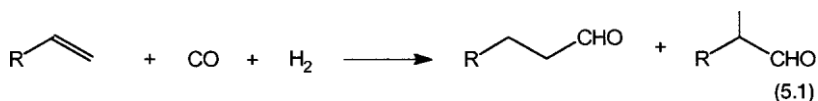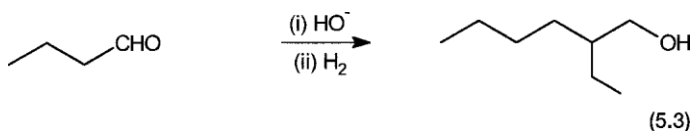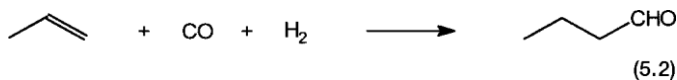# Hydroformylation

Hydroformylation, also known as oxo synthesis or oxo process, is an industrial process for the production of aldehydes from alkenes. This chemical reaction entails the net addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. This process has undergone continuous growth since its invention: Production capacity reached 6.6×10^6 tons in 1995. It is important because aldehydes are easily converted into many secondary products. For example, the resulting aldehydes are hydrogenated to alcohols that are converted to detergents. Hydroformylation is also used in speciality chemicals, relevant to the organic synthesis of fragrances and drugs. The development of hydroformylation is one of the premier achievements of 20th-century industrial chemistry.

The process entails treatment of an alkene typically with high pressures (between 10 and 100 atmospheres) of carbon monoxide and hydrogen at temperatures between 40 and 200 °C.[3] Transition metal catalysts are required. Invariably, the catalyst dissolves in the reaction medium, i.e. hydroformylation is an example of homogeneous catalysis.

Otto Roelen at Ruhrchemie AG discovered the hydroformylation or oxo reac- tion in 1938. As shown by reaction 5.1, the basic reaction is the addition of a hydrogen atom and a formyl group to the double bond of an alkene. The reaction works efficiently, mainly with terminal alkenes. With an optimal choice of ligands and process conditions, very high selectivity (>95%) for the desired isomer of the aldehyde could be achieved.

(5.1)

The aldehydes commercially produced this way are many. One of the most important is *n*-butyraldehyde. Isononyl aldehyde is also an important inter- mediate. As shown by reactions 5.2 and 5.3, propylene is hydroformylated to *n*-butyraldehyde which is then converted by aldol condensation and hydroge– nation to 2-ethyl hexanol.

$$\text{CH}_2=\text{CHCH}_3 \quad + \quad CO \quad + \quad H_2 \quad \longrightarrow \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$$

(5.2)

$$\text{propyl-CHO} \quad \xrightarrow[\text{(ii) } H_2]{\text{(i) } HO^-} \quad \text{2-ethylhexanol (OH)}$$

(5.3)

THE RHODIUM PROCESS

The high selectivity and mild conditions make the rhodium process more at- tractive than the cobalt one for the manufacture of *n*-butyraldehyde. The high cost of rhodium makes near-complete catalyst recovery a must for the com- mercial viability of the process. As we shall see, this has been achieved by developing an elegant separation method based on water-soluble phosphines.

The Catalytic Cycle

The catalytic cycle and the catalytic intermediates for the rhodium-plus- phosphine-based process are shown in Fig. 5.1. It is important to note that hydroformylation with rhodium can also be effected in the absence of phos- phine. In such a situation CO acts as the main ligand (i.e., in Fig. 5.1, L = CO). The mechanistic implications of this is discussed later (Section 5.2.4).

The following points are to be noted. First of all, complexes 5.1, 5.3, 5.5, and 5.7 are 18-electron complexes, while the rest are 16-electron ones. Second, conversions of 5.3 to 5.4 and 5.5 to 5.6 are the two insertion steps. The selec- tivity towards *n*-butyraldehyde is determined in the conversion of 5.3 to 5.4. It is possible that a rhodium– isopropyl rather than rhodium– propyl complex is formed. In such a situation on completion of the catalytic cycle isobutyral- dehyde will be the product. In practice both the *n*-propyl and the *i*-propyl complexes of rhodium are formed, and a mixture of *n*-butyraldehyde and *i*- butyraldehyde is obtained. This aspect is discussed in greater detail in the following section. Third, the catalyst precursor 5.1 undergoes ligand dissocia-

TABLE 5.1 Process Parameters for Several Hydroformylation Processes

| Process parameters	Cobalt	Cobalt + phosphine	Rhodium + phosphine
Temperature (°C)	140–180	160–200	90–110
Pressure (atm)	200–300	50–100	10–20
Alkane formation	Low	Considerable	Low
Main product	Aldehyde	Alcohol	Aldehyde
Selectivity (%) to *n*-butyraldehyde	75–80	85–90	92–95
Isolation of catalyst	Difficult; $HCo(CO)_4$ is volatile	Less difficult	Less difficult; water-soluble phosphine a major advancement
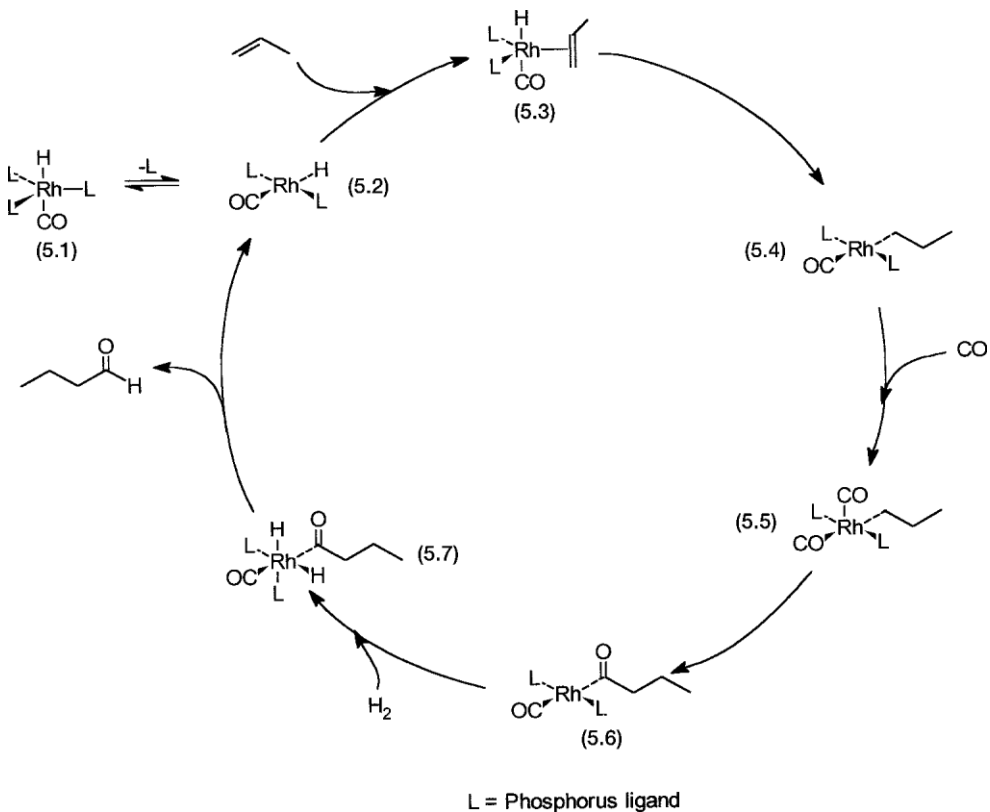
Figure 5.1 The basic catalytic cycle for the hydroformylation of propylene with Rh/ PPh3-based catalyst. In step 5.3 to 5.4 anti-Markovnikov addition is assumed.

tion to generate 5.2, a coordinatively unsaturated species. Finally, conversion of 5.6 to 5.7 is an oxidative addition reaction, while the conversion of 5.7 to
5.2 occurs by reductive elimination.

Both 2-ethyl hexanol and isononyl alcohol are used, in combination with phthalic anhydride, as plasticizers for polyvinyl chloride resin. Hydroformyl- ation is also used for the manufacture of long-chain fatty alcohols. The linear alcohols are used in detergents and are more biodegradable than the branched ones. The Shell higher olefin process (SHOP) uses ethylene that is oligomeri- zed, isomerized, methathesized, and then hydroformylated to give long-chain fatty alcohols (see Section 7.4.1).

Three commercial homogeneous catalytic processes for the hydroformyla- tion reaction deserve a comparative study. Two of these involve the use of cobalt complexes as catalysts. In the old process a cobalt salt was used. In the modified current version, a cobalt salt plus a tertiary phosphine are used as the catalyst precursors. The third process uses a rhodium salt with a tertiary phos- phine as the catalyst precursor. Ruhrchemie/Rhone-Poulenc, Mitsubishi-Kasei, Union Carbide, and Celanese use the rhodium-based hydroformylation process. The phosphine-modified cobalt-based system was developed by Shell specifi- cally for linear alcohol synthesis (see Section 7.4.1). The old unmodified cobalt process is of interest mainly for comparison. Some of the process parameters are compared in Table 5.1.

Catalyst and Ligand Degradation

The lifetime of the rhodium precatalyst depends on the rate at which the metal complex $HRh(CO)(TPPTS)_3$ and the excess ligand TPPTS undergo decompo- sition. The catalyst lifetime is considerably increased by occasional addition of extra ligand. In general an increase in the reaction temperature and/or CO pressure results in a decrease in the catalyst lifetime.

With 5.1 as the precatalyst, the degradation products in the propylene hy- droformylation reaction are diphenylpropyl phosphine ($Ph_2PC_3H_7$), benzene, and less soluble rhodium complexes. These complexes are tentatively formu- lated as phosphido clusters. Formation of all the products could be rationalized by the hypothetical catalytic cycle shown in Fig. 5.6.
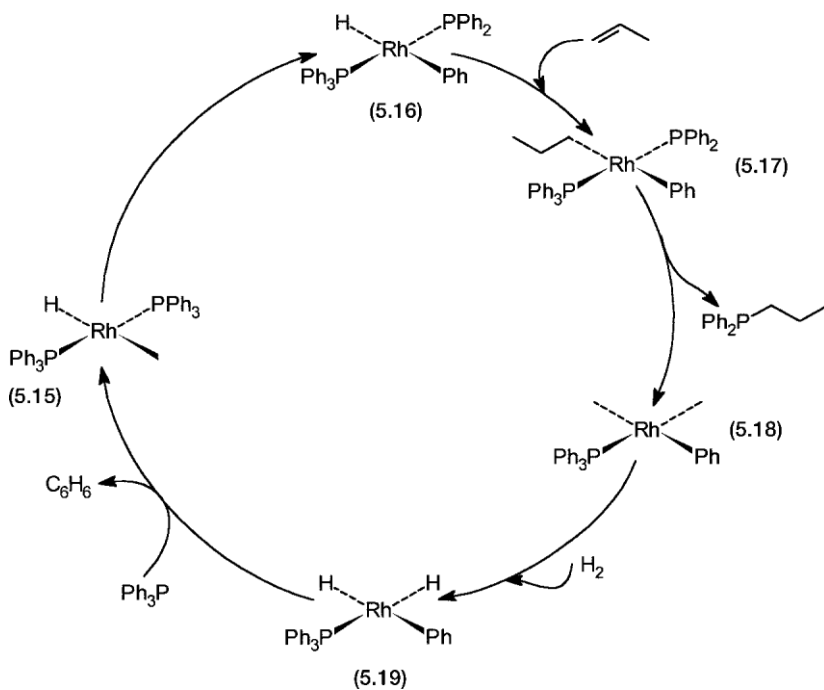
Figure 5.6 Catalytic cycle for the degradation of PPh3. Only four coordination sites around Rh are shown. In some of the hypothetical intermediates Rh may be five or six coordinated.

The basic assumption is the intramolecular oxidative addition of PPh$_3$ in the coordinatively unsaturated intermediate 5.15 to give the phosphido complex 5.16. This reacts with propylene to give 5.17, which undergoes reductive elimination to give Ph$_2$PC$_3$H$_7$ and the phenyl complex 5.18. The latter undergoes oxidative addition of dihydrogen to give 5.19. This in turn eliminates benzene reductively and regenerates 5.15. The vacant coordination sites of 5.15 and 5.18 are, of course, normally occupied by ligands such as PPh$_3$ or CO. Consequently, the rate of degradation in the presence of excess ligand would be very small.