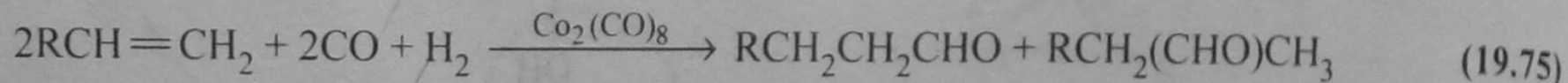


Hydroformylation⁴⁴

The reaction of an alkene with carbon monoxide and hydrogen, catalyzed by cobalt or rhodium salts, to form an aldehyde is called *hydroformylation* (or sometimes the *oxo process*):



It was discovered by Roelen in 1938 and is the oldest and largest volume catalytic reaction of alkenes, with the conversion of propylene to butyraldehyde being the most important. About 5 million tons of aldehydes and aldehyde derivatives (mostly alcohols) are produced annually making the process the most important industrial synthesis using a metal carbonyl complex as a catalyst.⁴⁵ The name hydroformylation arises from the fact that in a formal sense a hydrogen atom and a formyl group are added across a double bond. The net result of the process is extension of the carbon chain by one and introduction of oxygen into the molecule.

⁴³ Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. *Organometallics* **1986**, *5*, 724–730.

⁴⁴ Pruett, R. L. *J. Chem. Educ.* **1986**, *63*, 196–198.

⁴⁵ Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259–266.

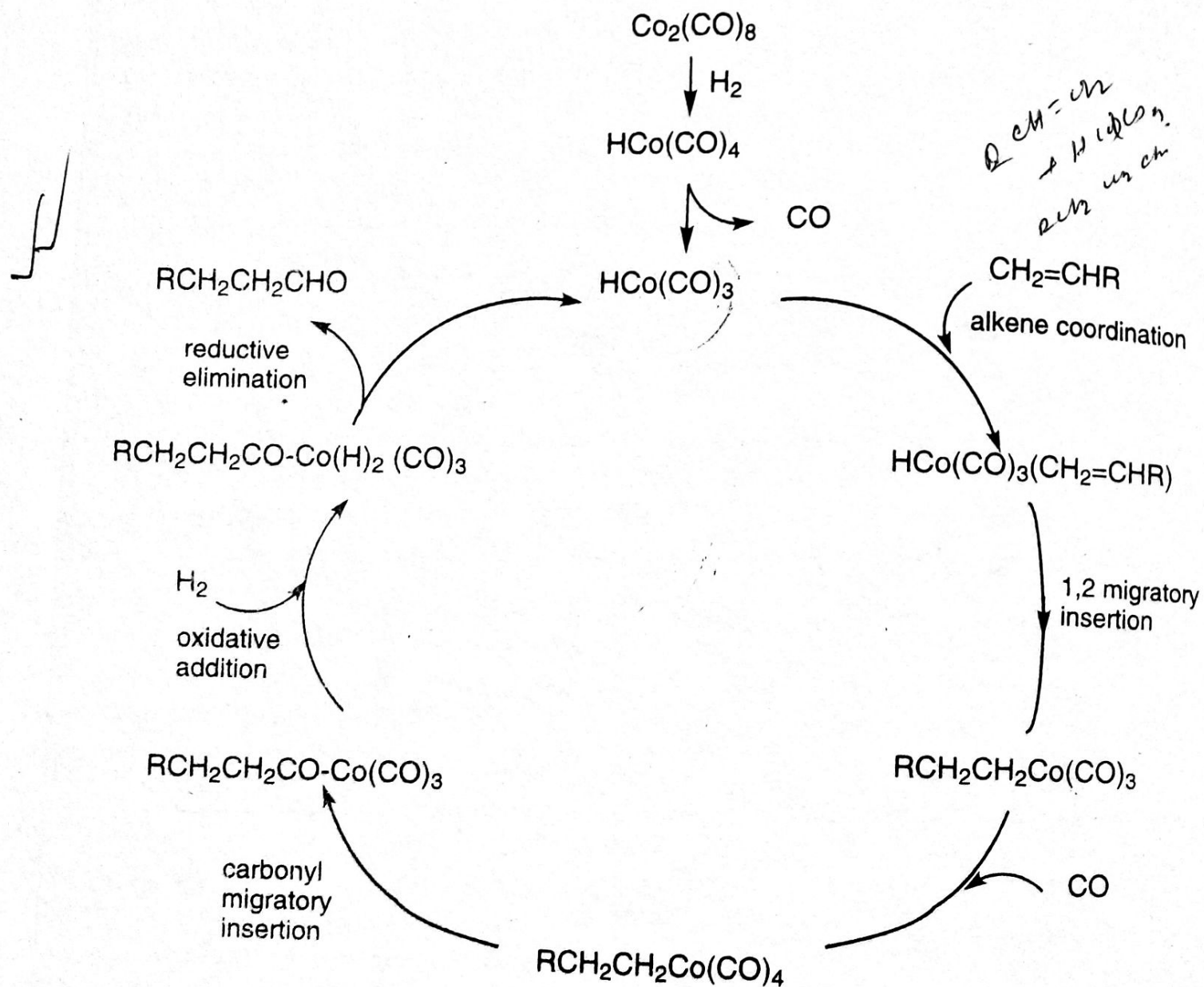
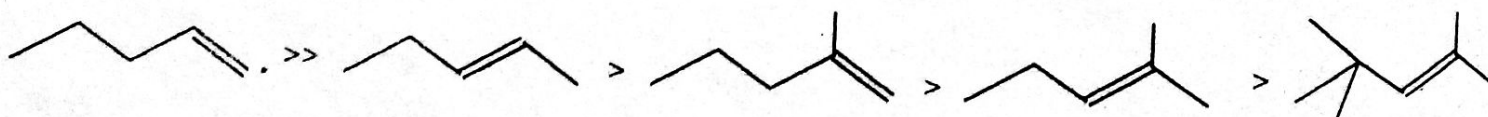


Fig. 13.1 Catalytic cycle for hydroformylation using $\text{HCo}(\text{CO})_4$

The general relative reactivity of alkenes for hydroformylation is as follows.



In Eq. 19.76 we see that $\text{Co}_2(\text{CO})_8$ reacts with H_2 to give $\text{HCo}(\text{CO})_4$ (an 18-electron species) which loses CO forming $\text{HCo}(\text{CO})_3$ (a 16-electron species) and creating a vacant coordination site. Alkene coordination recreates an 18-electron complex which undergoes migratory insertion of the olefin into the Co—H bond thereby creating another 16-electron complex and another vacant coordination site to which CO can become coordinated. A carbon monoxide ligand of $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4$ migrates to a position between the cobalt atom and the alkyl group—this is the critical step in the formation of the aldehyde. Reaction with H_2 or $[\text{HCo}(\text{CO})_4]^-$ releases the aldehyde and regenerates the catalytic cobalt complex. The process may be carried out so that the aldehyde products are reduced to give alcohols such as 1-butanol (which is used to make the plasticizer 2-1-ethyl-hexanol) or higher alcohols used for detergents or other plasticizers.

Some disadvantages are associated with the cobalt carbonyl catalyst when it is used to convert propylene to butyraldehyde: (1) temperatures of 140–175 °C and a pressure of 200 atmospheres are required; (2) branched chain aldehydes predominate over linear molecules which are more desirable (linear detergents are more biodegradable than are branched ones). A modified cobalt catalyst, $\text{HCo}(\text{CO})_3\text{PBU}_3$, developed by Shell improves the linear to branched ratio but gives a slower reaction and therefore is run at higher temperatures (175 °C and 50–100 atm). Union Carbide has improved the ratio even more with various rhodium catalysts. For example, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyzes the reaction at 90–110 °C and 12 atmospheres. A few years ago the company announced a new low-pressure hydroformylation rhodium catalyst modified with phosphites, $\text{P}(\text{OR})_3$, which works with less active alkenes such as 2-butene and 2-methylpropene.⁴⁷