HYDROFORMYLATION OVER HETEROGENIZED RHODIUM COMPLEXES
HYDROFORMYLATION OVER HETEROGENIZED RHODIUM COMPLEXES

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1. INTRODUCTION

1.1. General Introduction to Hydroformylation

Hydroformylation comprises the catalytic reaction of alkenes with equimolar amounts of carbon monoxide and hydrogen to yield an aldehyde with one more C-atom:

\[ \text{R-CH} = \text{CH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{RCH} = \text{CH}_2 \text{C-H} + \text{HCO} \]

This reaction, catalyzed by cobalt or cobalt compounds, was discovered by Roelen [1] during an investigation of Fischer-Tropsch reactions. Roelen also discovered that cobalt hydrocarbonyls are the active catalytic species in the hydroformylation reaction [2].

Hydroformylation has been used for commercial production of aldehydes since 1948 and has become a very important industrial process [3].
Complexes of Group VIII metals other than cobalt are also active as hydroformylation catalysts. Pt-Sn phosphine complexes, for example, show a good catalytic activity [4]; such catalysts are also highly enantioselective in combination with chiral phosphine ligands [5].

Slaugh and Millineau [6], and later on Osborn, Wilkinson and Young [7], found rhodium-phosphine complexes to be very active catalysts, the activity per metal atom being $10^2$-$10^4$ times higher than found for cobalt-based systems. Side reactions, like bond isomerization and hydrogenation of the alkene, are suppressed to a large extent by the addition of an excess of tertiary phosphine ligand.

The hydroformylation of propene (the so-called Low Pressure Oxo or LPO process), developed by Union Carbide and Davy Powergas [8], constituted the first industrial application of the rhodium-phosphine catalyst. It is a classic example of a successful homogeneous organometallic catalytic process. Compared with heterogeneous catalytic procedures, application of organometallic catalysts has the following advantages:

1. The catalytic efficiency (activity per metal complex) is high because every metal atom is available to the reactants. This is important because rhodium is very scarce and expensive.
2. The sensitivity to poisons is low.
3. Organometallic complex catalysts in general show a very high selectivity for the desired products (the aldehydes in this case).

However, the fact that metalorganic catalysts are applied homogeneously gives rise to difficulties in industrial applications, such as:

1. A complicated and therefore expensive separation of products and reactants from the catalysts is necessary, especially in processes involving the higher olefins.
2. The catalytic activity gradually decreases because of aggregation of the catalytic species.
3. The regeneration procedure for the spent catalysts is laborious and is accompanied by some loss of catalyst.

In view of these disadvantages efforts have been made to heterogenize the organometallic complexes, and to combine, in this way, the advantages of a soluble catalyst with those of a heterogeneous process. At Delft University of Technology several methods of heterogenization have been investigated:

1. Physical adsorption of the rhodium complex on an inorganic support, by Spek [9] and Tjan [10].
2. Chemical anchoring of the rhodium complex to the surface of a macroreticular styrene divinylbenzene diphenylphosphine resin, by de Munck et al. [11-14].
3. Rhodium catalysts in the supported liquid phase form (SLPC) by Gerritsen [15-22], de Munck [11,23,24], Herman [25] and Pelt [26-31].

A supported liquid phase catalyst consists of a catalyst dissolved in a liquid phase, capillary condensed in a porous support. The gaseous reactants diffuse through the residual, non-liquid filled, pore space as well as through the dispersed liquid phase, and undergo a homogeneous catalytic reaction in the liquid phase and/or a heterogeneous reaction at the gas/liquid interface. Next the produced aldehydes are transported out of the porous support by diffusion. The advantages are convenient catalyst handling, a large gas/liquid interfacial area, and easy separation of the products from the catalyst.

1.2. Scope of the Present Thesis

The thesis is organized as follows. In Chapter 2, several theoretical aspects of hydroformylation over rhodium complex catalysts are dealt with, and the reaction mechanisms hitherto proposed are critically evaluated. In Chapter 3 we present a literature review dealing with the state of the art with regard
to heterogenizing organometallic complex catalysts. The experimental part of the thesis starts with Chapter 4. Here the first goal is to investigate to what extent rhodium-SLP catalysts can be improved so that they can function at appreciably higher temperatures than hitherto possible. This may be achieved by the use of special ligands giving rise to a higher chemical stability. In Chapter 4 attention will be paid also to the behaviour of enantioselective SLP catalysts with chiral phosphine ligands. The performance of these systems will be demonstrated in the hydroformylation of butene-1.

Chapter 5 may be looked upon as an extension of Chapter 4, in that the knowledge generated in Chapter 4 is used in Chapter 5 to solve the difficult problem of the hydroformylation of allyl alcohol. The difficulties are:
1. The high boiling points of the alkene and of the reaction products, which can easily lead to condensation in the pores of the support material, resulting in leaching out of the rhodium complex.
2. The presence of a second functional group (OH group) in allyl alcohol leads to complicated side reactions, for instance the formation of acetals.

These difficulties are surmounted by applying higher temperatures and protection at the OH group.

The most radical solution of the problem of immobilization of organometallic complex catalysts is immobilization by chemical bonding of the complexes to the surface of heterogeneous supports via the ligands. Such chemically immobilized systems may be realized, but their production in general asks for a number of rather difficult and complicated organic reactions. The synthesis and the performance of such a catalyst will be discussed in the last chapter, Chapter 6.

References Chapter 1

1. O. Roelen, (Ruhrchemie AG), German Patent 849, 548 (1938).
2. THEORETICAL ASPECTS OF HYDROFORMYLATION OVER RHODIUM COMPLEX CATALYSTS

2.1. Introduction

The hydroformylation reaction, using cobalt compounds as catalysts, was discovered by Roeien in 1938 [1]. Extensive reviews have been published dealing with theoretical studies on the reaction mechanism and with technical developments [2-6].

Besides cobalt complexes, several other group VIII metal compounds are active as hydroformylation catalysts, such as Pt, Ir and Fe-carbonyl species. Rhodium carbonyl compounds, however, are by far the most active catalysts for this reaction. At Delft University of Technology the hydroformylation reaction has been studied for the last fifteen years, using heterogenized rhodium phosphine catalysts [7-12]. This is the reason for our special interest in the mechanistic aspects of rhodium-catalyzed hydroformylation.

In this chapter an outline is presented of the reaction mechanism, starting from the mechanism proposed originally by Wilkinson and co-workers (section 2.2). In section 2.3 recent developments concerning the Wilkinson mechanism are discussed. Catalyst deactivation, side reactions and ligand effects are dealt with in section 2.4. Finally, a critical evaluation of the preceding parts will be presented (2.5).
2.2. The Wilkinson Mechanism

Wilkinson et al. [13-18] introduced the supposition that homogeneous rhodium-catalyzed hydroformylation may proceed both by an associative and a dissociative mechanism, these mechanisms differing only in the number of PPh₃ ligands around the rhodium centre. These two major pathways may be summarized as follows:

Scheme I. Associative - and Dissociative Reaction Mechanism according to Wilkinson et al. [13-18]. L = PPh₃.

Yagupsky, Brown and Wilkinson [15] formulated the above mechanisms on the evidence of spectroscopic characterization (at ambient conditions) of most of the intermediates. They also prepared and isolated analogs of some of these intermediates, e.g. (PPh₃)₂Rh(CO)₂(C₂F₅)H, (PPh₃)₂Rh(CO)₂(C₂F₅)₂H and (PPh₃)₂Ir(CO)₂H, and demonstrated the separate reactions involved in the synthesis of these compounds. If too large an excess of phosphine is added the equilibrium is shifted to the inactive species HRh(CO)(PPh₃)₃ and hydroformylation activity declines.

The hydrogenation of the acyl species (see scheme I) was shown to be strongly inhibited by CO. Apparently, the formation of the five-coordinate dicarbonyl-acyl inhibits the oxidative addition of H₂ since a seven-coordinate species is unstable. As will be shown later on, this oxidative addition of H₂ is one of the most debatable elementary steps in the mechanism.

Wilkinson et al. [15] and Pruett and Smith [19] have shown that in the absence of excess phosphine and/or high CO pressure dissociation of a phosphine ligand occurs and that this ligand is progressively replaced by CO according to the following equilibria:

\[
\begin{align*}
HRh(CO)_2(PPh_3)_2 + CO & \rightleftharpoons HRh(CO)_2(PPh_3)_2 + PPh_3 \\
HRh(CO)_2(PPh_3)_2 + CO & \rightleftharpoons HRh(CO)_3(PPh_3) + PPh_3 \\
HRh(CO)_3(PPh_3) + CO & \rightleftharpoons HRh(CO)_4 + PPh_3
\end{align*}
\]

This phosphine dissociation decreases the selectivity to n-aldehyde and, as will be shown later on, causes deactivation of the catalyst. Thus, as more phosphine is displaced, either because of high temperature, high CO pressure or low phosphine concentration, the characteristics of the reaction system should become more like that of the simple metal carbonyl.
Wilkinson also studied the behaviour of the HRh(CO)(PPh)$^3$ complex in solution under various conditions. When a solution of this compound is treated with CO the dimeric complex [Rh(CO)$_2$(PPh)$_2$]$_2$ is formed. If CO is then swept out of the system a red dimer [Rh(CO)(PPh)$_3$)$_2$(S=solvent) is formed. The presence of excess PPh$_3$ inhibits the dimerization. On addition of H$_2$, HRh(CO)$_2$(PPh)$_2$ is formed back. In the absence of synthesis gas in solution another dimer is formed which is not capable of activating molecular hydrogen. M. Yagupsy, Brown, G. Yagupsy and Wilkinson [20] showed this complex to be

\[ \text{PPh}_3 \quad \text{PPh}_3 \]
\[ \text{OC-Rh-Rh-CO} \]
\[ \text{PPh}_3 \quad \text{PPh}_3 \]

Replacement of PPh$_3$ by CO eventually leads to the formation of dirhodiumhexacarbonyl, which can easily result in the formation of Rh(0).

2.3. Recent Developments

As mentioned earlier, most results of hydroformylation studies are explained in terms of the Wilkinson mechanism. However, this mechanism requires some modifications.

The first stages of the catalytic cycle have been studied by (among others) Kastrup et al. [21] and Brown et al. [22]. $^{31}$P NMR has been shown to be a useful research tool which allowed the determination of the rate of phosphine dissociation from HRh(CO)(PPh)$_3$ in the presence of excess triphenylphosphine at various temperatures [21]. Related studies under a CO atmosphere [22] at 0°C demonstrated that the equilibria shown in scheme I have to be formulated as follows:

Scheme II.

\[ \text{H} \quad \text{Ph}_3\text{P-Rh-PPh}_3 \]
\[ \text{CO} \quad \text{+CO} \quad \text{HPPH}_3 \quad \text{Trans} \quad 85\% \]
\[ \text{+PPh}_3 \quad \text{CO} \]
\[ \text{-CO} \quad \text{-PPh}_3 \]
\[ \text{Ph}_3\text{P-Rh-CO} \]
\[ \text{CO} \]
\[ \text{Ph}_3\text{P-Rh-PPh}_3 \]
\[ \text{HPPH}_3 \quad \text{Ph}_3\text{P-Rh-CO} \quad 85\% \]
\[ \text{Ph}_3\text{P-Rh-PPh}_3 \]
\[ \text{CO} \]
\[ \text{HPPH}_3 \]
\[ \text{OC-Rh-PPh}_3 \]
\[ \text{CO} \]
\[ \text{15\%} \]

As mentioned earlier, most results of hydroformylation studies are explained in terms of the Wilkinson mechanism. However, this mechanism requires some modifications.

The first stages of the catalytic cycle have been studied by (among others) Kastrup et al. [21] and Brown et al. [22]. $^{31}$P NMR has been shown to be a useful research tool which allowed the
Kastrup et al. favour HRh(CO)(PPh₃)₂ as the key intermediate, while Brown et al. believe it to be the dicarbonyl species HRh(CO)₂(PPh₃)₂. The latter group studied the effect of excess CO or triphenylphosphine on the square-planar intermediate HRh(CO)(PPh₃)₂ using the isomerization of Z-[1,2-d] styrene as a probe reaction. Under hydroformylation conditions (ambient pressure, 1:1 H₂/CO, room temperature) the isomerization was faster than hydroformylation although the isomerization was almost 100 times slower than in the absence of CO. In the presence of a 5M excess of triphenylphosphine, hydroformylation was more than six times faster than isomerization, and again the isomerization reaction was suppressed to a similar extent. The authors concluded that HRh(CO)(PPh₃)₂ is not an intermediate in the hydroformylation cycle as it is intercepted by triphenylphosphine or CO rather than by alkene.

On the other hand, HRh(CO)₂(PPh₃)₂ is an "18-electron species" and therefore it is not to be expected to be capable of accepting an alkene prior to losing a ligand. It appears from the bulk of known evidence that intermediates with more than 18 valence electrons are rare - if present at all - in catalytic cycles. This may be considered to support the arguments given by Kastrup et al. to accept the 16-electron species HRh(CO)(PPh₃)₂ as the active compound in the Π-addition of the alkene to the metal centre.

This Π-addition of the alkene to the metal centre is the second step in the hydroformylation mechanism. Pino [23] states that, on the basis of the results in hydroformylation, no conclusions can be drawn about the structure of this intermediate. Either Π-complexation of the substrate to the metal atom occurs, followed by insertion into the M-H bond, or there is a direct addition of an M-H bond to a double bond through a 4-centre transition state, the stereochemical consequences being the same in both cases.

Rh-acyl complexes have been studied by ¹³C NMR. These studies provide insight into the origin of the favourable normal: branched selectivity exhibited by the catalyst [24]. On treatment of a solution in toluene of HRh(CO)₂(PPh₃)₂ with oct-1-ene under a ¹³CO atmosphere at 0°C, followed by cooling to -95°C, a single complex was observed:

```
\[
\begin{array}{c}
\text{n C₈H₁₇} \\
\text{OC} \\
\text{Rh} \\
\text{OC} \\
\text{PPh₃}
\end{array}
\]
```

The acyl carbon signal showed broadening and the P coupling to the terminal carbonyl was lost on raising the temperature to -30°C owing to phosphine exchange. At higher temperatures both the acyl and terminal carbonyl signals were broadened, with loss of rhodium coupling, indicating dynamic CO exchange. With ¹³C-s-styrene two acyl complexes were observed at -20°C, corresponding to iso- and n-acyls in a 91:9 ratio, close to the ratio produced in hydroformylation under similar conditions. On warming to +20°C, the ratio changed to favour the normal isomer. The methyl and methine signals of the iso-acyl complex were broadened, suggesting that rapid acyl-alkyl equilibration was taking place. It has been stated that the acyl complexes accumulate during hydroformylation, with their hydrogenolysis being the rate-determining step [14]. On the basis of the observed acyl-alkyl equilibration, the same authors point out that the selectivity could well be controlled by the relative rates of hydrogenolysis of the acyl complex after loss of a CO or phosphine ligand,
rather than arising from the stereochemistry of the initial alkyl complexes or being the result of two competing cycles involving associative and dissociative pathways.

By far the most discussed and doubted part of the Wilkinson mechanism is the hydrogen activation step. Wilkinson suggested an oxidative cis-addition of $H_2$ to the metal centre, on the analogy of the oxidative addition of $H_2$ to $(\text{PPh}_3)_3\text{RhCl}$. Johnson et al. [25] studied the stereoselective oxidative addition of hydrogen to iridium (I) complexes, for example:

```
L CO
Ir + H_2
```

1

```
L CO
Ir H X L
```

2

```
L CO
Ir H X L
```

The generally accepted mechanism involves a concerted cis-addition of $H_2$ along one of the ligand axes corresponding to a diagonal of the square complex, leading to formation of dihydride products, with the stereochemistries shown above, via pathways 1 and 2. Numerous other studies concerning this cis-addition were undertaken, for example by Vaska [26].

There are, however, other views on this step in the catalytic cycle. Morris and co-workers [27] synthesized $\text{Fe}(H_2)\text{H(dppe)}_2\text{BF}_4$, a compound in which the $H-H$ bond is still intact, the $H-H$ distance being slightly longer than in free $H_2$. This could imply that the hydrogenolysis of the acyl-Rh compound takes place via a 4 centre, 4 electron transition state:

```
\begin{align*}
\text{Rh} & \quad \text{C} & \quad \text{R} \\
\text{H} & \quad \text{Ir} & \quad \text{CO} \\
\text{H} & \quad \text{Ir} & \quad \text{CO} \\
\text{H} & \quad \text{Ir} & \quad \text{CO} \\
\end{align*}
```

A fundamentally deviating view, however, is that there is no $H_2$ addition to an acyl-Rh species at all, but that the hydrogen needed to form the aldehyde is supplied by another $H$-liganded Rh-complex, in which case a bimolecular mechanism is responsible for the hydroformylation reaction [28]:

```
L_x\text{Rh-C-R} + L_x\text{Rh-H} \quad \rightarrow \quad L_x\text{Rh-RhL_x} + \text{RCH}
```

```
L_x\text{Rh-RhL_x} + H_2 \quad \rightarrow \quad 2 L_x\text{Rh-H}
```

2.4. Side Reactions, Ligand Effects and Deactivation

2.4.1. Side reactions

The most important side reactions are:

1) Hydrogenation.

Reaction of the alkyl-Rh complex with hydrogen.
2) Isomerization.

Internal alkenes are more stable than 1-alkenes. The \( \Pi \) addition step is reversible and will result in isomerization of the 1-alkene to an internal alkene. Two isomerization mechanisms have been favored:

(a) addition and elimination of a kinetically long-lived metal hydride [29] and

(b) rearrangement through a transitory \( \Pi \)-allyl hydride [30]:

\[
\begin{align*}
\text{a)} & \quad M-H + R-CH_2-CH=CH_2 & \rightarrow & & \left[ R-CH_2-CH-CH_2 \right]_M & \rightarrow & R-CH=CH-CH_2 + M-H \\
\text{b)} & \quad R-CH_2-CH=CH_2 & \rightarrow & & HCR \begin{array}{c} \text{M} \\
\text{H} \\
\end{array} \text{CH} \text{CH}_2 & \rightarrow & -M-H \\
\end{align*}
\]

\[ R-CH=CH-CH_2 \]

Davies [31] found that isomerization of \( \text{C}_6\text{H}_{11}\text{CD}_2-\text{CH}=\text{CH}_2 \) yielded little if any \( \text{C}_5\text{H}_{11}\text{CD}=\text{CHCH}_2\text{D} \), the product of the \( \Pi \)-allyl mechanism. The first mechanism, therefore, seems to be the better description of the isomerization reaction.

3) Aldol condensation.

The formed aldehydes can react with each other in the following manner, catalyzed by either basic or acidic sites:

\[
\begin{align*}
2 \text{R}_1\text{CHO} & \rightarrow \text{R}_1\text{CH}+\text{R}_2\text{CHO} + \text{H}_2\text{O} \\
\text{(For example: R}_1=\text{C}_3\text{H}_7, \ R_2=\text{C}_2\text{H}_5) \\
\end{align*}
\]

2.4.2 Ligand Effects

The use of excess phosphine ligands serves a number of purposes, such as:

1) Increased catalytic stability [32].

2) Increased n/iso aldehyde ratio [13], at the cost, however, of the over-all activity.

Olivier and Booth [33] demonstrated the effects of various added ligands on the hydroformylation of propylene using \( \text{HRh(CO)}(\text{PPh}_3)_3 \) as the basic catalyst. The following order of reactivity was determined:

\[ \text{PPh}_3 > \text{Ph}_2\text{PBu} > (\text{Ph}_3\text{O})_3\text{P} > \text{Bu}_3\text{P} \]

With the exception of \( (\text{Ph}_3\text{O})_3\text{P} \), the reactivity apparently decreased with increasing basicity of the ligand and concomitant increasingly hydridic character of the M-H bond of the catalyst. The less basic phosphines also lead to higher n/i ratios than do the more basic ones. However, the inherent steric differences among ligands make quantitative assessment of the electronic effects difficult.

Hydroformylation using Rh catalysts in the presence of chelating diphosphine ligands has been studied by a number of groups [34,35]. The original assumption behind this work was that
the chelating phosphines remain firmly bonded to Rh throughout the catalytic cycle, thus favouring Wilkinson's associative pathway resulting in a higher n/iso ratio. This was obviously not the case and the discrepancy was explained in terms of the phosphine ligand in the intermediate

\[
\begin{array}{c}
\overset{\text{P}}{\underset{\text{HRh(CO)}_{2}}{\text{P}}}
\end{array}
\]

being constrained to a cis geometry as opposed to the more sterically demanding trans geometry of \(\text{HRh(CO)}_{2}(\text{PPh}_3)_{2}\). Kastrup et al. [36] explained the lower activity of these bidentate systems in the presence of excess ligand by showing the formation of \((\text{P}_2)_{2}\text{RhH}\), which is inactive in hydroformylation.

2.4.3. Deactivation

Catalyst life is impaired by extrinsic poisons such as strong acid, HCN, sulphur as \(\text{H}_2\text{S}\) or \(\text{CO}_2\), and \(\text{O}_2\) [37],[38]. Feed stream purification negates this potential problem. But rhodium catalyst life is also impaired by intrinsic deactivation. This phenomenon is evident in systems which have been under hydroformylation conditions for some time [39]. Recent studies have shown that the deactivation involves insertion of rhodium into a P-C bond of triphenylphosphine [40]. Insertion of olefin into the metal hydride bond produces a metal-alkyl complex, which reductively eliminates as alkylidiphenylphosphine. The mononuclear phosphido complex can also eliminate Ph as benzene, biphenyl, benzaldehyde, etc, with concomitant formation of polynuclear species [Scheme III]. These are more coordinatively and structurally stable than their mononuclear counterparts and possess significantly diminished catalytic activity. It is interesting to note that increased olefin concentration will decrease phosphido-bridged cluster formation, but will increase alkylidiphenylphosphine formation.

Scheme III.

A second way in which catalyst activity can decrease is the application of too high temperatures. The number of P-atoms around the metal atom will decrease and formation of inactive dimers will result. Eventually the Rh(I) is reduced to Rh(0) [20].

2.5. Conclusions

From our literature review we conclude that the Wilkinson mechanism is still accepted as the best framework description of the hydroformylation mechanism. Lots of new techniques have been
applied recently to study the reaction in more detail, such as high pressure IR spectroscopy [41], $^{31}$P NMR [36], $^{13}$C NMR [24] and, on the basis of kinetic data, the use of computer modelling [42].

The conclusions arrived at by the several investigators, however, vary greatly, and no reaction step in the mechanism is undisputed. There is even no agreement on the question which step is the rate-determining one.

Information on the rate-determining step may be gained from the kinetics of a catalytic reaction. The general rate equation reads:

$$r = k \cdot p_a^a \cdot p_b^b \cdot p_c^c \cdot e^{-E_a/RT}$$

where $E_a$ is the apparent activation energy and the quantities $a$, $b$ and $c$ are the reaction orders in hydrogen, carbon monoxide and alkene pressure, respectively. When a reactant is involved in an equilibrium step and the order in the pressure of that reactant is zero or nearly zero, it is very likely that the equilibrium is fully shifted to the right. In that case such a step is not rate-determining. When the reaction rate is first order in the pressure of a reactant, and all other steps are in near-equilibrium, it becomes very likely that the step in which the reactant in question is involved is the rate-determining one, the "equilibrium" in the steady state being strongly shifted to the left.

As mentioned earlier, it has been stated by, for example, Olivier and Booth [33] that the hydrogenolysis of the acyl intermediate is the rate-determining step. These authors found a zero order in carbon monoxide pressure and an order of one in the partial pressures of hydrogen and alkene. However, Herman [11], d'Oro et al. [43] and Gerritsen et al. [10], all working with a large excess of $\text{PPh}_3$, found the order in hydrogen to be close to zero. This points to the last (hydrogenation) step in the associative pathway being an equilibrium step fully shifted to the right. Hence, a rate-determining hydrogenation of the acyl compound is not very plausible.

From the above considerations we conclude, for the time being, that, at least in the presence of a large excess of $\text{PPh}_3$, the addition of the alkene in the $\pi$-bonded form to the rhodium centre, perhaps concomitant with the pushing aside of a $\text{PPh}_3$ ligand, is the rate-determining step.

Wilkinson et al. [20] stated that dimerization of the complex can lead to deactivation of the catalyst. The use of excess ligand hampers this reaction, thus stabilizing the catalyst, but dimerization can be suppressed even more effectively by isolating the active metal centres from each other. This can be accomplished by chemical immobilization of the catalyst. Since bidendate ligands are more firmly bound to the metal centre, such systems are thermally more stable. We advocate the application of a tridentate ligand in which, due to the steric factor, only two of the three phosphorus atoms can be placed on the metal centre, the third one acting as an intramolecular stabilizer.

On the basis of the literature studied this should be an active and thermally stable catalyst, provided no bimolecular step is required in the hydrogenation of the acyl intermediate. We shall return to this subject in Chapter 6.
References Chapter 2

1. O. Roeien, (Ruhrchemie AG), German Patent 849, 548 (1938).
3. HETEROGENIZATION OF RHODIUM COMPLEX CATALYSTS

3.1. Introduction

In recent years there has been an increasing interest in heterogenization of homogeneous catalysts as a means of combining the advantages of heterogeneous and homogeneous systems. The following factors play an important role in catalytic processes:

1) Separation of the catalyst from the products.
Homogeneous catalysis often involves a laborious and expensive separation step, often accompanied by some loss of catalyst activity, whereas heterogeneous catalysts can easily be separated from the products, by filtration when they are used in a batch reactor, or by a continuous separation method when they are used in a fixed bed reactor. It should be noted that three of the commercially successful homogeneously catalyzed processes, namely the LPO process [1,2], the Monsanto process for carbonylation of methanol [3] and the Wacker process for the oxidation of ethene [4], owe part of their success to the relatively low boiling points of the products.

2) Thermal Stability.
Heterogeneous catalysts, such as pure metals on supports and metal oxides, are often much more thermally stable than homogeneous catalysts, which are often organometallic complexes.

3) Side reactions of the catalyst.
Metal complexes in solution can conglomerate, which can result in the formation of inactive oligomers.

These three factors highlight the advantages of heterogeneous catalyst systems. Homogeneous catalysis, of course, also has advantages, such as:

4) Efficiency.
Heterogeneous catalysts are only active in the surface or subsurface area, whilst in homogeneous catalysts all molecules are, in theory, available for the reaction. So the efficiency is much higher in the latter case.

5) Reproducibility.
Homogeneous catalysts have a very definite stoichiometry and structure; by contrast, the structure of the surface of heterogeneous catalysts is very difficult to reproduce because it is heavily dependent on the method of preparation.

6) Specificity and Controllability.
Homogeneous catalysts have, in general, only a limited number of types of active sites, in contrast with heterogeneous catalysts, which contain a great variety of surface defects and several different surface crystallographic planes, resulting in several sorts of active sites. These surface defects and the surface plane distribution are difficult to control, while in the case of homogeneous catalysts modification by, for example, other ligands can be accomplished much more easily.

7) Sensitivity to poisoning.
Heterogeneous catalysts are more frequently subject to poisoning by sulphur and phosphorus containing compounds than homogeneous catalysts, and to a much greater degree.

There are two major types of heterogenized homogeneous catalysts:

1) A solution of the metal complex, capillary condensed in the pores of an inorganic or organic porous support material (SLP catalysts).

2) A chemically immobilized metal complex on organic or inorganic support materials.

These two types of heterogenized homogeneous catalysts will be discussed in this chapter.
3.2. SLP Catalysts

Acres, Bond, Cooper and Dawson [5] and Rony [6] independently demonstrated the feasibility of dispersing non-volatile liquid catalyst solutions containing metal complexes within porous solids and performing gas-phase reactions over fixed beds of such catalysts.

In 1975 a research programme was started at Delft University of Technology with the objective to learn more about the application of organometallic complexes as catalysts in this so-called supported liquid phase (SLP) form. Hydroformylation of olefins over Wilkinson-type rhodium catalysts was chosen as test reaction [7-22].

In an SLP rhodium catalyst, schematically represented in Figure 1, HRh(CO)(PPh3)2 is dissolved in PPh3 or derivatives thereof, the so-called solvent-ligands. The solution is brought into the pores of support materials such as silica, alumina or macrorreticular resins (see Figure 1).

The function of the solvent-ligand is threefold:

a) Fixation of the catalyst.

The support material is chosen such that the pore walls are wetted by the solvent-ligand. Then, according to Kelvin’s law, a suction force is created which, for pores with diameters of a few nm, may become as high as 5 MPa. As a result, the solution is held strongly to the support by capillary forces.

b) Increasing the linear-to-branched ratio.

In the presence of carbon monoxide and an excess of PPh3, the following equilibria are shifted to the left:

\[
\begin{align*}
HRh(CO)(PPh_3)_3 & \rightleftharpoons HRh(CO)(PPh_3)_2 + PPh_3 \\
HRh(CO)_2(PPh_3)_2 & \rightleftharpoons HRh(CO)(PPh_3)_2 + CO \\
HRh(CO)_2(PPh_3)_2 & \rightleftharpoons HRh(CO)(PPh_3)_2 + PPh_3
\end{align*}
\]

Shifting of these equilibria to the left in general increases the number of bulky PPh3 ligands around the rhodium centre. As a result, the linear-to-branched ratio increases. Both steric and electronic effects explaining this shift have been suggested in the literature.

c) Stabilization of the catalyst.

Because of the presence of an excess of PPh3, the number of PPh3 ligands around the rhodium centre remains relatively large. This prevents the formation of catalytically less active or even inactive oligomers.

This type of catalyst has the following advantages compared with its homogeneous analogue:

a) Relatively easy separation of catalyst and products
b) Greater stability of the catalyst due to the excess PPh3
c) A large gas-liquid interfacial area and a shorter liquid phase diffusion path resulting in an efficient use of the catalytically active centres
d) Elimination of severe reactor corrosion problems [6].
However, two critical situations are encountered when working with SLPC's:

1) The catalyst can dry up due to evaporation of the solvent ligand. According to Herman [18], when working at 383 K, 50% of the PPh₃ will be evaporated after a period of 800 hrs. Therefore, measures must be taken to replenish the PPh₃ from a preconnected reactor filled with PPh₃ on a support. Another solution to this problem could be the use of solvent ligands with lower vapour pressures, such as tri (para-tolyl) phosphine [9].

2) The formation of aldol products and the solubility of the aldehydes in the solvent-ligand, as well as capillary condensation in the pores of the support, can result in leaching out of the expensive rhodium complex. Aldol condensation, however, can be largely circumvented by using supports with an extremely low aldol condensation activity, such as macroreticular resins or dehydroxylated silicas. It is clear that this problem is more severe when a high conversion per pass is applied. Unfortunately, a high conversion is necessary in order for this system to be industrially attractive. Furthermore, the hydroformylation of higher alkenes, producing high boiling products, will be very problematic.

We have to conclude that the two problems mentioned above are hard to avoid simultaneously. The first problem can be circumvented by using lower temperatures and/or higher pressures, while the second problem can be circumvented by applying higher temperatures and/or lower pressures. Besides, the temperature should not be above 383 K, because this results in deactivation of the catalyst. This implies that the temperature/pressure margin is relatively narrow. One of the potential solutions to this problem is the use of thermally more stable rhodium complexes, for example by applying bidentate phosphine ligands. This will be discussed in Chapter 4 of this Thesis.

3.3. Chemically Immobilized Systems

The SLPC systems can only be used when the reactants and the products are in the gas phase. This has the advantage that a continuous separation of the catalyst and the products can be achieved without the need to regenerate the catalyst by filtration or other laborious procedures. This is one of the reasons why at Delft University of Technology this technique has been investigated.

Most efforts in heterogenizing homogeneous catalysts, however, are in the field of the chemical immobilization of metal complexes. There are a few reasons for favouring this last technique:

1) Chemically immobilized systems can be tested in a batch reactor, which does not require very expensive equipment.
2) It can be used for the synthesis of higher boiling products.
3) Ligand evaporation is no longer a problem.

There are two types of chemically immobilized systems, viz.:

1) The metal complex is linked to the support through attachment to one or more of its ligands.
2) A chemical bond between the support and the metal centre is created.

The first of the two classes most resembles the homogeneous analogue, so this technique will be discussed here. Furthermore, most of the catalysts of category 2 are chemically unstable and relatively inactive.
3.3.1. Chemical immobilization on organic supports

The most important type of organic support material consists of cross-linked polystyrene. It offers several advantages:
1) It is easily functionalized.
2) Unlike metal oxide surfaces, most hydrocarbon polymers are chemically inert and therefore do not interfere with the catalytic group.
3) Styrene-based polymers can be prepared with a wide range of physical properties.

An essential disadvantage of styrene-based polymers is that they have poor mechanical properties, which prevents them from being used in stirred reactors, in which they would be pulverized.

Two types of styrene based polymers are used. In the first type, a commercial polymer is functionalized, whereas in the second the monomers styrene, divinylbenzene and a functionalized styrene are copolymerized.

A well-known example of the first route is the synthesis of diphenylphosphine functionalized polystyrene. At Delft University of Technology this was done by de Munck [12] in the following manner:

\[
\begin{align*}
\text{PCI} & \quad \text{BF}_3 \cdot \text{ET}_2 \cdot \text{O} \\
\text{HRh(CO)}(\text{PPh}_3)_3 & \rightarrow \\
\text{PPh}_2 & \quad \text{Li} \\
\text{PCl}_3 & \quad \text{O} \\
\text{PPh}_2 & \quad \text{CO} \\
\text{PPh}_3 & \quad \text{Rh} \\
\end{align*}
\]

The second route to functionalized polystyrene is to polymerize a functionalized monomer. Homopolymerization of the monomer produces a linear product in which every segment carries a functional group, while copolymerization with styrene and divinylbenzene also produces a polymer, but now with only a proportion of the monomer groups being functionalized. However, p-styryldiphenylphosphine is considerably more reactive than styrene itself so there is a tendency for multiple units of phosphinated monomers to be formed in the early stages of the polymerization. Therefore, it is very difficult to prepare a copolymer in this way with all the phosphinated residues completely isolated from each other. So, for hydroformylation catalysts copolymerization does not seem to be an attractive route to chemically immobilized systems.

3.3.2. Chemical immobilization on inorganic supports

The major advantages of inorganic supports over their organic counterparts are their better mechanical and thermal stabilities coupled with reasonable heat transfer properties. Very often the upper limit of the thermal stability of organic polymer-supported complex catalysts is set by the polymer rather than the metal complex [23].

Silica is by far the most widely used inorganic support material for chemical immobilization of organic functional groups. Well-known organic reactions have been applied to modify the silica surface, which consists of polar silanol groups and unreactive siloxane bonds, such as:
1) Reactions with alcohols [24]:

\[
\begin{align*}
\text{Si-OH} + \text{HO-R} & \rightarrow \text{Si-OR} + \text{H}_2\text{O} \\
\end{align*}
\]
2) Reactions with Grignard reagents [25]:

\[
\begin{align*}
\text{Si-OH} & \xrightarrow{\text{SOCl}_2} \text{Si-Cl} & \xrightarrow{\text{RMg X}} \text{Si-R} \\
\end{align*}
\]

3) Reactions with organosilanes [26-29]:

\[
\begin{align*}
\text{Si-OH} + (\text{CH}_3)_{3-n} & \xrightarrow{X_n} \text{Si-O-Si-R} \\
\end{align*}
\]

\(X = \text{Cl, OE t.}\)

Method 2 has the disadvantage of creating unstable bonds, while method 2 produces magnesium salts that remain partially adsorbed to the silica surface.

Method 3 is particularly useful when \(n=1\), because the surface coverage can be defined well, using elemental analysis. The reaction with organosilanes produces stable bonds and the reactant can easily be separated from the functionalized silica.

In Chapter 6 of this thesis the synthesis of a chemically fixed rhodium hydroformylation catalyst will be presented, applying method No. 3.

References Chapter 3


4. HYDROFORMYLATION OF 1-BUTENE OVER A RHODIUM/SLP CATALYST
APPLYING BIDENTATE PHOSPHINE LIGANDS

4.1. Introduction

As discussed already in Chapter 2, one of the methods to immobilize an (originally homogeneous) organometallic catalyst is by preparing a so-called SLP (supported liquid phase) catalyst. When dealing with a rhodium hydroformylation catalyst in the SLP form, several authors [1-16] made use of \( \text{HRh(CO)}(\text{PPh}_3)_3 \) dissolved in \( \text{PPh}_3 \) (the solvent-ligand) and capillary condensed this solution into the pores of heterogeneous support materials like silica and gamma-alumina.

In order to study the influence of the type of ligand on the performance of the catalyst, Gerritsen et al. [5] explored, besides \( \text{PPh}_3 \), several other ligands. These alternative ligands were used as the solvent-ligand but, being present in large excess, they rapidly and fully exchanged with the \( \text{PPh}_3 \) ligands around the rhodium centre. Out of nine trials, three attractive ligands emerged:

- **Tri(p-tolyl)phosphine.** A catalyst based on this phosphine showed a stable performance up to 139°C. At 90°C the activity was 20% lower than with \( \text{PPh}_3 \) as the ligand. The rate of reaction was 78 cm\(^3\) propylene/g Rh.s and, under comparable conditions, a normal-to-iso ratio of 6.9 was arrived at, against 8.9 with \( \text{PPh}_3 \).

- **(S(+)-(2-phenylbutyl)diphenylphosphine.** A catalyst provided with this type of ligand appeared to be stable, but up to a maximum temperature of 112°C only. Moreover, the activity was a factor of about 10 lower as compared with \( \text{PPh}_3 \)-liganded catalysts, under comparable conditions. The normal-to-iso ratio was 7.8.

- **Tri(2-cyanoethyl)phosphine.** Catalysts containing this ligand showed a stable performance up to a reaction temperature of 130°C, but the activity was a factor of about 100 lower than found with \( \text{PPh}_3 \)-liganded catalysts.

Applying Rh-SLP catalysts it would be desirable to operate at reaction temperatures far above 90°C, for a number of reasons. First, it is uneconomic to be forced to dissipate the high exothermic heat of reaction (-138 kJ.mol\(^{-1}\)) at relatively low temperature levels. Secondly, the combination of a low reaction temperature with a high alkene conversion per pass may lead to capillary condensation (followed by solution) of the produced aldehydes into the pores of the catalyst and this, in turn, leads to soaking of the catalyst. In the case of propylene hydroformylation, for instance, it can be calculated that the alkene conversion per pass should not exceed 21.4% in an experiment at 90°C and at 1.57 MPa total pressure (propene/H\(_2\)/CO = 1/1/1).

It will be clear that, from a practical point of view, such low conversions are uneconomic. The only solution of the problem lies in increasing the reaction temperature and this asks for types of ligands which render the catalyst a very high stability at higher temperatures. At the same time, however, the ligand should have a low vapour pressure at these higher temperatures. It was shown, among others, by Herman [9] that, when operating with \( \text{PPh}_3 \) as the solvent-ligand above 90°C, too
much $\text{PPh}_3$ evaporated out of the catalyst per unit time, causing the catalyst to dry up, whereas at the same time the aldehydes became contaminated with triphenylphosphine.

All these reasons prompted us to explore the use of still other ligands. In this chapter we will show that the use of 1,4-bis(diphenylphosphino)butane, $(\text{Ph}_2\text{P})-(\text{CH}_2)\text{CH}_2\text{CH}_2\text{PPh}_2^\text{3}$, can be quite successful. Such bidentate ligands give rise to a stronger bonding between the phosphorus atoms and the rhodium centre of the catalyst and hence the thermal stability of the catalyst will increase. Moreover, it will appear that the application of this type of ligands is interesting from a theoretical point of view, especially with respect to the kinetics of the hydroformylation reaction.

1-Butene was chosen as the alkene to be hydroformylated. The linear hydroformylation product of 1-butene, n-pentanal (n-valeraldehyde) is an intermediate in the production of a plasticiser with low volatility, di-isodecylphthalate (DIDP). The iso-product, 2-methylbutanal (iso-valeraldehyde) is of practical significance as it can be directly dehydrated to isoprene.

4.2. Experimental

4.2.1. Materials

HRh(CO)(PPh$_3$)$_3$ was prepared by the method of Ahmad et al. [16]. Triphenylphosphine (Merck, West Germany, 99%) was used as received. Tri(p-tolyl)phosphine (Janssen, Belgium, 98%), triphenylphosphine oxide (Merck, West Germany, 98%) and 1,4-bis(diphenylphosphino)butane (Janssen, Belgium, 98%) were used as received.

Benzene (Merck, West Germany, 99%) was dried over molecular sieve 3A, from Union Carbide, USA. 1-Butene, helium, nitrogen, hydrogen and carbon monoxide were obtained from Hoek Loos NV, The Netherlands. These gases were freed from traces of oxygen, water and carbon dioxide over a BASF catalyst R3-11, molecular sieves 3A, and sodium hydroxide on asbestos ("Ascarite"), respectively. Hydrogen was freed from traces of oxygen and water over Pd-on-alumina (from BASF, Germany) and over molecular sieves, type 3A.

The catalyst support material was silica 000-3E (from Ketjen, The Netherlands). The BET surface area appeared to be 203 $\text{m}^2.\text{g}^{-1}$ and the pore volume was 0.85 $\text{cm}^3.\text{g}^{-1}$. The maximum in the pore-volume distribution was at a pore radius of 5.7 nm.

4.2.2. Catalyst preparation

The rhodium SLP catalysts were prepared by dry impregnation of the support with a solution of RhH(CO)(PPh$_3$)$_3$ and of the phosphine ligands in benzene, according to a method first described by Gerritsen et al. [2]. Before impregnation, the support material was dried at 393 K for 16 hrs. in air. Impregnation was carried out in the apparatus shown in Figure 1.

A known amount of HRh(CO)(PPh$_3$)$_3$, together with the solvent ligands, was dissolved into benzene at 343 K under nitrogen, to prevent the oxidation of the phosphine (vessel A). The amount of the phosphine solvent-ligands corresponds with the desired degree of pore filling and the amount of rhodium complex to the desired $P$/Rh ratio. The total liquid volume was taken equal to the pore volume of the support material present in vessel B. A small additional quantity of the solvent was added to compensate for evaporation during the impregnation step. The catalyst solution was added dropwise to the stirred support. During impregnation the support is kept at 343 K under nitrogen.
Fig. 1. Catalyst preparation apparatus. A = catalyst solution holder; B = support holder; C = magnetic stirrer; D = oil bath.

The impregnated catalyst was taken out of the apparatus and dried from the solvent benzene at 363 K under flowing nitrogen during 16 hrs. Next the nitrogen atmosphere was replaced by air, after cooling down the catalyst to room temperature. Finally, the catalyst was stored at 253 K.

Degrees of pore-filling were adjusted at about $\delta = 0.2$. This value was controlled by measuring the pore volume of the support before and after filling; use was made of a micro-BET apparatus by measuring the total amount of liquid nitrogen taken up by the catalyst at 78 K, up to a relative $N_2$ pressure of about 0.995.

4.2.3. The hydroformylation apparatus

The hydroformylation experiments were performed in a continuous-flow fixed-bed equipment, suitable for total pressures up to 2 MPa and for reactor temperatures up to 473 K (see Figure 2).

Fig. 2. Fixed-bed continuous-flow apparatus for the hydroformylation of alkenes. A = purification unit. FCI = flow indicator. PIC = pressure indicator, PIA = pressure indicator and alarm, TI = temperature indicator, TIA = temperature indicator and alarm. Items 1-10 see text.

The gases passed a thermal flow meter and controller (Brooks type 5810/5835). The liquid butene was pumped from the
reservoir (1) by a piston pump (2) to the evaporator (3). Flow pulsations in the liquid flow were damped by a pulse damper and by a pressure valve and a membrane.

After having passed the evaporator, the gas mixture was led through heated tubes to the fixed bed (4), which consisted of a stainless steel tube of 0.20 m length and 0.01 m inner diameter. The reactor was placed in an air-fluidized bed oven (5). The temperature was kept constant by means of an Eurotherm thyristor controller to within 0.5 K. The reactor pressure was measured to within 0.02 MPa. The reactor can be bypassed by means of the four-way valve (6).

The gaseous product stream was passed through heated, stainless steel tubes to the heated back pressure regulator (7). Analysis of the product mixture was performed by an on-line gas chromatograph (8), samples being taken directly from the gas stream with a sample loop (0.5 cm³) and injected into the gas chromatograph by a pneumatically actuated Carle valve.

After passing the water cooled condensor (9), the gas stream was led through a soap film meter (10) and then vented to the atmosphere.

The gas chromatographic analysis was performed with two apparatus. The first is an isothermal self-constructed apparatus, used to determine eventual hydrogenation and isomerization of the alkene. The GC contained a column (3 m length, 0.003 m inner diameter) filled with Spherosil XOB-75, mesh size 100-120. The column temperature was 343 K. The GC was equipped with a flame ionisation detector and a Hewlett Packard 5701A electrometer. The second apparatus was a temperature programmable gas chromatograph (Hewlett Packard 5710A) equipped with flame ionisation detectors, to determine the conversion of the alkene to alkanals (linear and branched) and eventually formed aldol products. In the apparatus we used a column of 4 m length and inner diameter 0.0021 m, filled with 25% OV 101 on Chromosorb W-HP, mesh size 80 - 100. The column temperature was programmed from 343 K to 473 K. Peak areas were recorded and integrated by a microcomputer Digital LCI 11/03.

The operation of the hydroformylation equipment was semi-automatic, which means that the set-points were adjusted manually, and that the samples were taken automatically. Safety was ensured by installing pressure and temperature devices; if a pre-set maximum or minimum allowable value was exceeded, a shut-down followed.

At the start of each experiment the reactor temperature was raised stepwise to 363 K under a mixture (50/50) of hydrogen and carbon monoxide in a period of about 2 hours.

4.2.4. Vapour pressure measurements

Vapour pressures of the phosphine ligands were obtained from simultaneous torsion effusion measurements and mass loss effusion measurements and were fitted independently into the following equation [17]:

\[ \ln \left( \frac{p_{\text{lig.}}}{p_{\text{lig.}}^0} \right) = - \frac{\Delta G^{\circ}(\theta)}{\theta} + \Delta H^{\circ}(\theta) \cdot \left( \frac{1}{\theta} - \frac{1}{T} \right) \]

in which \( p_{\text{lig.}} \) is the saturated vapour pressure of the ligand, in Pa, \( \theta \) is a reference temperature, in K, and \( p_{\text{lig.}}^0 \) is a standard pressure, taken to be 1 Pa. \( \Delta G^{\circ}(\theta) \) is the standard free enthalpy of vaporization and \( \Delta H^{\circ}(\theta) \) is the standard enthalpy of vaporization. The measurements were carried out in the pressure region of 0.1 - 1 Pa and in the range of temperatures from 264 K to 459 K. The measurements have been performed in the Chemical Thermodynamics Group of the University of Utrecht, in cooperation with Prof. Dr. A. Schuijff and coworkers. The results for triphenylphosphine oxide and 1,4-bis(diphenylphosphino)butane were published in the Journal of Chemical Engineering Data [18]. In section 4.3 these results will be compared with data obtained earlier bij de Kruijf et al. [19] for other solvent-ligands, viz. triphenyl- and tri(p-tolyl)phosphine.
4.3. Results

4.3.1 The performance of SLP catalysts with 1,4-bis(diphenylphosphino)butane

The structure of rhodium complexes, prepared by exchange of the PPh₃ ligands in HRh(CO)(PPh₃)₃ for bidentate ligands of the general composition PPh₂(CH₂)ₙPPh₂, was investigated earlier by Kastrup et al. [20]. Two structures are found which are in mutual equilibrium:

\[
\text{(A)} \quad \text{Rh-PPh₂(CH₂)n-PPh₂} \quad \text{CO} \quad \text{Rh-PPh₂(CH₂)n-PPh₂}
\]

\[
\text{(B)}
\]

For \( n = 2 \) the equilibrium lies almost exclusively to the left, and the corresponding bicyclic system is inactive for hydroformylation. For \( n = 3 \), a larger amount of the right-hand side monocyclic species is found and, consequently, the complex will be more active in this case. For values of \( n \) larger than 3 the equilibrium shifts more and more to the right. However, for very large values of \( n \) stabilization, as a result of the chelating effect, will decrease and the phosphorous-rhodium bond becomes less firm. This is the reason that we have chosen for the use of 1,4-bis(diphenylphosphino)butane (\( n = 4 \)) in our catalytic experiments.

According to the method described in section 4.2.2., a number of catalysts have been prepared; the composition of three representative samples is given in Table 1.

### Table 1. Composition of catalysts used in the hydroformylation of 1-butene, in mmol per 5 gram of catalyst support.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRh(CO)(PPh₃)₃</td>
<td>0.0551</td>
<td>0.0544</td>
<td>0.055</td>
</tr>
<tr>
<td>tri(p-tolyl)phosphine</td>
<td>1.656</td>
<td>1.931</td>
<td>0.546</td>
</tr>
<tr>
<td>(Ph₂P)₂-(CH₂)₄-PPh₂</td>
<td>2.203</td>
<td>1.634</td>
<td>4.362</td>
</tr>
</tbody>
</table>

In all three cases tabulated, the amount of silica used was 5 gram. The particle size was in between 0.35 mm and 0.42 mm.

In the experiments reported in this Chapter, the reactor was operated differentially (conversion per pass lower than 5%) and hence the reaction rate (\( r \)) can be expressed by

\[
r = \frac{\xi}{(W/F)}
\]

where \( W \) is the weight of rhodium in the reactor in gram, \( F \) is the alkene flow expressed in cm³ alkene (at 0.1 MPa and 293 K) per second, \( \xi \) is the alkene conversion, and \( r \) is the reaction rate, consequently expressed in cm³ alkene converted (at 0.1 MPa and 293 K) per gram of rhodium per second.

Aldehydes being the only products observed, the conversion of alkene (\( \xi \)) was calculated from:

\[
\xi = \frac{A_p}{A_p + B_p + A_0}
\]

where \( A_p \) and \( A_0 \) are the integrated peak areas for aldehyde and alkene, respectively, and \( B_p \) is an internal normalization factor.
correcting for the difference in thermal conductivity between aldehyde and alkene.

The kinetics were studied in the flow reactor at a total pressure of 1.2 MPa, and partial pressures of hydrogen, carbon monoxide and 1-butene of 0.4 MPa. The total gas flow was kept constant at 2.5 cm$^3$ (STP) s$^{-1}$.

First of all, the stability of the catalyst (sample II) was tested. At a reactor temperature of 145°C, both at an alkene conversion of 5% and 8%, a perfect catalytic stability was observed and after one week no sign of deactivation of the catalyst could be observed. The activity of the catalyst at 145°C amounted to 45 cm$^3$ 1-butene (STP) converted per g of rhodium per second. As expected, this activity is lower than the one found with monodentate rhodium complexes as a catalyst. The activity is about equal to what has been found in the hydroformylation of propene under comparable conditions at a reaction temperature of 100°C [3, 4]. The observed normal-to-iso ratio at 145°C was 5. An experiment performed at 180°C resulted in a relatively rapid deactivation of the catalyst.

4.3.2. The kinetics of the reaction

The reaction kinetics have been studied in the temperature range of 95 to 140°C. All results could be expressed in the form of a power rate law:

$$ r = k_0 \cdot P_H^a \cdot P_{CO}^b \cdot P_{1\text{-butene}}^c \cdot \exp \left( - \frac{E_{app}}{RT} \right) $$

(4)

where $r$ is the reaction rate per unit weight of rhodium and $a$, $b$ and $c$ are the orders in hydrogen pressure, carbon monoxide pressure and 1-butene pressure, respectively. $E_{app}$ is the apparent activation energy.

The reaction orders have been determined at the relatively low temperature of 97°C. This has the advantage of a nearly 100% selectivity to the formation of the $n$- and iso-aldehyde; isomerization of 1-butene to cis- and trans 2-butene was absent and only a very small fraction of 1-butene was hydrogenated to n-butane.

The experiments were performed at a total pressure of 1.2 MPa and partial pressures of hydrogen, carbon monoxide and 1-butene of 0.4 MPa each. The total gas flow was kept constant at 2.5 cm$^3$ (STP) s$^{-1}$. The reaction order for each reactant was found by halving the partial pressure of that reactant and bringing the total pressure to 1.2 MPa by the addition of helium to the gas flow. The reaction orders found in experiments with catalysts I, II and III (see Table 1), together with the apparent activation energies, are brought together in Table 2. Arrhenius plots are collected in Figure 3. All data in Table 2 and in Figure 3 are related to the kinetics of 1-butene conversion to both $n$- and iso-aldehyde.

Table 2. The kinetics of the hydroformylation of 1-butene to iso-and $n$-valeraldehyde (kinetics related to the 1-butene conversion). The reaction orders in hydrogen pressure ($a$), carbon monoxide pressure ($b$) and 1-butene pressure ($c$) are given at 97°C and 1.2 MPa total pressure. $E_{app}$ is the apparent activation energy. $A$ is the catalytic activity, expressed in cm$^3$ 1-butene.g Rh$^{-1}$.s$^{-1}$, at a reaction temperature of 97°C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ratio Rh-complex/No.</th>
<th>bidentate ligand/tri(p-tolyl)phosphine</th>
<th>$H_2$</th>
<th>CO</th>
<th>$1-C_{H_2}$</th>
<th>$E_{app}$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1 : 30 : 40</td>
<td></td>
<td>0.35</td>
<td>0.06</td>
<td>1.44</td>
<td>65.5</td>
<td>3.5</td>
</tr>
<tr>
<td>II</td>
<td>1 : 35.5 : 30</td>
<td></td>
<td>0.35</td>
<td>0.28</td>
<td>1.38</td>
<td>67.3</td>
<td>1.7</td>
</tr>
<tr>
<td>III</td>
<td>1 : 9.9 : 79.3</td>
<td></td>
<td>0.32</td>
<td>0.14</td>
<td>1.44</td>
<td>66.2</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Fig. 3. Arrhenius plots for the hydroformylation of 1-butene over catalysts I, II and III. The natural logarithm of the conversion rate to n- and iso-valeraldehyde is plotted against 1000/T.

The kinetic data for the formation of n-valeraldehyde is presented in Table 3a. The differences with what is found for the kinetics of the conversion of n-valeraldehyde plus iso-valeraldehyde (Table 2) are marginal. Table 3b represents the kinetics for the formation of the iso-valeraldehyde. Here the differences with the data in Table 2 are larger, especially with respect to the order in the carbon monoxide pressure. We return to this point in the section Discussion.

For all three catalysts a remarkable nearly constant normal-to-iso ratio is found in the whole temperature range investigated (97 to 140°C); see Table 4. Halving the partial hydrogen or n-butene pressures hardly influenced this ratio. However, an increase of the partial carbon monoxide pressure by a factor of two resulted in a decrease of the normal-to-iso ratios (see Table 4).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ratio Rh-complex/</th>
<th>bidentate ligand/</th>
<th>$H_2$ (a)</th>
<th>CO (b)</th>
<th>1-CO</th>
<th>$E_{app}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1 : 30 : 40</td>
<td>0.35</td>
<td>-0.06</td>
<td>-1.4</td>
<td>66.6</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>1 : 35.5 : 30</td>
<td>0.35</td>
<td>-0.31</td>
<td>-1.4</td>
<td>61.1</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>1 : 9.9 : 79.3</td>
<td>0.35</td>
<td>-0.19</td>
<td>-1.4</td>
<td>64.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 3b.

Table 4. The n-valeraldehyde/iso-valeraldehyde ratios in the hydroformylation of 1-butene over catalysts I, II and III.

<table>
<thead>
<tr>
<th>Catalyst No.</th>
<th>n/iso ratio</th>
<th>n/iso ratio, on increasing the partial CO pressure (factor 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5.0 to 5.5</td>
<td>3.85 to 4.24</td>
</tr>
<tr>
<td>II</td>
<td>5.5 to 6.0</td>
<td>4.07 to 4.44</td>
</tr>
<tr>
<td>III</td>
<td>4.9 to 5.0</td>
<td>3.87 to 3.95</td>
</tr>
</tbody>
</table>
We finally remark that both the kinetics and the normal-to-iso ratios found when applying 1,4-bis(diphenylphosphino)butane-ligated catalysts differ appreciably from the results arrived at in the hydroformylation of 1-butene over triphenylphosphine-ligated catalysts by Pelt et al. [21-27]. We return to this important point in the section Discussion.

4.3.3. Vapour pressure measurements

The thermodynamic quantities describing the vapour pressures of the solvent-ligands (see eq. 1 in section 4.2.4.) are brought together in Table 5.

Table 5. Experimental values of \( \Delta G^0(\theta) \), \( \Delta H^0(\theta) \) and of \( \theta \).

<table>
<thead>
<tr>
<th>( \theta ) (K)</th>
<th>( \Delta G^0(\theta) ) (J.mol(^{-1}))</th>
<th>( \Delta H^0(\theta) ) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPP</td>
<td>378.06</td>
<td>4358</td>
</tr>
<tr>
<td>TPPO</td>
<td>398.86</td>
<td>3039</td>
</tr>
<tr>
<td>BDPPB</td>
<td>443.22</td>
<td>3377</td>
</tr>
<tr>
<td>TPTP</td>
<td>325.28</td>
<td>2935</td>
</tr>
</tbody>
</table>

In Table 5 the mean values of the thermodynamic quantities are presented, calculated from torsion effusion measurements and mass loss effusion measurements. For details we refer to ref. [17], [18] and [19]. TPTP stands for tri(p-tolyl)phosphine, TPPO for triphenylphosphine oxide, BDPPB for 1,4-bis(diphenylphosphino)butane and TPP for triphenylphosphine.

In Table 6 the relative pressures of the solvent-ligands are brought together, calculated from equation (1) and making use of the thermodynamic quantities in Table 5.

Table 6. Pressure-temperature values for TPPO, BDPPB, TPTP and TPP. The standard pressure, \( p^0 \), is 1 Pa.

<table>
<thead>
<tr>
<th>( \frac{p}{p^0} )</th>
<th>Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>385.34 425.99 372.16</td>
</tr>
<tr>
<td>0.2</td>
<td>391.99 434.44 378.61</td>
</tr>
<tr>
<td>0.3</td>
<td>395.95 439.53 328.48</td>
</tr>
<tr>
<td>0.4</td>
<td>398.86 443.22 385.28</td>
</tr>
<tr>
<td>0.5</td>
<td>401.13 446.13 387.48</td>
</tr>
<tr>
<td>0.6</td>
<td>403.00 448.53 389.29</td>
</tr>
<tr>
<td>0.7</td>
<td>404.60 450.58 390.84</td>
</tr>
<tr>
<td>0.8</td>
<td>405.99 452.37 392.19</td>
</tr>
<tr>
<td>0.9</td>
<td>407.22 453.96 393.39</td>
</tr>
<tr>
<td>1.0</td>
<td>408.34 455.40 394.47 360.86</td>
</tr>
<tr>
<td>2.0</td>
<td>408.34 455.40 369.26</td>
</tr>
<tr>
<td>3.0</td>
<td>408.34 455.40 374.36</td>
</tr>
<tr>
<td>5.0</td>
<td>408.34 455.40 380.98</td>
</tr>
<tr>
<td>7.0</td>
<td>408.34 455.40 385.48</td>
</tr>
<tr>
<td>9.0</td>
<td>408.34 455.40 388.90</td>
</tr>
<tr>
<td>10.0</td>
<td>408.34 455.40 390.36</td>
</tr>
</tbody>
</table>
All results are plotted in a $\ln(p/p^0)$-against-$10^3/T$ graph in Figure 4. The vapour pressures of TPP, BDPBP and TPTP are equilibrium pressures of the liquid state. For TPPO we are dealing with equilibrium pressures of the solid state.

![Graph](image)

**Fig. 4.** The natural logarithm of the relative solvent-ligands, plotted against $1000/T$. $p^0 = 1$ Pa.

- Line A: triphenylphosphine [19].
- Line B: triphenylphosphine oxide [18].
- Line C: 1,4-bis(diphenylphosphino)butane [18].
- Line D: tri(p-tolyl)phosphine [19].

4.4. Discussion

4.4.1. Kinetics and reaction mechanism

The type of SLP catalyst we are dealing with in this research is characterized by a pore-filling with the bidentate ligand 1,4-bis(diphenylphosphino)butane and with tri(p-tolyl)phosphine, both in large excess in proportion to the amount of hydridocarbonyl-tris(triphenylphosphine)rhodium I. From a study by Pelt and coworkers [23] we know that, next to this, the pores in the catalyst become filled with a certain amount of the aldehydes produced during reaction. It can be estimated from their study that, at the lowest reaction temperature applied in our work (97°C) and at a 1-butene conversion of 18.5%, when 50% of the pore volume is filled by the phosphines, the other 50% is filled by the aldehydes. At the highest temperature (145°C) this high degree of pore-filling would be realized only at a 1-butene conversion of about 50%. Taking into account that in our research the 1-butene conversion was much lower (mostly less than 5%) we estimate that the pore-filling with aldehydes was not exceeding 12% at the lowest temperature and not exceeding 5% at the highest temperature applied.

Notwithstanding the fact that the amount of aldehydes in the catalyst pores is relatively small, dilution of the solution of the catalyst in the solvent-ligands by the aldehydes may have an influence on the reaction rate and on the kinetics. From the work by Pelt and coworkers [23] it follows that addition of aldehydes to the solvent-ligands has hardly any influence on the solubility of the reactants CO and H₂, but the 1-butene solubility is strongly increased by it, and the 1-butene solubility is proportional to the partial 1-butene pressure.

It is likely that the 1-butene solubility, increasing with increasing 1-butene conversion, will influence the 1-butene hydroformylation kinetics. The remarkable broken order in the 1-butene partial pressure, reported in section 4.3.2 (ca. 1.4), and also reported by Hamann in the hydroformylation of propene [9] and by Pelt in the hydroformylation of 1-butene [25], can now be explained as follows. According to the associative reaction mechanism (see Chapter 2) the $\pi$-addition of the alkene is one of the equilibrium steps, and in the presence of an excess of solvent-ligands this equilibrium is strongly positioned to the left. Hence, a first order behaviour in the 1-butene pressure is to be expected. However, with increasing rate of reaction more of
the aldehydes are formed and hence the amount of dissolved 1-butene increases with an increasing amount of aldehydes formed. This will result in a 'self-acceleration' of the reaction by which the order of one is surmounted, the rate of reaction being proportional to the amount of 1-butene dissolved.

A further discussion of the kinetics should start from equilibrium A $\rightleftharpoons$ B, represented in section 4.3.1. By the addition of tri(p-tolyl)phosphine the rate of reaction is strongly increased. Obviously, the monocyclic complex B will exchange its linearly bound 1,4-bis(diphenylphosphino)butane ligand for a tri(p-tolyl)phosphine ligand:

![Diagram of chemical reaction]

The constancy of the normal-to-iso ratio (see Table 4, section 4.3.2.), independent on the ratio tri(p-tolyl)phosphine/1,4-bis(diphenylphosphino)butane, is a strong argument in favour of the exchange of the linearly bound ligand only. The strongly chelating bidentate ligand forces the PH$_2$-groups in a cis-position around the rhodium centre, and due to this fact the normal-to-iso ratio is relatively low (5 to 6, against 8 to 12 with monodentate complexes), for sterical reasons (see below).

It also appeared that the normal-to-iso ratio hardly depends on the reaction temperature and on the degree of 1-butene conversion. These facts may be explained as well from the high stability of the chelating bidentate ligand around the rhodium centre.

According to the line of reasoning inherent the reaction mechanism of hydroformylation explained in Chapter 2, complex C is inactive and hence the first step should be the dissociation of the P(C$_6$H$_4$CH$_3$)$_3$ ligand. This step is followed by M-addition of the alkene which, via an interligand reaction with the H-ligand, is rapidly converted into a $\sigma$-bound n- or iso-alkyl group:

![Diagrams of chemical reactions]

$\sigma$-bound n-alkyl ligand

$\sigma$-bound iso-alkyl ligand
It is seen from the structure of complexes D and E that, due to the cis-position of the bulky PPh₂-groups, the sterical hindrance in the formation of an iso-alkyl group is much lower than in case we are dealing with two more bulky non-interconnected PPh₂ groups. Moreover, according to Kastrup [20], such PPh₂ groups are mainly in a trans-position, by which the sterical hindrance is strengthened.

The large influence of the partial CO pressure on both the catalytic activity and the normal-to-iso ratio is a well-known phenomenon. Pelt and coworkers [25], for instance, in studying 1-butene hydroformylation over a Rh-SLP catalyst containing RhH(CO)(PPh₃)₃ dissolved in PPh₃ as the solvent ligand, reported a positive order in the CO pressure of 0.22. The order in the CO pressure, as far as the formation of n-valeraldehyde is concerned, was about 0.1, whereas the order in CO pressure for the formation of iso-valeraldehyde was 1. Hence, by increasing the CO pressure, the formation of the branched aldehyde was favoured in Pelt’s study.

In studying the hydroformylation of propene over a Rh-SLP catalyst of analogous composition as Pelt’s catalyst, Herman [9] concluded that the partial pressure of CO shows only a slight influence on the rate of reaction, but, on the other hand, has a major impact on the normal-to-iso ratio; an increase of the partial CO pressure from 0.18 MPa to 0.36 MPa led to a decrease of the normal-to-iso ratio by a factor of 1.4.

We conclude that, obviously, CO does not play an important role in any rate-determining step of the reaction, but might play a role in an equilibrium step. However, when such equilibrium is strongly positioned to the right the influence of the CO pressure on the overall kinetics will be negligible. Of course, the CO pressure can have an influence on the number of PPh₃ ligands around the rhodium centre. When part of these PPh₃ ligands exchange for CO ligands the sterical hindrance by the PPh₃ ligands will be diminished and the normal-to-iso ratio will decrease.

It is interesting to note that in our research, by the use of bidentate ligands around rhodium, another situation is encountered; see Tables 2 and 3 in section 4.3.2. The order in CO pressure for 1-butene conversion (Table 2) appeared to be slightly negative. As can be seen from Table 3b in section 4.3.2, the influence of the CO pressure on the rate of formation of iso-valeraldehyde is positive. An explanation of these facts, which deviate from what has been found in Pelt’s and Herman’s work, should be given on the basis of the essential difference with PPh₃-ligated complexes, viz. the cis-position of the PPh₂ groups of the bidentate ligand in our study. We think this to be possible in the following manner. After complexes D and E have been formed, the o-bound alkyl groups will react with the CO-ligand (inter-ligand reaction) by which acyl-ligands are formed:

According to Evans, Osborn and Wilkinson [27] there are now two possibilities:
a. Complexes F and G react slowly with $H_2$ (rate-determining step). During this oxidative hydrogenation ($\text{Rh(I)} \rightarrow \text{Rh(III)}$), two $H$ ligands are taken up:

Obviously, CO addition to complex G to form complex K is less favoured than CO addition to complex F (slightly positive order in CO for the formation of the iso-aldehyde).

b. Complexes F and G react with CO, and a complex K is formed:

This complex K can no longer participate in the formation of aldehydes [27] and the higher the CO pressure the more of this complex will be formed.

Finally, the positive orders in hydrogen pressure (about 0.3; see Tables 2, 3a and 3b in section 4.3.2) have to be explained.

According to Wilkinson et al. [27] the oxidative hydrogenation step is the rate-determining one. This would be in accordance with first order kinetics in hydrogen pressure, which indeed has been found in the homogeneous hydroformylation of propene. But it is interesting to note that Cavalieri d'Oro et al. [28], in studying the hydroformylation of propene homogeneously with a relatively large excess of $\text{PPH}_3$ in toluene ($P/\text{Rh} = 150 \text{ mol/mol}$), arrived at a rate of reaction zero order in hydrogen. It might be that in both cases (first order or zero order) the hydrogenation step remains the rate-determining one. In the first order case (low number of $\text{PPH}_3$ ligands around rhodium) hydrogen should then be directly bound dissociatively by the rhodium centre. In the zero order case the hydrogen molecule is perhaps pre-dissociatively bound, this being a fast reaction leading to full saturation of all complexes with a $H_2$-ligand. (The occurrence of $H_2$-liganding is reported for, among others, tungsten and ruthenium organometallic complexes [29, 30].) The next and rate-determining step would then be the interligand reaction between the $H_2$-ligand and the acyl-ligand, to form the aldehyde and a $H$-ligand.

In our experiments the situation is more or less in between these two extremes (broken order in hydrogen). A possible explanation is that the competition between the reactions a: F (or G)$\rightarrow$H (or J) and b: F (or G)$\rightarrow$K, is promoted in favour of reaction a on increasing the hydrogen pressure (small positive order in hydrogen).
4.4.2. The vapour pressures of the solvent ligands

As demonstrated by Table 6 and in Figure 4 (section 4.3.3.) the relative pressures of the solvent-ligands applied in our catalysts are very low as compared to the vapour pressure of the generally preferred PPh₃ ligand. For instance, at 400 K (127°C) the partial pressure of PPh₃ amounts to about 20 Pa (0.15 mm Hg pressure). At the same temperature the partial pressure of tri(p-tolyl)phosphine is only 1.34 Pa (0.01 mm Hg pressure) and the partial pressure of 1,4-bis(diphenylphosphino)butane is only about 0.015 Pa (10⁻⁴ mm Hg pressure).

It follows that the large evaporation losses reported by Herman [9] when using PPh₃ as the solvent ligand, leading to total dry up of the catalysts in a period of ca. 400 hrs. at 110°C, will be much lower in our case. Referring to the partial pressure of tri(p-tolyl)phosphine (see above) the life-time of our catalyst will be a factor of about 15 longer, and the evaporation loss of 1,4-bis(diphenylphosphino)butane will be negligible. Therefore, the combined use of the two ligands employed by us might be attractive in applied catalysis in those cases where a very high normal-to-iso ratio is not necessary.

4.4.3. Experiments with DIOP as the solvent ligand

A chiral diphosphine ligand frequently used in asymmetric hydrogenation with Wilkinson type rhodium catalysts is 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (DIOP), introduced by Kagan and coworkers [31]:

Some preliminary experiments were performed by us with (-)DIOP in the hydroformylation of 1-butene with a rhodium SLP catalyst. This is interesting as a consequence of the enantioselective influence this solvent-ligand may have on the course of the hydroformylation reaction.

A rate of hydroformylation was found which, under comparable conditions, was 5 to 6 times lower than with 1,4-bis(diphenylphosphino)butane as the solvent-ligand, whereas the normal-to-iso ratio was about the same. This low activity prompted us to apply a relatively high reaction temperature. But it is known that for attaining a high enantioselectivity just very low reaction temperatures are needed (around 60°C, for instance). One might compensate for this by working at higher pressures, but this too has an adverse effect on the enantioselectivity.

In experiments at 90°C no enantiomeric form of isovaleraldehyde could be detected by us. Clearly, in the field of heterogeneous enantioselective hydroformylation with SLP catalysts further research is needed.

References Chapter 4

5. HYDROFORMYLATION OF ALLYL ALCOHOL AND THE TERTIARY BUTYL ETHER OF ALLYL ALCOHOL OVER RHODIUM-BASED SUPPORTED LIQUID PHASE CATALYSTS

5.1. Introduction

The industrial production of 1,4-butanediol is currently based on the Reppe reaction of acetylene with formaldehyde from which 1,4-butynediol is obtained [1]. Catalytic hydrogenation of this product results in the formation of the desired diol, which is used as a component in certain polyurethanes and polyesters and also for the production of butyrolactone and pyrrolidine.

Because of a growing market for 1,4-butanediol and the rapidly increasing cost of acetylene, it became attractive to search for alternative processes. A very attractive route, in principle at least, is the hydroformylation of allyl alcohol to 4-hydroxybutyraldehyde (see Figure 1).

Originally, the hydroformylation of allyl alcohol was performed with cobalt catalysts. However, the yield of 4-hydroxybutyraldehyde did not exceed 30% and the larger portion of the allyl alcohol isomerized to propionaldehyde [2-4]. Later on, Brown and Wilkinson studied the hydroformylation of allyl alcohol with hydridocarbonyltris (triphenylphosphine)-rhodium(I) as a catalyst, at 65 kPa and 25°C, but they did not specify the reaction products [5].

![Chemical equation and reaction diagram]

Fig. 1. Hydroformylation of allyl alcohol over a rhodium organometallic catalyst to 4-hydroxybutyraldehyde and 2-methyl-3-hydroxypropionaldehyde. Ring closure to 1-hydroxytetrahydrofuran.

The advantages of carrying out hydroformylation reactions applying heterogenized rhodium catalysts have been explained already in the preceding chapters. The first authors who demonstrated the viability of this principle in the case of allyl alcohol hydroformylation were de Munck et al., who used a supported liquid phase rhodium catalyst [6,7]. At first sight their mode of operation looks promising. Their SLP rhodium catalysts possess a high stability and the 4-hydroxybutyraldehyde selectivity is of the order of 80 to 97%. At the same time the undesired isomerization of allyl alcohol to propionaldehyde is prevented by selection of a silica support with a low aluminium content and by the use of rhodium complexes in the presence of excess phosphine.

However, a calculation based on the data presented in ref. [6] shows the allyl alcohol conversion per pass in de Munck et al.'s work to be of the order of 5% only, whereas the 4-hydroxybutyraldehyde productivity attained the very low value of about 0.02 grams per gram of catalyst per hour.
of 96C. An experiment, as shown in Figure 1, was conducted on a total pressure of

performing by van Milton were conducted at a total pressure of

hypothetical and theoretical work, at least in principle, if not in practice, as is
certainly the case of theoretical work, at least in principle, if not in practice, as is

in accordance with the results published by de Munk et al.,

a discrepancy exists at the mean dye-particle concentration of 0.08 g/l.

The study by de Munk et al., has been continued by van

In accordance with pre-arranged experiments, it is not agreeable by

to the fact that the experimental work, at least in principle, if not in practice, as is

formulation reactor.

composition in the product mix due to pH jump in the hydro-

the reaction on the basis of changes in the

prefered over a product size, as is
certainly the case of theoretical work, at least in principle, if not in practice, as is

in accordance with the results published by de Munk et al.,

a discrepancy exists at the mean dye-particle concentration of 0.08 g/l.

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the reaction on the basis of changes in the

prefered over a product size, as is
certainly the case of theoretical work, at least in principle, if not in practice, as is

in accordance with the results published by de Munk et al.,

a discrepancy exists at the mean dye-particle concentration of 0.08 g/l.

The study by de Munk et al., has been continued by van

In accordance with pre-arranged experiments, it is not agreeable by

to the fact that the experimental work, at least in principle, if not in practice, as is

formulation reactor.
A major problem which emerged from van Milligen's work is the occurrence of a number of parallel and consecutive reactions. First of all, these reactions may take place as soon as condensation of non-converted allyl alcohol and 4-hydroxybutyraldehyde occurs in the piping behind the reactor. It is unknown to what extent stainless steel walls of the piping play a catalytic role here. The reactions and products, which were gas chromatographically detected in relatively small amounts, are summarized in Figure 2.

In hydroformylation, be it homogeneous or heterogeneous, there is always the risk of disturbing aldol condensation reactions. But in the case of allyl alcohol hydroformylation, additional problems arise due to the presence of an extra functional group in the olefin and in the product, 4-hydroxybutyraldehyde. Besides ring closure, hemiacetals and acetals may be formed. For instance, 4-hydroxybutyraldehyde can dimerize:

$$2\text{HO-CH}_2\text{CH}_2\text{CHO} \rightarrow \text{HO-CH}_2\text{CH}_2\text{CH}-\text{O-CH}_2\text{CH}_2\text{CHO},$$

(hemiacetal)

or 4-hydroxybutyraldehyde can react with allyl alcohol from the feed:

$$\text{HO-CH}_2\text{CH}_2\text{CHO} + \text{HOCH}_2\text{CH} = \text{CH}_2 \rightarrow \text{HO-CH}_2\text{CH}_2\text{CH}_2\text{CHOCH}_2\text{CH} = \text{CH}_2,$$

(hemiacetal)

Likewise, addition of two mole equivalents of the alcohol, with the consequent formation of 1 mole equivalent of water, yields the corresponding acetals.

Hemiacetal and acetal formation was encountered indeed in van Milligen's study. Though in one of his experiments the catalytic activity and selectivity were nearly equal to the values mentioned by de Munck [6], a gradual lowering of the activity to 58% of the initial value was observed in a period of 120 hours, after which a stable production rate was observed. Notwithstanding the low partial 4-hydroxybutyraldehyde pressure of 0.9 kPa in his experiments, an increase of the degree of pore filling from 0.14 to 0.48 was noticed and this has to be attributed to the accumulation of the hemiacetal of 4-hydroxybutyraldehyde into the pores. In our opinion a second cause might be the accumulation of the mixed allyl alcohol/4-hydroxybutyraldehyde hemiacetal.
5.2. Gas-phase Hydroformylation of t-Butyl Allyl Ether

The problems arising from the presence of a reactive hydroxyl group, as sketched in the introduction, made us decide to start experiments with a compound in which this group is protected by reaction with iso-butene:

\[
H_2C=\text{CH}-\text{CH}_2\text{OH} + \frac{\text{H}}{\cdot} \overset{\text{CH}}{\text{C}=\text{CH}_2 \cdot \text{O}-\text{C} (\text{CH}_3)_3}{\text{CH}_3} \rightarrow H_2C=\text{CHCH}_2\cdot\text{O}-\text{C} (\text{CH}_3)_3
\]

After hydroformylation of this tertiary allyl ether, and reduction of the formed aldehyde function, the iso-butene can be eliminated by hydrolysis, catalyzed by an acid, resulting in the desired 1,4-butanediol (see Figure 2a). Because ethers in general are relatively inert to most reagents a tertiary butyl ether has been chosen, such a compound having a less strong ether bond.

\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_3\text{C}=\text{C}-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2+\text{CO}+\text{H}_2 \\
\text{CH}_3 & \quad \overset{\text{H}}{\text{C}=\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-C \quad \overset{\text{H}}{\text{C}=\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-C} \\
\text{H}_2 \text{ (Raney-Ni)} & \quad \text{H}_2 \text{ (Raney-Ni)} \\
\text{HO-} (\text{CH}_2)_4 \text{-OH} & \quad \overset{\text{acid}}{\text{acid}} \quad \text{HO-} (\text{CH}_2)_4 \text{-OH} \\
& \quad \overset{\text{hydrolysis}}{\text{hydrolysis}} \\
+ \text{iso-butene} & \quad \overset{\text{hydrolysis}}{\text{hydrolysis}} \\
\end{align*}
\]

Fig. 2a.

5.2.1. Synthesis of t-butyl allyl ether

The synthesis was carried out according to ref. [9]. 400 ml. allyl alcohol and 40 g dry Amberlyst 15 resin were placed in a 1000-ml capacity glass flask agitated by means of a magnetic stirrer. ("Amberlyst" is a Registered Trade Mark for a high-surface-area resin with acidic surface groups). A sketch of the experimental set-up is presented in Figure 3.

Fig. 3. A sketch of the experimental set-up for the synthesis of t-butyl allyl ether.

While stirring, a certain amount of iso-butene was introduced into the flask up to the point where the manometer mounted on the flask indicates two Atm. Dosing of iso-butene was then continued, keeping the pressure constant at two Atm. An exothermal reaction took place, as follows from the increase of temperature. Also an increase of the volume of the liquid by a factor of two was observed. This is due to the density of the
ether being much lower than the density of allyl alcohol, but also as a result of dissolution of iso-butene in the reaction mixture.

The reaction was completed after approximately 5 hours, when no more iso-butene was taken up. After releasing the pressure the product was decanted from the resin and distilled in order to remove dissolved iso-butene and unreacted allyl alcohol. After drying over anhydrous sodium carbonate the product was analyzed. The NMR spectrum confirmed that t-butyl allyl ether had been formed. A Karl Fischer titration showed that, notwithstanding the drying operation, still 0.17 mass percent water was present. From gas chromatographic analysis it was found that minute amounts of allyl alcohol and iso-butene were still present; taking this into account the purity of the product was calculated to be about 97%.

The reaction can be represented as follows:

\[ \text{H}_3\text{C}^-\text{C}^-\text{CH}_2 + \text{H}^+ \text{ (from Amberlyst)} \rightarrow \text{H}_3\text{C}^-\text{C}^-\text{CH}_3 \]

\[ (\text{CH}_3)_3\text{C}^+ \text{O}^-\text{CH}_2\text{CH}^-\text{CH}_2 + \text{H}^+ \rightarrow (\text{CH}_3)_3\text{C}^-\text{O}^-\text{CH}_2\text{CH}^-\text{CH}_2 \]

The second reaction step being reversible, the ether is very sensitive to acids; contact with acids results in decomposition into iso-butene and allyl alcohol. Furthermore, the ether should be handled with care as a consequence of its high volatility combined with poisonousness.

5.2.2. Preparation of the SLP rhodium catalyst

The SLP rhodium catalyst used for the hydroformylation of t-butyl allyl ether had the following composition:
- Rhodium complex: 0.05 g RhH(CO)(PPh₃)₃ (one molar part).
- Phosphine ligand: 0.232 g 1,4-bis(diphenylphosphino)butane (10 molar parts).
- Solvent ligand: 1.33 g tri(p-tolyl)phosphine (80 molar parts).
- Support material: 10 g silica 000-3E.

The 1,4-bis(diphenylphosphino)butane being present in excess, an exchange reaction will occur with the PPh₃ ligands of the rhodium complex. The choice of this bidentate ligand is based on our wish to make the catalyst more stable, especially at higher temperatures. After exchange, the phosphorus atoms are cis-coordinated around the rhodium centre. Hence, from a sterical point of view, it is to be expected that during hydroformylation more of the iso-aldehyde will be formed than when working with a PPh₃-liganded rhodium complex. This is a disadvantage when finally 1,4-butanediol has to be produced via d-aldehyde.

Tri(p-tolyl)phosphine has been chosen as a solvent-ligand instead of triphenylphosphine. From research carried out by Gerritsen et al. [10] it follows that this ligand is more suitable for hydroformylation at higher temperatures than triphenylphosphine, as a consequence of its lower vapour pressure.

A commercial type of silica, silica 000-3E, from Akzo, The Netherlands, was chosen as the support. Its specifications were as follows: \( S(\text{BET}) = 203 \text{ m}^2\cdot\text{g}^{-1} \), pore volume \( V_p = 0.85 \text{ cm}^3\cdot\text{g}^{-1} \), max. pore radius = 5.7 nm, and particle size in between 0.7 and 0.84 mm.

From experiments carried out by de Munck et al. [6] it is known that this type of silica has a very low activity for allyl alcohol isomerization to propionaldehyde under hydroformylation conditions.
Preparation of the catalyst was carried out in an apparatus shown in Figure 4, according to a procedure first published by Gerritsen et al. [11], the so-called dry impregnation method.

Fig. 4. Catalyst preparation apparatus. A = vessel containing the solution of the rhodium complex and the phosphine ligands in benzene. B = support holder. C = magnetic stirrer. D = oil bath.

All preparation steps to be described below were performed under flowing nitrogen as a shelter gas in order to prevent the oxidation by air of the rhodium complex to phosphine oxides and rhodium oxide and the phosphines to phosphine oxides.

The mixture of the rhodium complex and the phosphines indicated above, was dissolved in a small amount of benzene at 70°C. After drying in vacuo at 150°C for 3 hrs., a 10 g portion of the support was placed in vessel B. Next, the solution in vessel A was added dropwise to the magnetically stirred support at 70°C and the total volume of solution was taken equal to the total pore volume. The impregnated support still present in support holder B was dried at room temperature for 3 hrs. and finally stored in a vacuum desiccator. After total evaporation of the benzene the degree of pore filling was found to be about 10%.

5.2.3. Description of the hydroformylation equipment

The gas-phase hydroformylation of t-butyl allyl ether was studied in a continuous-flow apparatus schematically represented in Figure 5.

Fig. 5. Scheme of the continuous-flow apparatus. PC = pressure controller. PI = pressure indicator. FI = flow indicator. FC = flow controller. A = mixing chamber. B = evaporation vessel filled with t-butyl allyl ether. C = Pyrex glass tubular reactor, filled with 1 g of catalyst. D = gas chromatographic analysis section. E = back-pressure regulator. F = condensation vessel. G = soap film meter.
The apparatus is suited for total pressures up to 0.6 MPa and temperatures up to 200°C. Hydrogen, helium and carbon monoxide were purified by passing them over BASF catalyst R3-11, zeolite type 3A and sodium hydroxide on asbestos ("Ascarite"). The gases were metered by means of Brooks PFD 112 mass flow controllers and mixed in mixing chamber A before passing evaporator B. A schematic drawing of evaporator B is presented in Figure 6.

![Fig. 6. t-Butyl allyl ether evaporator B, constructed from Pyrex glass. A = thermostatted jacket. B = funnel for ether supply. C = inlet tube for carbon monoxide/hydrogen/helium mixture. D = sight glass. E = outlet tube for the carbon monoxide/hydrogen/He-gas enriched with ether. F = sprinkler.]

By means of the thermostatted jacket the ether temperature was kept constant at 42°C. After having passed the evaporator the gas mixture was led to the tubular reactor C (Figure 5). The reactor was placed in an air-fluidized bed oven permitting isothermal operation to within 0.5°C by applying a Eurotherm PID temperature controller.

The reaction products were periodically and automatically sampled by means of a Carle sampling valve and analyzed by means of a Packard gas chromatograph, type 429 FID, with programmable temperature control. The products were separated on a polar column packed with 10 w.% diethylene glycol succinate on Chromosorb W. The column was continuously flushed with helium at a flow rate of 30 cm³ (STP). min⁻¹.

5.2.4. Synthesis of 4-t-butoxybutyaldehyde (TBBA) and of 3-t-butoxy-2-methylpropionaldehyde (TBMPA)

In order to determine the gas chromatographic retention times of the products to be expected from heterogeneous hydroformylation of allyl t-butyl ether it was necessary to synthesize these compounds, as they were commercially not available.

A mixture of 10 g of allyl t-butyl ether, 0.5 g triphenylphosphine and 50 mg of RhH(CO)(PPh₃)₃ was prepared. The ether was hydroformylated homogeneously by injection of a CO/H₂ gas mixture at 40°C and one atm. pressure. After 48 hrs. the degree of conversion of the ether was 100%. The two aldehydes formed were separated by distillation under reduced pressure in a so-called "spinning band" apparatus. In accordance with ref. [9] the boiling point of TBBA was found to be 170.5°C at a pressure of 760 mm Hg, whereas the boiling point of TBMPA amounted to 152.3°C at the same pressure. NMR analysis of TBBA was in accordance with the structure: (CH₃)₃C-O-CH₂CH₂CHO. The purity of TBMPA was high enough to arrive at an unambiguous NMR spectrum.
5.2.5. Heterogeneous hydroformylation of allyl t-butyl ether over the SLP rhodium catalyst

After calibration of the mass flow meters, both the CO and the H₂ stream were adjusted at 15.87 cm³(STP) per minute. The temperature of the ether evaporator (see Figure 6) was adjusted at 42°C. Under these conditions the CO/H₂ gas mixture, after being pressurized to 1.4 Atm., is enriched with ether vapour. This brings the ether flow to 3.2 cm³(STP) per minute. From Figure 7 it can be seen that the ether flow as a function of the gas flow through the ether showed a relatively high fluctuation around the line representing the (expected) linear relationship. This introduces an unwanted uncertainty in the absolute values of the ether conversions to be reported below.

![Graph showing ether flow as a function of gas flow through the ether](image)

Fig. 7. Calibration of the t-butyl allyl ether flow as a function of the gas flow through the evaporator. Total pressure 1.4 Atm. Temperature of the ether: 42°C.

After a short running-in period, characterized by a small increase of the conversion followed by a small decrease, the t-butyl allyl ether conversion was measured at 100, 110, 120 and 130°C. It is important to note that the selectivity to TBBA plus TEMPA was very high. This is illustrated by the gas chromatogram in Figure 8.

![Gas chromatogram of product stream](image)

Figure 8. Gas chromatographic analysis of the product stream during hydroformylation of t-butyl allyl ether over the rhodium SLP catalyst at 100°C. 1 = iso-butene. 2 = allyl alcohol. 3 = t-butyl allyl ether. 4 = TEMPA. 5 = TBBA. 6 = heavy products.

Peaks number 1 and 2 in the chromatogram, allyl alcohol and iso-butene, are caused by the presence of these compounds as an impurity in the t-butyl allyl ether. Peaks 4 and 5 represent the products TEMPA and TBBA, respectively, and peak 6 points to a very small amount of byproducts, probably aldol condensation products. It follows from Figure 8 that a (TBBA + TEMPA)-selectivity of about 93% was arrived at. Conversions and normal/iso ratios are given in Table 1.

![Table showing conversions and normal/iso ratios](image)
Table 1. t-Butyl allyl ether hydroformylation over the rhodium SLP catalyst. Total pressure 1.4 Atm. CO/H₂ ratio: 1. CO/ether ratio: about 5.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>10³/T (K⁻¹)</th>
<th>Total conversion per pass (%)</th>
<th>Selectivity to (TBBA + TBMPA) (%)</th>
<th>normal to iso ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.68</td>
<td>7.71</td>
<td>93</td>
<td>13.02</td>
</tr>
<tr>
<td>110</td>
<td>2.61</td>
<td>8.99</td>
<td>93</td>
<td>10.66</td>
</tr>
<tr>
<td>120</td>
<td>2.54</td>
<td>11.11</td>
<td>93</td>
<td>5.46</td>
</tr>
<tr>
<td>130</td>
<td>2.48</td>
<td>12.75</td>
<td>93</td>
<td>4.95</td>
</tr>
</tbody>
</table>

As a consequence of the low conversions per pass the reactor operated differentially. In such a case the conversions are a direct measure of the rate of reaction, and hence:

\[ \text{conversion} = A \cdot \exp\left(\frac{-E}{RT}\right) \]

where \( A \) is the pre-exponential constant, \( E \) the apparent activation energy (in kJ.mol\(^{-1}\)), \( R \) the gas constant \((8.3146 \times 10^{-3} \text{ kJ.deg}^{-1}.\text{mol}^{-1})\) and \( T \) the absolute temperature (in degrees Kelvin).

From the Arrhenius plots the following values for the apparent activation energies have been calculated:

- rate of (TBBA + TBMPA) production: \( E(\text{app.}) = 21.6 \text{ kJ.mole}^{-1} \)
- rate of TBBA production: \( E(\text{app.}) = 18.8 \text{ kJ.mole}^{-1} \)
- rate of TBMPA production: \( E(\text{app.}) = 31.6 \text{ kJ.mole}^{-1} \)

At first sight these values are relatively low. Gerritsen et al., for instance, found for hydroformylation of propene over a rhodium SLP catalyst an apparent activation energy of 79 kJ.mole\(^{-1} \) [12]. De Munck et al., in studying the hydroformylation of allyl alcohol under about the same conditions, arrived at 40
These last authors rightly remarked that introduction of a hydroxyl group on the gamma carbon atom in propene strongly accelerates the rate of hydroformylation; also a lowering of the apparent activation energy from 79 to 40 kJ.mole\(^{-1}\) was observed.

We did not make a very profound study of the reaction orders in the \(H_2\), CO and aldehyde-ether pressures. In accordance with the results of foregoing investigators the impression was gained that the order in hydrogen pressure is about zero, in carbon monoxide pressure about 0.1 to 0.2, and in the pressure of the aldehyde-ether about 1.4. This points to the first step in the mechanism, the \(\pi\)-addition of the double bond to the rhodium centre, to be rate-determining in the presence of excess phosphine. The weak positive influence of the CO pressure on the reaction rate is connected with the partial displacement of phosphine ligands around the rhodium centre by carbon monoxide ligands, by which the catalytic activity slightly increases.

We finally remark that the productivity of our rhodium-SLP catalyst was relatively high as compared with the productivity mentioned by de Munck et al. for the case of allyl alcohol hydroformylation \[6\]. At 90\(^\circ\)C, under conditions comparable with the conditions of our experiments, these authors arrived at a productivity of 4-hydroxybutyraldehyde of 52 g per g of rhodium per hour. At 100\(^\circ\)C we found an aldehyde-ether production, starting from t-butyl allyl ether, of 217 g per g of rhodium per hour. This high productivity, in combination with the low apparent activation energy mentioned above, again points to a high reactivity of the double bond in the hydroformylation of t-butyl allyl ether.

Returning to Table 1 it is seen that a 100\(^\circ\)C a surprisingly high normal-to-iso ratio was arrived at. In section 5.2.2. we just anticipated a low normal-to-iso ratio, the bidentate bis(diphenylphosphino)butane ligand being cis-coordinated around the rhodium centre. It is, however, generally found that the longer the chain of the alkene to be hydroformylated the higher will be the normal-to-iso ratio. After all, the accommodation of an iso-alkyl group with a long carbon chain to the rhodium centre is sterically hindered. Apparently the same is true for t-butyl allyl ether, \(H_2C=CH-CH_2-O-(CH_3)\), with its relatively long chain length at the right hand side of the double bond, accompanied by the bulky, branched tertiary-butyl group.

5.3. Further Processing of TBBA and TEMPA

For the production of 1,4-butanediol, starting from TBBA, the aldehyde group has to be reduced to an alcohol group. This can easily be performed by reduction with hydrogen, preferably with Raney nickel as a catalyst. De-etherification of the t-butoxy butyl alcohol can be realized by flowing the alcohol, diluted with an excess of water, over a bed of a heterogeneous acidic catalyst, for instance Amberlyst (see section 5.2.1.). It is to be expected that this will be accompanied by dehydration and ring closure to tetrahydrofuran.

According to ref. \[6\] TEMPA can be oxidized by air at 70\(^\circ\)C to 3-t-butoxy-2-methyl-propionic acid. This acid, in turn, can be de-etherified by treatment with a solution of phosphoric acid in methanol at 80\(^\circ\)C. The product, methyl methacrylate, can be polymerized by free radical polymerization to a stiff transparent plastic known as Lucite or Plexiglas.
5.4. Conclusions

It has been shown in this chapter that the problems encountered in the hydroformylation of allyl alcohol may be circumvented efficiently by shielding of the hydroxyl group via etherification with iso-butene. Hydroformylation of the obtained t-butyl allyl ether is then possible over a rhodium-SLP catalyst. At temperatures around 100°C a high selectivity is arrived at and the normal/iso ratio in the hydroformylation product is high as well. However, the procedure is hampered by condensation of the high boiling hydroformylation products in the pores of the support, accompanied by dissolution of these products in the solvent-ligand. This problem would be solved if the reaction temperature could be increased to 160 to 170°C; soaking of the catalyst would be avoided in this way. However, until now the highest temperature at which Rh-SLP catalysts have been found to be capable of functioning has been about 140°C; above that temperature deterioration of the catalyst takes place. Moreover, it is to be expected that at such high temperatures the selectivity to TBBA and TEMPA becomes less favourable, as well as the normal/iso ratio.

It is to be recommended, therefore, to carry out the t-butyl allyl ether hydroformylation in a slurry reactor in the liquid phase at temperatures below 100°C. In order to facilitate the separation of the catalyst in that case, use can perhaps be made of a heterogeneous catalyst whose surface is covered with chemically immobilized active rhodium complexes. The synthesis and performance of such catalysts will be described in the next chapter.

References Chapter 5

6. The Synthesis and Performance of a Chemically Immobilized Rhodium Hydroformylation Catalyst

6.1. Introduction

Why Chemical Immobilization?

At Delft University of Technology the attention has been focussed mainly on hydroformylation by means of SLP catalysts. The advantages of this type of catalysts are:
- A high selectivity to the linear aldehyde is obtained.
- A stable performance up to 140°C is arrived at.

There are, however, some disadvantages as well, especially when converting higher alkenes to aldehydes, such as:
- Soaking of the catalyst by capillary condensation of the products in the pores of the support material cannot always be circumvented.
- Drying up of the catalyst by evaporation of the phosphine ligand asks for special measures.
- Dimerization of the catalytically active centers, which causes deactivation at higher temperatures, may occur.

Therefore we thought it to be worthwhile to study chemical immobilization as well. De Munck [1] applied this method by chemical immobilization of rhodium complexes on porous polystyrene/diphenylphosphine resins, but addition of extra triphenylphosphine was necessary to arrive at a satisfactory stability and selectivity.

An immobilized rhodium hydroformylation catalyst should ideally meet the following requirements:
1) There should be no need for addition of extra free triphenylphosphine, otherwise drying up remains a problem as is the case with SLP catalysts.
2) The dimerization reaction should be suppressed to a great extent.

Requirement 1

From our experiences with bidentate ligands, as discussed in Chapter 4, we arrived at the conclusion that the bond between the rhodium center and the phosphorous atoms is much stronger than the monodentate phosphine-rhodium bond. The use of bidentate ligands might exclude the need for the use of extra triphenylphosphine. However, the SLP systems operate with a high P:Rh ratio (100, for instance). It will be clear that a P:Rh ratio of only 2, as will be present in an immobilized bidentate system, will probably be too low to maintain a good stability.

Therefore we introduced an additional phosphine group, meant for intramolecular stabilization:

![Diagram of immobilized rhodium hydroformylation catalyst]

This third phosphine ligand will replace one of the other phosphine groups when it dissociates. From a study of T.E. Nappier et al. [2] it follows that, for sterical reasons, it will be impossible to have the three phosphines around the rhodium center at the same time.
Requirement 2
In order to prevent the active rhodium centers to interact, the following two conditions are imperative:
- The surface coverage of the proposed tridentate phosphine complex should be low.
- The support material should possess large wide pores and a stiff backbone structure.

The distance between the rhodium complexes will then be too large for any interaction to take place. Therefore, we selected a porous low loaded silica, type S 980 A 2.3, from Shell, which meets these requirements.

6.2. The Synthesis of the Chemically Immobilized Rhodium Catalyst

6.2.1. Synthesis route 1

At first our attention was focussed on the following system:

The following synthesis scheme was tried:

Fig. 2.

The compound is an immobilized form of the well-known bis(2-diphenylphosphinoethyl)phenylphosphine (triphos). The synthesis of this compound has been known for almost 20 years [3] and the compound is commercially available, but it is not possible to introduce a para-substituted group selectively, in order to couple it to the silica surface. Therefore, the compound...
was synthesized with a bromine atom at the para position on the phenyl ring bound to the central phosphorus atom (III).

The first step is the synthesis of 4-bromophenyl-dichlorophosphine(I) from bromobenzene and phosphorus-trichloride, catalyzed by aluminiumtrichloride. This is a classical example of a Friedel-Crafts acylation. The ortho-para directing activity of the bromine atom, combined with the bulky trichlorophosphine and bromine groups, results in the almost exclusive formation of the para compound.

One of the two possibilities to synthesize compound III is the conversion of I into 4-bromophenylphosphine (II), followed by the addition of two equivalents of vinyldiphenylphosphine. However, compound II is extremely difficult to handle (it is pyrophoric and very toxic) and the yield of this reduction reaction is very low. Therefore we decided to follow the route A-D-E-F (see Figure 3).

First we convert I into 4-bromophenyldibutylphosphite (IV) by means of an alcoholysis reaction [5]. This is necessary because I gives very poor results in the reaction with vinylmagnesiumbromide. IV is converted into 4-bromophenyldivinylphosphine (V) by means of a Grignard reaction. Compound IV gives a much better yield in this reaction than I.

The second step is a nucleophilic addition reaction in which potassium tertiary butoxide functions as a catalyst. The reaction mechanism is shown in Figure 4.

A possible side reaction, the nucleophilic substitution of the diphenylphosphide anion on the phenylring carrying the bromo atom, does not occur to a great extent, probably because of the very low concentration of this ion.

Fig. 4.

The immobilization of III
There are a number of methods at our disposal to immobilize III on silica:

1) The reaction of the Grignard - or lithium compound (VI and VIA, respectively) with a chlorinated silica. This route is not very attractive because it cannot be controlled whether the compounds VI or VIA are formed, so the possibility exists that the compound is coupled in a wrong way or not at all.

2) The reaction of VI or VIA with an excess of dichlorodimethylsilane to yield bis(2-diphenylphosphinoethyl)-(4-chlorodimethylsilylphenyl)phosphine (VII). The structure of
VII can be cleared up applying, for example, NMR spectroscopy and the coupling of a monochlorosilane compound to the silanol groups of the silica is a very common reaction.

The formation of the Grignard compound VI, however, proved to be impossible. After addition of a solution of III in THF to magnesium no reaction occurred. After three days boiling in THF the magnesium had reacted and a green colour, characteristic of a Grignard compound, emerged. The colour disappeared when dichlorodimethylsilane had been added. The reaction product was a white oily liquid, only soluble in THF. However, the $^1$H NMR spectrum showed a much too low number of aromatic protons, so we concluded that because of the excessive boiling the magnesium had broken one or more of the phosphorus-phenyl bonds, analogous to the way alkali metals do.

Therefore we tried a lithiation reaction using tertiary butyllithium. The reaction of the lithiated compound with dichlorodimethylsilane, unfortunately, did not give the desired product.

Conclusions concerning synthesis route 1
It is possible to synthesize bis(2-diphenylphosphinoethyl)-4-bromophenylphosphine in 4 steps. The shorter route via 4-bromophenylphosphine is not attractive for practical reasons. Attempts to immobilize the compound were unsuccessful. The formation of the Grignard compound as well as the lithiation proved to be impossible. The reasons for this failure are not clear.

Experimental
All experiments were carried out under nitrogen. The solvents were dried over zeolites, and ether and THF were distilled over lithiumaluminiumhydride prior to use. $^1$H NMR was used to verify the structures of the compounds.

4-bromophenyldichlorophosphine (I)
In an all-glass apparatus consisting of a 500 ml three-necked flask equipped with a thermometer, a condenser and a dropping funnel, are placed 209 grams (1.54 moles) of phosphorus trichloride (distilled prior to use), 78 grams (0.5 moles) of bromobenzene and 70 grams (0.52 moles) of aluminiumtrichloride. The mixture was refluxed during 4 hours and pyridine (42 grams, 0.52 moles) was slowly added to the reaction mixture. The mixture separated into two layers. The top layer contained the molten pyridine-aluminiumchloride complex. The layers were separated and the bottom layer was distilled under reduced pressure, using a 15 cm Vigreux column.

Boiling point: 90-110°C; p: 0.3-1.0 mm Hg.
Yield: 32 grams (25%).

4-bromophenylphosphine (II) [7]
In an all-glass apparatus consisting of a 100 ml three-necked flask equipped with a thermometer, a condenser and a dropping funnel, a suspension of 810 mg lithiumaluminiumhydride in diethyl ether was slowly added. The reaction mixture was then refluxed for 1 hour. Then, under cooling, 5 ml of water was slowly added. Attempts to filtrate the hydrolyzed mixture, however, were unsuccessful. The filter was clogged and probably that was the reason why we were not able to obtain pure II.

4-bromido-n-butylphosphite (IV) [8]
A solution of 47.5 grams (0.18 moles) of I and 47.9 grams (0.4 moles) N,N dimethylaniline in 100 ml diethyl ether were placed in a three-necked flask equipped with a thermometer, a dropping funnel and a condenser. A solution of 28.6 grams (0.3 moles) n-butanol in 100 ml of diethyl ether was slowly added at a temperature of -30°C. After that, the mixture was refluxed for 1 hour. The dimethylaniline hydrochloride formed was separated from the solution by filtration and, after removal of the solvent, the
residue was distilled under reduced pressure, using a 15 cm Vigreux column.

Boiling point: 133-136°C; p: 0.3-0.4 mm Hg

Yield: 66%.

The $^1$H NMR spectrum was in accordance with the expected structure.

4-bromophenyldivinylphosphine (V) [3]

In a 1 litre three-necked flask, equipped with a condenser, a thermometer and a dropping funnel, a solution of 40.7 grams (0.12 moles) in 150 ml toluene was placed. 400 ml of a one molar solution of vinylmagnesium bromide in THF was slowly added. No increase of temperature was detected. The solution was refluxed for 4 days. After that, the mixture was hydrolyzed with a 10% aqueous solution of ammonium chloride. The water layer was washed three times with diethyl ether and once with hot toluene. The combined organic fractions were dried on anhydrous sodium sulphate. After filtration and evaporation of the solvents the residue was distilled under reduced pressure, using a 15 cm Vigreux column.

Boiling point: 115-125°C; p: 1.6-2.0 mm Hg.

Yield: about 15%.

The $^1$H NMR spectrum was in accordance with the desired structure.

Bis(2-diphenylphosphinoethyl)-4-bromophenylphosphine (III) [3]

In a 100 ml flask, containing a condenser, are placed 4.52 grams (0.019 moles) of V, 6.98 grams (0.038 moles) of diphenylphosphine, and a small amount of potassium tertiary butoxide in 30 ml of benzene (or THF). This mixture was refluxed for 24 hours. After evaporation of the solvent, the residue was recrystallized from a mixture of benzene and methanol. The product was a white solid with a low melting point (below room temperature).

Yield: 8.63 grams (75%)

Elemental analysis.

Theoretically:  

C: 66.6  

H: 5.2

Found:  

C: 65.1  

H: 5.2

The $^1$H NMR spectrum showed a slightly impure product, but did leave little doubt that the compound was the desired one.

6.2.2. Synthesis route 2

The failure of synthesis route 1 made us look for other possibilities. This led to the successful synthesis scheme 2:

\[ \text{PCl}_3 + 2 \text{HN(Et)}_2 \rightarrow \text{Et}_2\text{N-PCl}_2 \]  

(A)

\[ 2 \text{H}_2\text{C=CHHgBr} \rightarrow 2 \text{MgBrCl} \]  

(B)

\[ \text{LiAlH}_4 \rightarrow \text{H-P(CH}_2\text{CH}_2\text{PPh}_2)_2 \]  

(C)

\[ \text{EtOH} \rightarrow \text{EtN-PCCH}_2\text{CH}_2\text{PPh}_2 \]  

(D)

\[ \text{U.V} \rightarrow \text{H-P(CH}_2\text{CH}_2\text{PPh}_2)_2 \]  

(E)

Fig. 5.
The final product has the following advantages over the initial system:

1) The bond between the silica and the ligand is aliphatic instead of aromatic, which makes the catalyst resistant to the following side reaction in hydroformylation:

\[
\begin{align*}
\text{L}_n\text{-Rh-PPh}_3 & \rightarrow \text{L}_n\text{-Rh-Ph} \text{PPh}_2 \\
\text{Ph} & \rightarrow \text{L}_n\text{-Rh-CH}_2\text{CH}_2\text{R} \text{PPh}_2 \rightarrow \text{L}_n\text{-Rh-Ph-CH}_2\text{CH}_2\text{R} \text{Ph}
\end{align*}
\]

Fig. 6.

In the initial compound this side reaction may lead to bond breaking between the ligand and the support material.

2) The use of ethoxysilane instead of chlorosilane makes it easier to remove the side products. Ethoxysilane produces ethanol and chlorosilane hydrochloric acid, which requires addition of pyridine. The pyridine hydrochloride formed is very difficult to remove from the functionalized silica and can have a negative effect on the performance of the catalyst.

The first step (see Figure 5) is the synthesis of diethylaminodichlorophosphine \((A)\), a selective aminolysis reaction.

The diethylamino-phosphorus bond is relatively resistant to Grignard reagents, and hence a selective Grignard reaction to diethylaminodivinylphosphine \((B)\) is possible. Two synthesis receipts have been investigated (see below).

The next step is again a nucleophilic addition reaction as described earlier when discussing synthesis scheme 1, but this time sodium hydride is used as a catalyst. This results in the formation of diethylaminobis(2-diphenylphosphinoethyl)phosphine \((C)\).

The reduction of compound \(C\) to bis(2-diphenylphosphinoethyl)phosphine \((E)\) by means of lithiumaluminiumhydride proved to be incomplete; a very impure product was the result. Compound \(E\) is a liquid with a very high boiling point, so purification by means of either crystallization or distillation was not possible. Therefore we converted compound \(C\) to ethoxy bis(2-diphenylphosphinoethyl)phosphine \((D)\) by means of an alcoholysis reaction. Reduction of \(D\) with lithiumaluminiumhydride does give compound \(E\) in a fairly high yield and purity.

There are various methods by which organophosphorus-substituted silanes can be prepared. One of them is based on the addition of secondary phosphines, phosphine oxides or phosphine sulphides to alkenyl silanes, alkenyl alkoxysilanes, alkenyl chlorosilanes or polyalkenylpolysiloxanes, under the influence of irradiation by ultraviolet light. This reaction produces the required products in a very high yield \([14]\). The high yield and purity is necessary because the compound formed is an undistillable liquid and purification would be very difficult. In this way we synthesized (2-ethoxydimethylsilylethyl)bis(2-diphenylphosphinoethyl)phosphine \((F)\). The chemical immobilization is a standard reaction which is used very often for the preparation of well-defined chemically bonded stationary phases for HPLC \([9]\).

Chlorosilanes usually give higher surface coverages, but in our case this is not very important, because we want isolated sites, and consequently a low coverage is necessary. We aimed to realize one site per 25 nm\(^2\) (compound \(G\)).

The remaining silanol groups on the surface of the support material might be able to react (unwanted) with the rhodium complex \(HRh(CO)(PPh)_3\). Therefore we decided to perform an "endcapping" by means of addition of an excess of ethoxytrimethylsilane to produce compound \(H\). In the last step the catalyst is prepared by a ligand exchange reaction with \(HRh(CO)(PPh)_3\).
Experimental

Diethvlaminodichlorophosphine (A) [10]

In a 500 ml three-necked flask equipped with a condenser, a dropping funnel and a thermometer, was placed 110 grams (0.8 moles) of phosphorus trichloride. Under vigorous stirring 100 grams (1.4 moles) diethylamine was slowly added while the temperature was kept at -20°C by means of a dry ice/acetone bath. Afterwards 300 ml of diethyl ether was added and the mixture was stirred at room temperature. The diethylammonium chloride formed was filtered off and washed twice with 100 ml diethyl ether. The solvent was removed and the residue was distilled under reduced pressure using a 15 cm Vigreux column.

Boiling point: 73-75°C; p: 14-15 mm Hg.

B.p (lit): 73-74°C, at 13 mm Hg [10].

Yield: about 50%.

The 1H NMR spectrum shows the methyl signal as a triplet around 1.2 ppm and the CH₂ group as a sextet around 3.35 ppm, due to the coupling with the phosphorus nucleus.

The proton-decoupled 31P NMR spectrum shows a singlet at 162.4 ppm only, implying that only one phosphorus compound is present in the product.

Diethvlaminodivinvlphosphine (B) [11][12]

Two synthesis methods were applied:

1) 500 ml of a one molar solution of vinylmagnesiumbromide in THF was slowly added to a vigorously stirred solution of 0.25 moles of A in 400 ml diethyl ether cooled to -78°C. The mixture was then allowed to warm slowly to room temperature and stirred overnight. The reaction mixture was then poured into a vigorously stirred mixture of 0.55 moles of EDTA, 2.3 moles of sodium hydroxide, 750 ml of deoxygenized water, and 500 ml of diethyl ether, held at room temperature, and after the addition stirring was continued for another 5 minutes. According to the literature [11] two layers should separate. This, however, proved not to be the case. Using a considerable amount of diethyl ether some product was collected, but the yield did not exceed 5%, while the literature claimed a yield of about 50%. Therefore we abandoned this "sophisticated" receipt and returned to a more straightforward method, viz. that of Issleib and Becker [12].

2) The addition method is about the same. Instead of stirring at room temperature overnight, the solution was refluxed for one hour. This method, however, did not include a hydrolysis step. The magnesiumbromidechloride formed was filtered off and washed with diethyl ether. The solvents were removed and the residue was distilled under reduced pressure.

Boiling point: 62-65°C; p: 14-15 mm Hg.

B.p (lit): 64-65°C at 15 mm Hg [11].

Yield: about 40%.

The 1H NMR spectrum was in accordance with the expected structure.
Diethylaminobis(2-diphenylphosphinoethyl)phosphine (C) [11]
A solution of 11.8 grams (0.0636 moles) of diphenylphosphine, 5.0 grams (0.0318 moles) of B and 75 mg of sodium hydride in 100 ml of THF was boiled under reflux for five days. The reaction mixture was diluted with 100 ml of diethyl ether and then washed with three 25 ml portions of water. The ether layer was dried over anhydrous magnesium sulphate. Solvent was removed from the filtered ether solution to give a clear viscous liquid. Addition of cold ethanol produced a white solid. 
Melting point: 54-55°C; lit.: 49-51°C. Yield: about 80%.
Elemental analysis.

Theoretically: 72.6 7.2 2.6
Found: 71.7 6.8 2.2

The ¹H NMR spectrum:
CH₃ group amine function: triplet 0.8 ppm (6H)
CH₂ group amine function: multiplet 2.5-3.0 ppm (4H)
ethylene groups: multiplet 1.2-2.4 ppm (8H)
aromatic protons: multiplet 6.9-7.5 ppm (20H).

Ethoxylbis(2-diphenylphosphinoethyl)phosphine (D)
A mixture of 13.2 grams (25 mmol) C, 15 ml ethanol and 100 ml toluene was refluxed for 24 hours. After removal of the solvent the residue was treated with cold ethanol to yield a white solid (analogous to the method described in ref. 11). Melting point: 78-79°C. Yield: about 90%.
Elemental analysis.

Theoretically: 71.7 6.6
Found: 71.3 6.4.

The ¹H NMR spectrum of this (new) compound:
CH₃ group: triplet 1.0 ppm (6H)
ethylene groups: multiplet 1.3-2.4 ppm (8H)
CH₂ group: multiplet 3.2-3.8 ppm (2H)
aromatic protons: multiplet 6.8-7.6 ppm (20H).

Bis(2-diphenylphosphinoethyl)phosphine (E)
The reduction was carried out in analogy to the method described in ref. [13], except for the fact that we used THF instead of diethyl ether. At first we attempted the reduction of compound C, but it hardly reacted. Therefore we applied the same method starting from compound D:
A solution of 20 mmol (10.04 grams) of D in 40 ml of THF was slowly added to a stirred suspension of 20 mmol (0.8 grams) of lithiumaluminiumhydride in 20 ml of THF. After the addition was completed, the mixture was refluxed for 24 hours. The mixture was diluted with 50 ml of diethyl ether and then hydrolyzed by the successive addition of 2 ml of water, 2 ml of a 15% solution of sodium hydroxide in water, and finally 6 ml of water. After filtration the solvent was removed and a brownish oily liquid remained. The product was nearly pure, but some D was still present. It was removed by extraction with hot ethanol. Yield: about 65%.
In the $^1$H NMR spectrum the signals of the ethoxy group were completely vanished. A small multiplet at 4.7-5.0 ppm had emerged.

- $^1$H : 4.7-5.0 ppm (1H)
- $\text{CH}_2-\text{CH}_2$ : 1.3-2.3 ppm (8H)
- aromatic protons : 6.9-7.5 ppm (20H).

(2-ethoxydimethylsilyl)bis(2-diphenylphosphinoethyl)-phosphine (P) [14]

A mixture of 2.3 grams (5 mmol) of E and 0.6 grams (20 mmol) of vinyl(dimethylethoxysilane) was irradiated by a UV lamp for three days. After removal of the excess vinyl(dimethylethoxysilane) a bleak-yellow viscous liquid remained.

Yield: about 100%.

Fig. 9a:
The proton-decoupled $^{31}$P NMR spectrum:
Triplet at -16 ppm (the central phosphorus atom (1P))
Doublet at -13 ppm (the outer phosphorus atoms (2P))

Fig. 9b:
The $^1$H NMR spectrum shows four "clusters" of signals: the first, at 0.2-0.5 ppm is a combination of the signals of the $\text{CH}_3$-Si groups (singlet) and the $\text{Si}-\text{CH}_2$-R group (multiplet). The second, very complex signal from 1.3-2.6 ppm is a combination of the resonances of the $\text{PCH}_2-\text{CH}_2$P (multiplet), $\text{CH}_3$ (of the ethoxy function, triplet) and the $\text{CH}_2$P (multiplet) groups. The third signal is a quartet (the methylene group of the ethoxy function) at 3.7-4.1 ppm. The fourth signal at 7.2-8.0 ppm can be attributed to the aromatic protons.

The product is far from pure, but the impurities can be removed, after the coupling of the ligand to silica, by means of a Soxhlet extraction.
The coupling of compound F to silica [9]
A mixture of 100 ml toluene, 0.18 grams (impure) of compound F and 15 grams of silica was kept at 100°C for 48 hours. Occasionally the mixture was stirred. After filtration the functionalized silica (G) was extracted with benzene in a Soxhlet apparatus for a period of 48 hours. The silica was then dried in vacuo at 150°C for 24 hours. Elemental analysis showed the carbon content to be 0.01% for the pure silica and 0.483% for the functionalized silica.

The "endcapping" reaction
A mixture of 100 ml toluene, 8 grams (70 mmol) of ethoxytrimethylsilane and 10 grams of G was kept at 45°C for 72 hours. The further procedure was identical to that of the functionalization reaction. Elemental analysis of the product showed a carbon content of 3.1%.

Coupling of the rhodium complex by ligand exchange [1]
The elemental analysis showed the presence of about $1.2 \times 10^{-5}$ moles of ligand per gram H. Therefore 3 grams of H was stirred with a solution of $3.6 \times 10^{-5}$ moles of $\text{HRh(CO)(PPh}_3)_3$ and $1.08 \times 10^{-5}$ moles of $\text{PPh}_3$ in 25 ml of toluene for two hours at 65°C under a hydrogen atmosphere. Addition of $\text{PPh}_3$ is necessary to stabilize the rhodium complex in solution. The silica-supported catalyst is separated from the solution and carefully washed with 3x50 ml toluene and 2x50 ml diethyl ether, in order to remove excess rhodium complex and $\text{PPh}_3$. The filtrate, however, did not contain any rhodium complex, pointing to a total exchange. The catalyst was dried in vacuo at room temperature for 24 hours. The compound appeared to be extremely air-sensitive and therefore it was stored under nitrogen at -20°C.

Conclusions
Synthesis route 2 proved to be successful; a chemically immobilized intramolecularly stabilized hydroformylation catalyst has been synthesized in nine reaction steps. Unfortunately, the concentration of the ligands was too low for analysis by solid-phase $^{31}$P NMR, and hence we had to rely entirely on elemental analysis. Therefore we also synthesized a silica-supported catalyst with a high ligand coverage (a carbon content of 7.2% was detected). With this sample we succeeded in obtaining a $^{31}$P solid-phase NMR spectrum, which showed some impurities to be present.

*The silica was obtained from Shell, type No S 980 A 2.3.
Particle size: between 0.35 and 0.42 mm.
BET surface area: 205 m$^2$/gram.
Mean pore diameter: 16 nm.
Before use the silica was dried in vacuo at 150°C for 24 hours.
Figure 10 shows the spectrum of the **highly-covered** functionalized silica. *(It was not possible to obtain a reproducible spectrum of the catalyst itself.)

Although the impurities probably do little harm to the performance of the catalyst, it makes the interpretation of the spectrum, which, even in the absence of impurities, would be a very complex matter, almost impossible.

One particular phenomenon is worth noticing. \( \text{H}_{3}\text{Rh}(\text{CO})(\text{PPh}_3) \) as well as the functionalized silica \( H \) are relatively stable in air at room temperature, whereas our silica-supported catalyst is very sensitive to oxygen indeed. A possible explanation might be that at low temperatures the structure of the catalyst is as follows (Figure 11):

![Chemical structure](image)

Fig. 11.

According to a study by Taqui Khan and Martell [15], triphos is capable of forming this type of complexes with cobalt(I) and nickel(II) ions. It might be possible this to be the case for rhodium(I) as well. Due to the extreme ring tension a high sensitivity to all kinds of poisons is present.

At higher temperatures, however, the ring tension will become too large and dissociation of one of the phosphorus ligands will occur. As a result an active catalyst is formed. Further evidence for this will be presented in the discussion in section 6.3 of this Chapter.

6.3. The Performance of the Chemically Immobilized Silica-Supported Rhodium Catalyst

6.3.1. Experimental

The materials and apparatus used to test the performance of the catalyst have been described already in Chapter 4. Again, butene-1 was chosen as the alkene to be hydroformylated.

6.3.2. Results

First we tested the activity, selectivity and stability of the catalyst at standard conditions (total flow 150 ml/min; \( \text{CO} : \text{H}_2 : \text{butene-1} = 1 : 1 : 1 \); total pressure 1.2 MPa; reaction temperature: 363 K). The catalyst maintained a relatively stable performance for a period of about 24 hours and then deactivated very rapidly. A representative example of our experimental results is shown in Figure 12. The activity of the catalyst appeared to be relatively high (butene-1 conversion about 30 \( \text{cm}^3(\text{STP}) \cdot \text{g Rh}^{-1} \cdot \text{s}^{-1} \)) whereas a triphenylphosphine-based SLP catalyst with a pore filling of about 0.5 does not exceed an activity of about 10 \( \text{cm}^3(\text{STP}) \cdot \text{g Rh}^{-1} \cdot \text{s}^{-1} \). The selectivity for the formation of \( n \)-valeraldehyde is rather low, the normal-to-iso-ratio being about 2. An SLP catalyst (with monodentate ligands) usually produces a normal-to-iso ratio of about 10.

As found for most other rhodium-based hydroformylation catalysts, the selectivity for the formation of aldehydes was close to 100% in the temperature range from 90 to 120°C. At higher temperatures, isomerization to butene-2 did increase slightly, as well as the formation of aldol products.
Fig. 12.

Kinetics
The reaction kinetics have been studied in the temperature range from 80 to 110°C. All results could be expressed in the form of a power-rate law:

$$r = k_0 \cdot p_{H_2}^a \cdot p_{CO}^b \cdot p_{C_4}^c \cdot \exp(-E_a/RT)$$

where $r$ is the reaction rate per unit weight of rhodium and $a$, $b$ and $c$ are the orders in hydrogen pressure, carbon monoxide pressure and butene-1 pressure, respectively. $E_a$ is the apparent activation energy.

The Arrhenius plots are shown in Figure 13:

Fig. 13.

The natural logarithm of the conversion rate to $n$- and iso-valeraldehyde, as well as the total aldehyde production, are plotted against 1000/T.

The apparent activation energy is approximately 56 kJ.mol$^{-1}$. 
The reaction orders have been determined at 96°C, a temperature at which a nearly 100% selectivity to the formation of aldehydes is observed. The reaction order for each reactant was found by halving the partial pressure of that reactant and bringing the total pressure to 1.2 MPa by the addition of helium to the gas flow.

The reaction orders found were:

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>i</th>
<th>t</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>C₄⁻</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

n = linear aldehyde production
i = branched aldehyde production
t = total aldehyde production

Discussion
In short, the kinetics, as compared with that of the SLP catalyst mentioned before, may be summarized as follows (see Table 1).

The first remarkable result is the deactivation occurring suddenly after a period of about 24 hours. This can possibly be explained from the formation of aldol products which, due to their high boiling points, accumulate in the pores of the support which eventually become totally filled up. Then the reactants are no longer capable of reaching the catalytically active centers.

<table>
<thead>
<tr>
<th></th>
<th>SLP [16]</th>
<th>SiO₂⁻ supported catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eₐ (kJ/mol)</td>
<td>79</td>
<td>56</td>
</tr>
<tr>
<td>order in H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>i</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>t</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>order in CO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>i</td>
<td>1</td>
<td>0.0</td>
</tr>
<tr>
<td>t</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>order in C₄⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>i</td>
<td>1.7</td>
<td>1.0</td>
</tr>
<tr>
<td>t</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>reaction rate at 90°C in cm³ C₄⁻/g.Rh.s</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>n:i ratio</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

The activity of the catalyst is about three times as high as that of the SLP system. An explanation of this phenomenon might be the strongly deviating structure of our intramolecularly stabilized rhodium catalyst:
HRh(CO)(PPh₃)₃ is inactive in hydroformylation; dissociation of one of the triphenyllphosphine ligands is necessary in order to create a catalytically active complex. This implies that in the presence of a large excess of phosphine ligands (as is the case in SLP catalysts) only a small amount of the rhodium complexes will participate in the catalytic cycle. In our system, however, nearly all rhodium complexes are in the active form.

The selectivity of the catalyst towards the linear aldehyde is rather low, and Figure 14 shows the reason why: the catalytically active compound has the two phosphorus particles coordinated in a cis position. Therefore the vacant place where the alkene addition takes place is relatively spacious, which results in a low selectivity (hardly any sterical hindrance). In the monodentate SLP catalysts the phosphine ligands are coordinated in a trans position, which, for sterical reasons, favours production of the linear aldehyde.

The apparent activation energy is lower than found with monodentate SLP systems. For the bidentate SLP catalysts (with 1,4-bis(diphenylphosphino)butane as the solvent-ligand) the value lies between these extremes, so the larger space for the addition reaction of the alkene could be an explanation.

Finally, by far the most remarkable observation are the uncommon reaction orders. In homogeneous hydroformylation with rhodium complex catalysts a reaction order of 1 in alkene is usually found; we found the same value for our immobilized system. The SLP catalysts usually show an alkene order of about 1.4 (see Chapter 4). The explanation presented for this phenomenon is that, due to the higher alkene pressure, the solvent-ligand is diluted with the aldehydes formed, which in turn improves the solubility of the alkene. Therefore the real order (1) increases to 1.4.

When using a large excess of phosphine ligand the reaction order in hydrogen usually is close to zero. Our system is no exception to the rule, because our effective phosphine concentration is high due to the intramolecular stabilizer combined with the chelating effect.

The carbon monoxide order, however, differs appreciably from that found for other hydroformylation catalysts. Pelt, for instance [16], found an order of 0.1 in the formation of the linear aldehyde and an order of 1 in the formation of the branched aldehyde. We found an order of zero in both cases! Perhaps the space around the active site offers an explanation. In the five-ring chelating system there is little discrimination between the following intermediates:
The addition of CO, preventing the oxidative addition of hydrogen, could be equally disturbing for both the branched and the linear compound. In the monodentate systems the active site is much smaller, the phosphine ligands being in a trans position. The more bulky iso-product is considerably less affected by carbon monoxide than the linear product, due to sterical factors.

Conclusions
We were able to synthesize and test the performance of an intramolecularly stabilized chemically immobilized rhodium hydroformylation catalyst with isolated sites. The fact that, notwithstanding the isolated nature of the sites, it produces aldehydes in a relatively very good yield, makes it improbable that a bimolecular hydrogenation step is involved in the catalytic cycle, as suggested by Collman and coworkers [17].

The sudden deactivation of the catalyst after a period of about 24 hours has been explained by the accumulation of aldon products in the pores of the support material. This can be avoided by applying our catalyst at the solid/liquid interface. Further work in this direction is needed.

Gas-phase hydroformylation will probably remain restricted to the lower alkenes. Despite the fact that the maximum temperature could be raised to about 140°C (see Chapter 4) such temperature is much too low to be able to hydroformylate alkenes larger than pentene in an efficient way.

In our opinion, research in the field of chemically heterogenized homogeneous catalysis should concentrate on catalysis at the liquid-solid interface. At such interface accumulation of high-boiling byproducts is less likely than at the gas-solid interface.

References Chapter 6

SUMMARY

The industrial application of rhodium-phosphine based catalysts in the hydroformylation of the alkenes has increased dramatically during the last forty years. In order to understand the performance of the catalyst a lot of research has been carried out concerning the reaction mechanism. Chapter 2 of this thesis is a review dealing with the various theoretical aspects of hydroformylation with rhodium-based catalysts, such as the reaction mechanism, the occurrence of side reactions, deactivation of the catalyst etc.

Hydroformylation is a homogeneous catalytic process, and often a laborious separation of the products from the catalyst is necessary, in most cases attended by some loss of the (very expensive) rhodium. Immobilization of the rhodium complex on a support has the advantage of circumventing this undesirable aspect. In Chapter 3 an outline is given on the way in which immobilization of homogeneous catalysts can be accomplished. Our attention was mainly focussed on two methods of immobilization:
1) Capillary condensation of a solution of the complex in a porous support, giving rise to the so-called Supported Liquid Phase Catalysts (SLPC).
2) Chemical anchoring of an organometallic complex to an organic or inorganic support via chemically bonded ligands.

During the last 15 years the application of SLP-rhodium-triphenylphosphine catalysts in the heterogeneous gas-phase hydroformylation of various alkenes, using a continuous flow system with a fixed bed reactor, has been a major field of research in the Catalysis Department of Delft University of Technology. One of the major limitations when using these systems is the relatively low maximum operating temperature of about 115°C. When alkenes containing more than 4 C-atoms are hydroformylated, soaking of the catalyst may take place, unless a very low (and, therefore, less economic) conversion per pass is applied. The use of bidentate solvent-ligands like 1,4 bis(diphenylphosphino)butane (this thesis) increases the maximum operating temperature because the chelating effect of this ligand creates a much firmer phosphine-rhodium bond. The performance of these bidentate-based SLP catalysts in the hydroformylation of butene-1, in comparison with the "traditional" triphenylphosphine-based systems, is discussed in Chapter 4.

In Chapter 5 the hydroformylation of allyl alcohol is the central issue. This hydroformylation may be used as an alternative route for the production of the industrially attractive compound 1,4-butanediol, which is formed by the reduction of the hydroformylation product \( \gamma \)-hydroxybutyraldehyde. Due to the high boiling points of the aldehydes formed, soaking of the catalyst is a severe problem, as well as the presence of a reactive OH-group which causes the formation of undesired by-products like, for instance, hemi-acetals and acetals. These problems can be circumvented to a large extent by applying higher temperatures and shielding-off of the OH-group of allyl alcohol by means of reaction with isobutene to form tert-butyl allyl ether. After hydroformylation of the ether and reduction of the aldehyde formed, the ether bond can be broken by acid hydrolysis to form the desired product, 1,4-butanediol.

The final chapter, Chapter 6, deals with the synthesis and performance of a chemically immobilized catalyst. Use was made of a tridentate phosphine ligand, chemically bonded to silica, capable of forming an intramolecularly stabilized active rhodium compound. The kinetics of hydroformylation with this catalyst is compared with the kinetics found for the SLP systems, again using butene-1 as the alkene to be hydroformylated. A mechanistic explanation of the differences arising in the kinetics is presented.
De industriële toepassing van rhodium-fosfine katalysatoren is de laatste veertig jaar sterk toegenomen, met name voor de hydroformylering van alkenen. Teneinde de werking van deze katalysatoren beter te leren begrijpen is er veel onderzoek gedaan naar o.a. het reactiemechanisme. Hoofdstuk 2 van deze dissertatie is een "review", betrekking hebbend op de diverse theoretische aspecten van hydroformylering met deze rhodiumkatalysatoren, zoals het reactiemechanisme, het optreden van nevenreacties, de desactivering van de katalysator, etc.

Hydroformyleren is een homogeen katalytisch proces en het is meestal bewerkelijk om de katalysator van de produkten te scheiden. Dit gaat vaak gepaard met enig verlies van het zeer kostbare rhodium. Het immobiliseren van het rhodiumcomplex op een drager heeft het voordeel dat deze ongewenste stap achterwege kan blijven. In Hoofdstuk 3 worden enkele mogelijkheden besproken om een dergelijke immobilisatie tot stand te brengen. Onze aandacht ging vooral naar de volgende twee opties:

1) Kapillaircondensatie van een oplossing van het katalytisch actieve complex in een poreuze drager, hetgeen leidt tot de zogenaamde Supported Liquid Phase Katalysatoren.

2) Het chemisch verankeren van een metaalorganisch complex aan een organische of anorganische drager via chemisch gebonden liganden.

Binnen de afdeling Katalyse van de Technische Universiteit Delft is de toepassing van SLP rhodium-trifenylfosfine katalysatoren in de heterogene gasfasehydroformylering van diverse alkenen, dynamisch beproefd in een vast-bed reactor, gedurende de laatste 15 jaar een belangrijk onderzoeksterrein geweest. Een van de grootste beperkingen van deze systemen is de relatief lage maximum temperatuur die kan worden toegepast (ca. 115°C). Indien alkenen met meer dan 4 C-atomen worden gehydroformylerd kan door ophoping van de reactieprodukten in de poriën van de drager de katalysator worden uitgespoeld, tenzij een betrekkelijk lage (en, derhalve, minder economische) conversie wordt gehanteerd. Uit ons onderzoek blijkt dat het gebruik van bidentaat oplosmiddel-liganden, zoals het 1,4 bis(difenylfosfino)buteen, tot gevolg heeft dat deze maximum temperatuur wordt verhoogd omdat het chelertend effect van dit ligand een sterkere fosfine-rhodium binding oplevert. In Hoofdstuk 4 is het gedrag van deze bindentaat-SLP katalysatoren vergeleken met dat van de "traditionele" trifenylfosfine-SLP systemen. Inderdaad blijken nu hogere reactietemperaturen mogelijk te zijn.

In Hoofdstuk 5 is de hydroformylering van allylalcohol het centrale thema. Dit kan een alternatieve route opleveren voor de produktie van de industriëel aantrekkelijke verbinding 1,4-butaandiol, welke gevormd wordt door reductie van het hydroformyleringsproduct γ-hydroxybutyraldehyde. Het uitspoelen van de katalysator (hetgeen te wijten is aan de hoge kookpunten van de gevormde aldehyden) en de aanwezigheid van een reactieve OH-groep, die aanleiding geeft tot de vorming van ongeneeslijke nevenprodukten zoals semi-acetalen en acetalen, zijn grote problemen. Deze kunnen voor een belangrijk deel worden omzeild door een hogere reactietemperatuur te kiezen en door het afschermen van de OH-groep in allylalcohol door verethering met isobuteen (reactie met isobuteen levert tertiair butylallylether op). Na hydroformylering van de ether en reductie van het gevormde aldehyde can de etherbinding door zure hydrolyse verbroken worden en ontstaat het gewenste 1,4-butaandiol.

Het laatste hoofdstuk, Hoofdstuk 6, beschrijft de synthese en het katalytisch gedrag van een chemisch geimmobiliseerde rhodium katalysator. Er werd gebruik gemaakt van een tridentaat fosfineligand, chemisch gebonden aan silica. Dit ligand is in staat tot de vorming van een intramoleculair gestabiliseerd actief rhodiumcomplex. De kinetiek van de buteenhydroformylering
met deze katalysator werd vergeleken met de kinetiek gevonden bij gebruik van SLP systemen, waarbij eveneens buteen-1 als het te hydroformyleren alkeen werd toegepast. Een mechanistische verklaring voor de optredende verschillen wordt gepresenteerd.

NASCHRIFT

Aan het totstandkomen van dit proefschrift hebben vele mensen een bijdrage geleverd. Een aantal van hen wil ik hier met name noemen.
- Het personeel van de servicegroepen van het Gebouw voor Scheikunde.
- De medewerkers van de analyse-afdeling van DSM.
- De NMR-groep van Professor W.S. Veeman van de Katholieke Universiteit Nijmegen, voor de vaste stof $^{31}$P NMR metingen aan de chemisch geimmobiliseerde katalysator.
- Dr. F. van Rantwijk voor zijn kritische belangstelling en zinvolle suggesties.
- Ir. Henk Swaan voor zijn inzet tijdens zijn afstudeerperiode.
- Drs. Kees Witmans en Drs. Joost Cornelissen voor hun medewerking en bovenal voor hun prettige gestoordheid die de werksfeer zeer ten goede kwam.
- Ir. Hans van Stralen voor zijn bewonderenswaardige betrokkenheid bij het onderzoek, waaraan hij een fundamentele bijdrage heeft geleverd.
- Professor Scholten voor zijn hulpvaardigheid en geduld.
CURRICULUM VITAE


Van november 1984 tot en met oktober 1985 was ik in dienst van ZWO (later NWO), en werd ik in de gelegenheid gesteld in de werkgroep Katalyse van de vakgroep Chemische Technologie van de TU Delft dit promotieonderzoek te verrichten.

1. Algemeen wordt aangenomen dat homogene katalyse met organometalcomplexen aanleiding geeft tot produktselectiviteiten die gunstiger zijn dan in de heterogene katalyse (1). Men is er zich echter onvoldoende van bewust dat dit alleen geldt voor eenvoudige organische moleculen (met weinig koolstofatomen) in de voeding van de katalytische reactor. Voor de omzetting van bijvoorbeeld hogere alkenen en gesubstitueerde alkenen zijn de selectiviteiten vaak laag (2).

(2) Dit proefschrift, hoofdstuk 5.

2. Toekomstige research op het gebied van katalyse met geheterogeniseerde organometalcomplexen zal zich vooral moeten richten op reacties aan de fasegrens vast-vloeibaar.

3. In de katalytische Wacker-oxidatie van alkenen tot aldehyden of ketonen speelt de reoxidatie van Pd(0) met behulp van een redoxkoppel en zuurstof een belangrijke rol.

In de literatuur wordt vaak ten onrechte geen melding gemaakt van het feit dat de concentratie van de redoxcomponenten, bijvoorbeeld van Cu(I) en Cu(II), onder bepaalde omstandigheden invloed kan hebben op de kinetiek van de reaktie (1).


CURRICULUM VITAE


Van november 1984 tot en met oktober 1988 was ik in dienst van ZWO (later NWO), en werd ik in de gelegenheid gesteld in de werkgroep Katalyse van de vakgroep Chemische Technologie van de TU Delft dit promotieonderzoek te verrichten.

5. Uit het feit dat rhodium-SLP katalysatoren met bidentaatfosfineliganden een lagere normaalso-verhouding van aldehyden opleveren dan analoge katalysatoren met monodentaatliganden, kan worden gekonkludeerd dat het aktieve complex slechts twee fosfineliganden bevat en niet drie (1).


6. In de opleidingen tot wetenschappelijk onderzoeker of tot technoloog moet meer aandacht worden geschonken aan wetenschaps-historische en wetenschapsfilosofische aspecten.

7. Het onder goed medisch toezicht verstrekken van gratis heroïne aan verslaafden zal de aanwas van nieuwe verslaafden doen teruglopen en het sociaal isolement van deze mensen verminderen.

8. Het positief diskrimineren van minderheden door overheid en bedrijfsleven zal de negatieve diskriminatie onder de bevolking doen toenemen en dus helaas zijn doel voorbij schieten.

9. Het is triest te moeten konstateren dat het erg gemakkelijk is negatieve stellingen te formuleren over de staat van ons huidig hoger onderwijs.

10. Daar het aanvaarden of verwerpen van ideologieën een individuele zaak behoort te zijn, moet er naast de scheiding van kerk en staat ook een scheiding doorgevoerd worden tussen staat en wetenschap. De wetenschap is immers een van de meest agressieve en dogmatische religieuze instellingen van dit moment. Zo'n scheiding zou wel eens het enige middel kunnen zijn dat ons overblijft om menselijker te worden dan tot nu toe het geval was.

Stellingen bij het proefschrift van P. Groen, 7-12-1989,
TU Delft.