as rhodium oxide were highly active as hydroformylation catalysts, although the ratio of normal:iso aldehydes was lower than those obtained with commercial cobalt systems. However in the 1960s Wilkinson's group at Imperial College, London, and Pruet's group at Union Carbide found, independently, that rhodium com-

pounds containing organophosphines could convert alkenes to aldehydes at mild temperatures and pressures, and with high selectivity to linear aldehydes (2,3). An extension of this work resulted in the commercial exploitation of the rhodium Low Pressure Oxo (LPO) process by Union Carbide, Davy McKee and Johnson Matthey. The principal industrial application of this process is the hydroformylation of propylene to butyraldehyde. This



Metal	Activity
Rhodium	$10^3 - 10^4$
Cobalt	1

Ruthenium, Platinum	10^{-2}
Manganese	10^{-4}
Iron	10^{-6}
Chromium, Molybdenum, Tungsten, Nickel	0

primary product can be converted to the plasticiser alcohol 2-ethylhexanol, via aldol condensation/hydrogenation, or to butanol. Since the LPO process was introduced commercially in the 1970s it has been immensely successful. It has been used for the production of over one million tonnes of butyraldehyde, and is licensed to 12 companies in 9 countries, Table II.

In addition to the development being timely with respect to feedstock costs, the commercial success of the process can be attributed to a number of technical features:

- [1] The high activity of rhodium complexes.
- [2] The presence of a large excess of triphenylphosphine contributes to the high selectivity to aldehydes, in particular the desired product n-butyraldehyde, and it also suppresses hydrogenation.
- [3] In addition, the presence of triphenylphosphine renders the catalyst thermally stable and confers longevity on the catalyst, while the low volatility of the catalyst means that the product can be stripped from the reactor with a minimal rhodium loss, of less than 1ppm.
- [4] An efficient reactant purification system eliminates catalyst poisons and extends the catalyst lifetime.

Overall the process provides a graphic example of how a relatively expensive platinum group metal catalyst can successfully compete

with a significantly cheaper cobalt catalyst.

On a commercial scale, the rhodium and cobalt catalyst systems are to some extent complementary in that rhodium catalysts are only suitable for the hydroformylation of low molecular weight alkenes, whereas the cobalt systems can be applied to the hydroformylation of high molecular weight feedstocks and are particularly attractive where alcohols are the desired products, Table III.

Limitations to the rhodium process result from the availability of methods of separating the catalyst from the product. In the production of butyraldehyde the product is distilled out of the reactor at low temperatures which do not cause catalyst degradation. For higher molecular weight products higher temperatures are required, and at temperatures greater than 120°C severe catalyst degradation can occur, Table IV. Thus if rhodium catalysts are to be used commercially for the production of compounds of interest to the detergent and aroma industry, an alternative strategy is required.

An approach which has attracted a great deal of attention from research workers investigating hydroformylation and related reactions is the use of chemically anchored catalysts. After some preliminary work in this

Company	Location
Union Carbide	Texas, U.S.A.
Tenneco	Texas, U.S.A.
Neste Oxo	Sweden
Huels	West Germany
CNTIC	China (2)
TSK	Japan
Kyowa Yuka	Japan
Chisso	Japan
Lucky	South Korea
Polimex	Poland
Nan Ya Plastics	Taiwan
Oxochimie (planned)	France

Table III Commercial Hydroformylation Processes			
	Cobalt	Modified Cobalt	Rhodium Low Pressure
Catalyst	[HCo(CO) ₄]	[HCo(CO) ₃ (PBu ₃)]	[HRh(CO)(PPh ₃) ₃]
Temperature, °C	110–180	160–200	100
Pressure, bars	200–300	50–100	<20
Products	Aldehydes	Alcohols	Aldehydes
Normal : branched aldehyde ratio	2–4	7	>10
n-product yield, per cent	67	67*	90
Aldehyde yield, per cent	90	80*	98
Alkanes, per cent	1	15	0.9
Other by-products, per cent	9	5	1.0
Catalyst costs		Similar	

* Aldehyde and Alcohol

area Johnson Matthey decided against this approach, for a variety of reasons, including:

- [a] The difficulty of producing a catalyst with reproducible activity and selectivity, which implied that catalyst costs would be extremely high.
- [b] Many of the heterogenised catalysts were more air sensitive than their homogeneous analogues.
- [c] Metal was slowly lost from the catalyst, and in many cases the metal could not be recovered in a cost effective manner.
- [d] Neighbouring group effects such as chelation, arising from a high surface concentration of organophosphines, caused slower rates of reaction.

We were attracted to the idea of utilising a water soluble catalyst system, with a view to locating the catalyst in the aqueous phase and the feedstock and product in the organic phase. We concentrated on rhodium catalyst systems, with a few less successful diversions into ruthenium and platinum systems. The standard which we wished to match in terms of rate and selectivity was the triphenylphosphine-modified rhodium homogeneous system, and we chose dodec-1-ene as a convenient model substrate.

Our first task was to devise a water-soluble phosphine ligand which located the rhodium in the aqueous phase, yet was similar to

triphenylphosphine. The sulphonated triphenylphosphine-rhodium systems which had been investigated by Rhône Poulenc and by Wilkinson gave rise to extremely slow rates of reaction at moderate pressures, and we selected carboxylated triphenylphosphines as ligands. We observed measurable rates at 80°C and about 6 atmospheres hydrogen-carbon monoxide with a ten-fold molar excess of carboxylated phosphine over rhodium.

At the conception of the project we had appreciated that we would need to use some "special" effect to enhance the rate in the two liquids system relative to the homogeneous system. For the system containing two liquid phases, mass transfer control is likely to

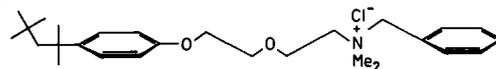
Table IV Catalyst Solution Degradation
Phosphido bridged rhodium species
Alkyl diphenylphosphine complexes
Triphenylphosphine oxide
Benzene, benzaldehyde
Heavy organics

Table V
Hydroformylation of Dodec-1-ene
Surfactant/Phase Transfer Agent Variation

Surfactant/phase transfer agent	Selectivity n:i	Total aldehydes per cent	Colour of organic phase	Colour of aqueous phase
18-crown-6 ^(a)	3	88	yellow	yellow
PhCH ₂ N ⁺ Bu ₃ ⁿ Cl ⁻	7	76	yellow	brown
Bu ₄ ⁿ N ⁺ Cl ⁻	6	73	yellow	brown
Bu ₄ ⁿ N ⁺ OH ⁻	6	90	yellow	brown
C ₁₆ H ₃₃ ⁺ PBu ₃ ⁿ Br ⁻	6	64	deep purple	colourless
Aliquat 336 (C ₁₀ H ₂₁) ₃ N ⁺ MeBr ⁻	2	78	deep purple	colourless
Benzethonium chloride ^(b)	5	82	yellow	colourless
Tween 61	4	72	yellow	colourless
Span 40	5	80	yellow	colourless
Sodium dodecyl sulphate	4	80	yellow	brown
Brij 35 C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₂₃ OH	14	87	colourless	brown
CTAB C ₁₆ H ₃₃ N ⁺ Me ₃ Br ⁻	115	76	colourless	yellow
C ₁₄ H ₂₉ N ⁺ Me ₃ Br ⁻	70	78	colourless	clear orange
C ₁₆ H ₃₃ N ⁺  Br ⁻	60	70	pale yellow	yellow

^(a) In pH10 KHCO₃ + KOH buffer

All runs at 80°C, 5.1–5.5 atms 1:1 H₂:CO, organic:aqueous = 1:2, organic = dodec-1-ene (10g) unless otherwise stated, aqueous = pH10 NaHCO₃ buffer

^(b) Benzethonium chloride = 

dominate, which contrasts with the homogeneous hydroformylation system where kinetic control is operative.

At this time there was a burgeoning interest in the use of phase transfer agents in organic synthesis, and there were many reports that surfactant systems would induce micelle formation and promote liquid-liquid transport. Accordingly we set out to investigate the effect of a range of these amphiphilic reagents on the two liquid phase hydroformylation reaction, see Figure 2 and Table V. For those reagents with a high affinity for organic solvents, high rates of reaction were obtained, as measured by conversion to aldehydes and by hydrogen/carbon

monoxide uptake. However, the reaction effectively took place in the organic phase, with high concentrations of rhodium observed in the organic. For quaternary ammonium salts (Quat.) of the type RN⁺Me₃X⁻ (R=C₁₀-C₁₆ alkyl, X=halide, acetate etc), under basic conditions reasonable reaction rates were obtained, as shown in Table VI. These rates were about half that of the homogeneous rhodium system at 80–100°C and about 6 atmospheres hydrogen-carbon monoxide (4).

In the more favourable cases rhodium loss to the organic phase was lower than 1ppm. Dependent on the R group, rapid phase separation could be achieved. Alternatively, a fairly

Table VI
Effect of Surfactants

Surfactant	Substrate	Time, hours	Conversion, per cent	n:i	Efficiency, per cent
None	Hex-1-ene	3	2	7	—
$C_{12}H_{25}N^+Me_3Br^-$	Hex-1-ene	1	44	73	85
None	Dodec-1-ene	3	2	6	—
$C_{12}H_{25}N^+Me_3Br^-$	Dodec-1-ene	1	78	20	91
None	Hexadec-1-ene	3	0.5	—	—
$C_{12}H_{25}N^+Me_3Br^-$	Hexadec-1-ene	1	73	22	89

Conditions: $[Rh]_{aq} = 300$ ppm, 4- $Ph_2PC_6H_4COOH$, P:Rh = 10:1, $C_{12}H_{25}NMe_3Br$:Rh = 20:1 in pH10 buffer at 80°C, 5.5 atms 1:1 H_2 :CO

stable emulsion could be obtained. Using a particular reactor conformation it was possible to achieve extremely high selectivities to normal aldehydes, with normal:iso ratios in the region of 300.

Rhodium loss to the organic phase, and selectivity both to total aldehydes and normal aldehydes were highly dependent on the organic phase composition, the reactor system and the rate of stirring. The selectivity to total aldehydes was dependent on the organic phase composition, which can be explained in terms of the relative solubility of carbon monoxide. High selectivity to normal aldehydes was promoted when relatively poor mixing of the liquid phases occurred, and poor mixing also minimised rhodium loss.

The fact that the mixing of the two liquid phases plays such an important part in the course of the reaction can be interpreted in terms of the formation of metastable aggregates. The pH of the aqueous phase is basic under reaction conditions, and in these circumstances the carboxylated phosphine is in an anionic form. It is possible to imagine an organised array containing catalyst, surfactant and substrate molecules (Figure 3). Under these highly organised conditions the approach of the polar alkene group will be favoured sterically for a 1-alkene, and likewise the forma-

tion of a linear alkyl and acyl will be favoured over the branched species for the two phase system relative to the homogeneous system. In this way it is possible to rationalise the extremely high normal:iso ratios that are obtained under poor mixing conditions, when the formation of highly organised assemblies is favoured.

Some work was carried out in elucidating the reaction mechanism. Through varying the hydrogen to carbon monoxide ratio it was found that at low partial pressures of carbon monoxide the normal:iso ratio is extremely high, with moderate selectivity to total aldehydes; increasing this partial pressure

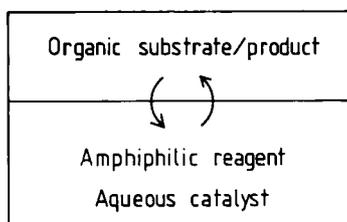
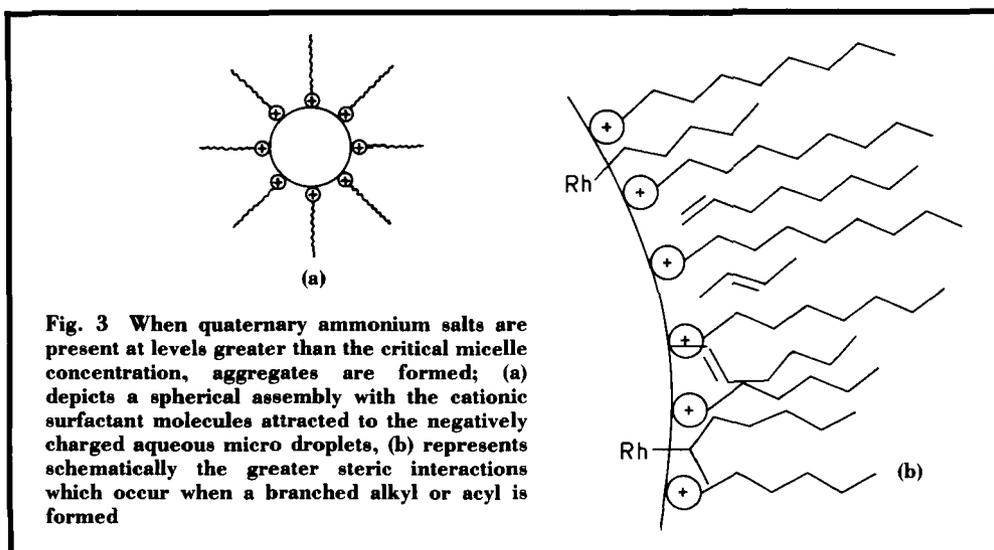


Fig. 2 The effect of a range of amphiphilic (phase transfer or surfactant) reagents has been investigated as a means of enhancing reaction rates and reducing rhodium loss to the organic phase



results in a decrease in normal:iso, but an increase in selectivity to total aldehydes. This indicates that it is not the initial attack of hydride to alkene which determines the ratio of linear to branched aldehydes, but that there is a pathway

for the interconversion of iso-alkyl and normal-acyl compounds where the relative proportions of each are determinable by the partial pressure of carbon monoxide. The accepted hydroformylation pathway is given in Figure 4.

Table VII
Comparison of Rhodium Water-Soluble Catalyst Systems

Ligand	$\text{PPh}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$	$\text{P}(\text{C}_6\text{H}_4\text{SO}_3)_3(\text{M}^+)_3$
Rhodium, ppm	<300	300–700
Ligand : Rhodium	10	20–40
Additive (A:Rh)	Quat. (20:1)	none
pH	10	7–8
Buffer	bicarbonate	phosphate
Total pressure, atmospheres	10	>60
Temperature, °C	100	>125
Efficiency, per cent	95	<95
Selectivity, per cent	90	<90
Normal:Iso	100 to 20	12 (for 1-hexene)

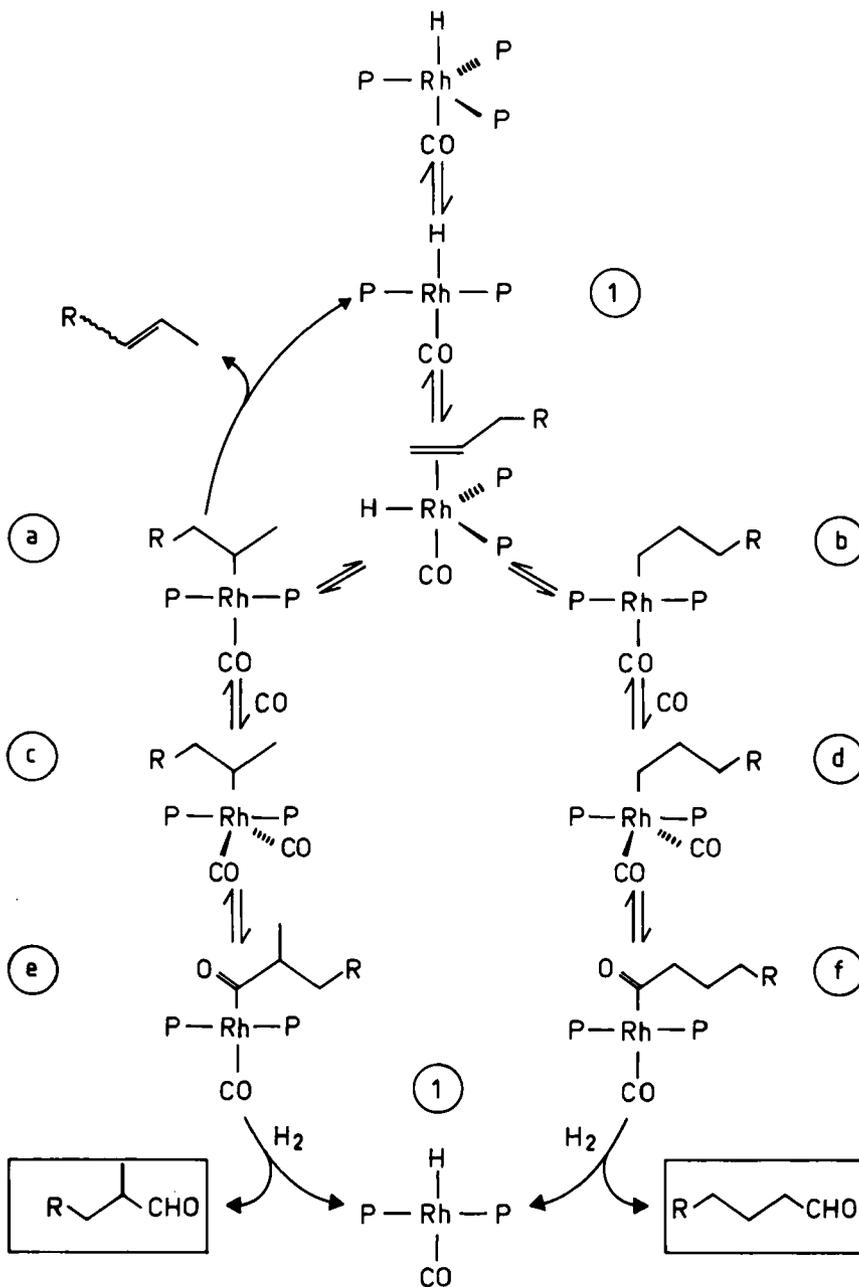


Fig. 4 The widely accepted mechanism for the hydroformylation of alkenes using rhodium catalysts is depicted. It involves the dissociation of a phosphine to give a sixteen electron species (1), followed by co-ordination of an alkene and the formation of linear and branched acyls. The mechanism permits the interconversion of branched alkyl (a) and linear acyl (f) species. Reductive elimination results in the formation of normal and iso aldehydes, and regenerates (1)

In this mechanism there is a route for the interconversion of branched alkyl (a) and linear acyl (f) species, which is consistent with the observations made above. Thus by modifying the microstructure of the liquid assembly, through the addition of surface active agents and the polarity of the organic solvent, it is possible to effect high selectivities to total aldehydes.

Other features which make this system attractive are that high normal:iso ratios can be achieved at relatively low phosphine concentrations (less than 1/10 of that of the conventional triphenylphosphine-rhodium system). Minimal losses of phosphine, surfactant and rhodium occur, and the phosphine and surfactant are not degraded under the reaction conditions.

A related water soluble system has been developed by Rhône Poulenc and Ruhr Chemie (5). This system utilises sulphonated triphenylphosphine as a water solubilising ligand and operates at higher temperatures and pressures than the truly homogeneous rhodium-phosphine. A comparison of the sulphonated and carboxylated phosphine systems is given in Table VII.

The Destruction of Polychlorinated Biphenyls

In an earlier issue of this journal attention was drawn to the possibility of disposing of persistent aromatic pollutants, including polychlorodibenzo-*p*-dioxins (PCDDs), by an oxidation process which utilised catalytic quantities of ruthenium tetroxide (1).

Since that time there has been a growing awareness of the potential danger to human health posed by polychlorinated biphenyls (PCBs), compounds with similar structures to the PCDDs. PCBs were widely used in the past as insulators in electrical transformers and capacitors. They are very stable, and therefore difficult to get rid of when they are no longer required. Burial in a landfill site cannot be regarded as a permanent solution as leaching into the drainage system may occur. Incineration, the usual alternative method of disposal, requires temperatures of around 1200°C and risks the possibility that even more toxic polychlorinated dibenzofurans could be formed if the process conditions are not controlled satisfactorily. Although various chemical

The trisulphonated triphenylphosphine-rhodium catalyst is operated commercially by Ruhr Chemie for the hydroformylation of propylene and the complexity of these reaction systems suggests that the design of an industrial plant for the hydroformylation of high molecular weight alkenes will not be trivial. However, the mild operating conditions which result from the use of the 4-diphenylphosphino-benzoate-rhodium catalyst, together with the high selectivities attained, mean that this system has considerable potential for the manufacture of aldehydes in the fine organic chemicals markets.

Acknowledgements

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methods of detoxification have been reported the unreactivity of PCBs generally necessitates the use of extreme conditions. However, a simple, efficient method for the oxidative destruction of PCBs has now been reported by investigators at the University of East Anglia and at Queen Mary College, London (2).

Their procedure makes use of ruthenium tetroxide as an oxidising agent, and complete destruction can be achieved. The rate of destruction of individual polychlorinated biphenyl isomers varies, resistance to degradation depending on the degree of chlorination of the biphenyl. The method is said to be suitable for the detoxification of laboratory equipment, and to have possible application for the large scale treatment of commercial waste fluids.

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