## COBALT-BASED HYDROFORMYLATION

The catalytic cycle for the cobalt-based hydroformylation is shown in Fig. 5.7. Most cobalt salts under the reaction conditions of hydroformylation are con- verted into an equilibrium mixture of $Co_2(CO)_8$ and $HCo(CO)_4$. The latter un- dergoes CO dissociation to give 5.20, a catalytically active 16-electron inter- mediate. Propylene coordination followed by olefin insertion into the metal– hydrogen bond in a Markovnikov or anti-Markovnikov fashion gives the branched or the linear metal alkyl complex 5.24 or 5.22, respectively. These



**Figure 5.7** Catalytic cycle for the hydroformylation of propylene with cobalt catalyst. The inner and outer cycles show the formation of linear and branched isomers.

complexes can undergo CO insertion into the metal– alkyl bonds to give 5.25 and 5.23, respectively. The product aldehydes are generated from these species by reaction with both dihydrogen and $HCo(CO)_4$. Under the catalytic conditions the latter reaction is insignificant compared to the former.

The cobalt and rhodium catalysts have one important difference

between their respective mechanisms. Unlike in the rhodium-catalyzed process, there is no oxidative addition or reductive elimination step in the cobalt-catalyzed hy- droformylation reaction. This is reminiscent of the mechanistic difference be-tween rhodium- and cobalt-based carbonylation reactions (see Section 4.2.3). The basic mechanism is well established on the basis of in situ IR spectroscopy, kinetic and theoretical analysis of individual reaction steps, and structural char- acterization of model complexes.

Both $Co(CO)_4(COPr^n)$ and $Co(CO)_4(COPr^i)$ have been isolated, and their reactions with $H_2$ as well as $HCo(CO)_4$ have been studied. On the basis of such studies participation by intermediates such as 5.23 and 5.25 in the catalytic cycle is firmly established. The reactions of $HCo(CO)_4$ with $Co(CO)_4(COPr^i)$ and $Co(CO)_4(COPr^n)$ are about 20– 30 times faster than the corresponding re-actions with dihydrogen at 25°C. However, as already mentioned, at high tem- perature (>100°C) and pressure (>100 bar), reaction with dihydrogen is the main product-forming step.

For the other catalytic intermediates, there are spectroscopic data and/or strong theoretical arguments in favor of their existence. Thus $Co(CO)_3(COMe)$, an analogue of 5.23 and 5.25 has actually been observed spectroscopically at low temperature by the matrix isolation technique. A similar experimental tech-nique has also established the formation of $Co(CO)_3(Me)$, an analogue of 5.22 and 5.24.

In the Shell process (SHOP) phosphine-modified cobalt-catalyzed hydrofor- mylation is one of the steps in the synthesis of linear alcohols with 12– 15 carbon atoms (see Section 7.4.1). Two important characteristics of this reaction should be noted. First, the phosphine-modified precatalyst $HCo(CO)_3(PBu^n)$ is less active for hydroformylation than $HCo(CO)_4$ but more active for the sub- sequent hydrogenation of the aldehyde. In this catalytic system both hydrofor- mylation and hydrogenation of the aldehyde are catalyzed by the same catalytic species. Second, the phosphorus ligand-substituted derivatives are more stable than their carbonyl analogues at higher temperatures and lower pressures (see Table 5.1).

In situ IR spectroscopic studies have been carried out on the $CO_2(CO)_8$ plus $PBu^n$–based catalytic system with ethylene or $n$-octene as the olefins.

Unlike in the case of $Co_2(CO)_8$, where $HCo(CO)_4$ and $Co(CO)_4(COR)$ may

be observed, in the presence of PBu$^n$, no Co(CO)(PBu$^n$)(COR) or

$Co(CO)_3(PBu^n))(R)$ types of complexes could be seen. This presumably is because of low concentrations of such intermediates under operating conditions. The mechanism of hydroformylation is assumed to be similar to the one shown in Fig. 5.7. Very little direct mechanistic evidence at a molecular level is avail- able on the aldehyde hydrogenation reaction.

## OTHER HYDROFORMYLATION REACTIONS

Apart from the processes discussed so far, there are other industrial and pat- ented processes where hydroformylation reactions are employed. A few selected ones are summarized in Table 5.2.
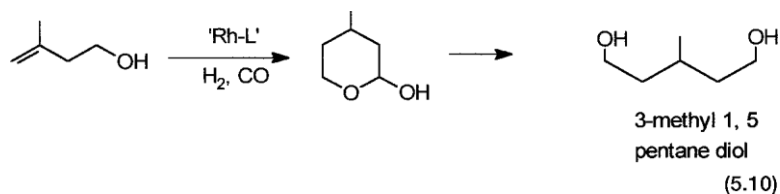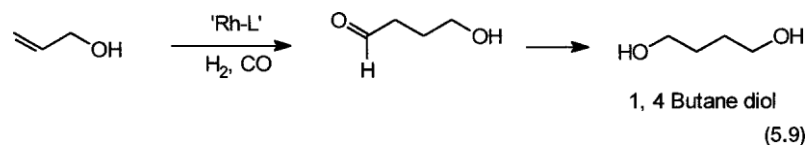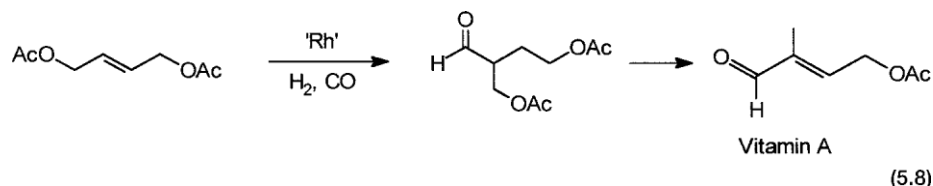


Vitamin A

(5.8)



1, 4 Butane diol

(5.9)



3-methyl 1, 5 pentane diol

(5.10)

TABLE 5.2   Hydroformylation Reaction Processes

| Manufacturer | Product | Process |
|---|---|---|
| Mitshubishi Kasei | Isononyl aldehyde for isononyl alcohol, which is used in polyvinyl chloride resin as a plasticizer alcohol | Rhodium catalyst with triphenyl phosphine oxide as a weakly coordinating ligand; catalyst separated from the products by distillation |
| BASF Hoffman-LaRoche | An intermediate for Vitamin A synthesis | Rhodium catalyst without phosphorus ligand; Reaction 5.8 |
| ARCO | An intermediate for 1,4-butanediol | Rhodium catalyst with chelating phosphorus ligand; hydroformylation of allyl alcohol followed by hydrogenation of the resultant aldehyde; Reaction 5.9 |
| Kuraray | An intermediate for 3-methyl 1,5-pentane diol | $Rh_4(CO)_{12}$ with phosphorus ligand as the precatalyst; hydroformylation of 2-methyl buten-4-ol followed by hydrogenation; Reaction 5.10 |