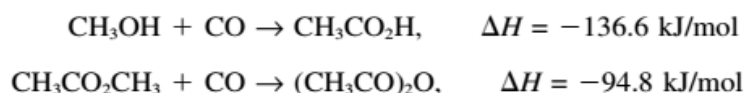


CARBONYLATION

In this chapter we discuss the mechanistic and other details of a few industrial carbonylation processes. These are carbonylation of methanol to acetic acid, methyl acetate to acetic anhydride, propyne to methyl methacrylate, and benzyl chloride to phenyl acetic acid. Both Monsanto and BASF manufacture acetic acid by methanol carbonylation, Reaction 4.1. The BASF process is older than the Monsanto process. The catalysts and the reaction conditions for the two processes are also different and are compared in the next section. According to reaction, the carbonylation of methyl acetate to acetic anhydride is a productive industrial process produced by Eastman Kodak. Shell recently commercialized the carbonylation of propyne (methyl acetylene) in methanol to give methyl methacrylate. The Montedison carbonylation process for the manufacture of phenyl acetic acid from benzyl chloride is noteworthy for the clever combination of phase-transfer and organometallic catalyses. Hoechst has recently reported a novel carbonylation process for the drug ibuprofen.



They are important for the Monsanto and BASF processes. The methanol carbonylation reactions aptly demonstrate many of the basic principles mentioned in Chapter 2. We begin our discussion with these reactions.

MANUFACTURE OF ACETIC ACID

There are various major by-products of reactions in the BASF and Monsanto processes. In the former it is the Fischer – Tropsch-type liquid phase reaction, which contributes to the formation of products such as alkyl acetates, methane etc. In the Monsanto process it is the homogeneous water-gas shift reaction that produces CO₂ and H₂ as byproducts. Also note that the Monsanto process is superior in terms of selectivity, metal usage and operating conditions.

The Monsanto Process—The Catalytic Cycle

The basic catalytic cycles for the Monsanto process and the catalytic intermediates are shown in Fig. The reaction mixture can be supplemented with a variety of rhodium salts as precatalysts. They are easily transformed to complex in the presence of I y CO. The following points about the catalytic cycles deserve special attention.

TABLE Comparison of Process Parameters for Methanol Carbonylation Processes

	BASF	Monsanto
Metal concentration	10^{-1} mole/liter of cobalt	10^{-3} mole/liter of rhodium
Temperature	230°C	180–190°C
Pressure (atm)	500–700	30–40
Selectivity (%) based on		
1. Methanol	90	>99
2. CO	70	90
Byproducts	CH ₄ , glycol acetate, and other oxygenated hydrocarbons	CO ₂ , H ₂
Effect of hydrogen	Amount of byproduct increases	No effect
Promoter CH ₃ I	Essential	Essential

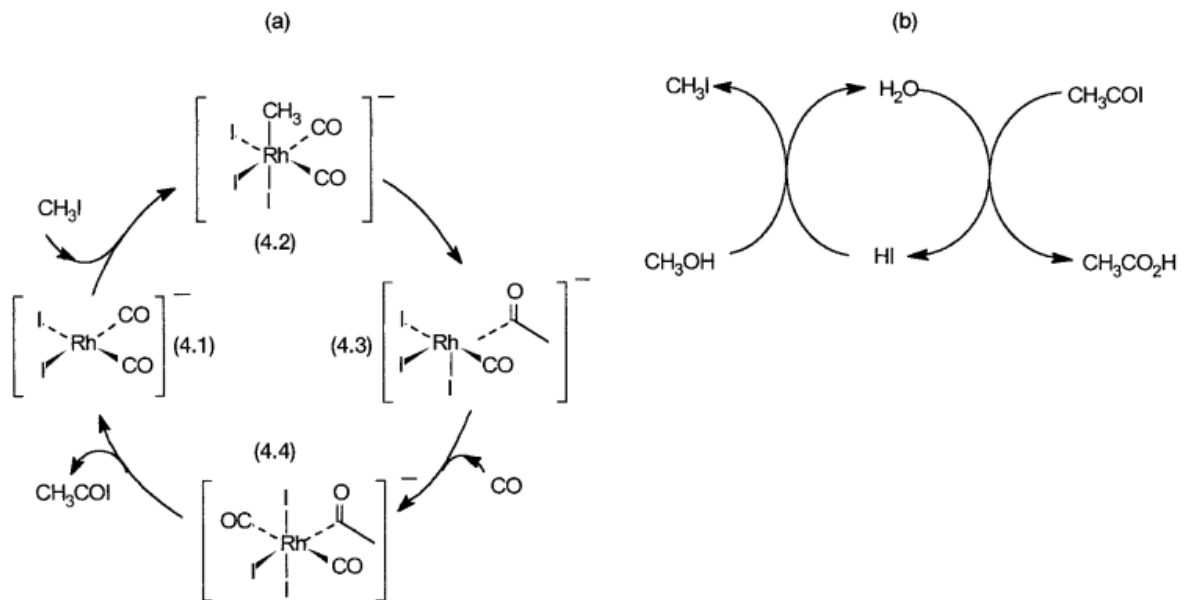


Figure. Monsanto process

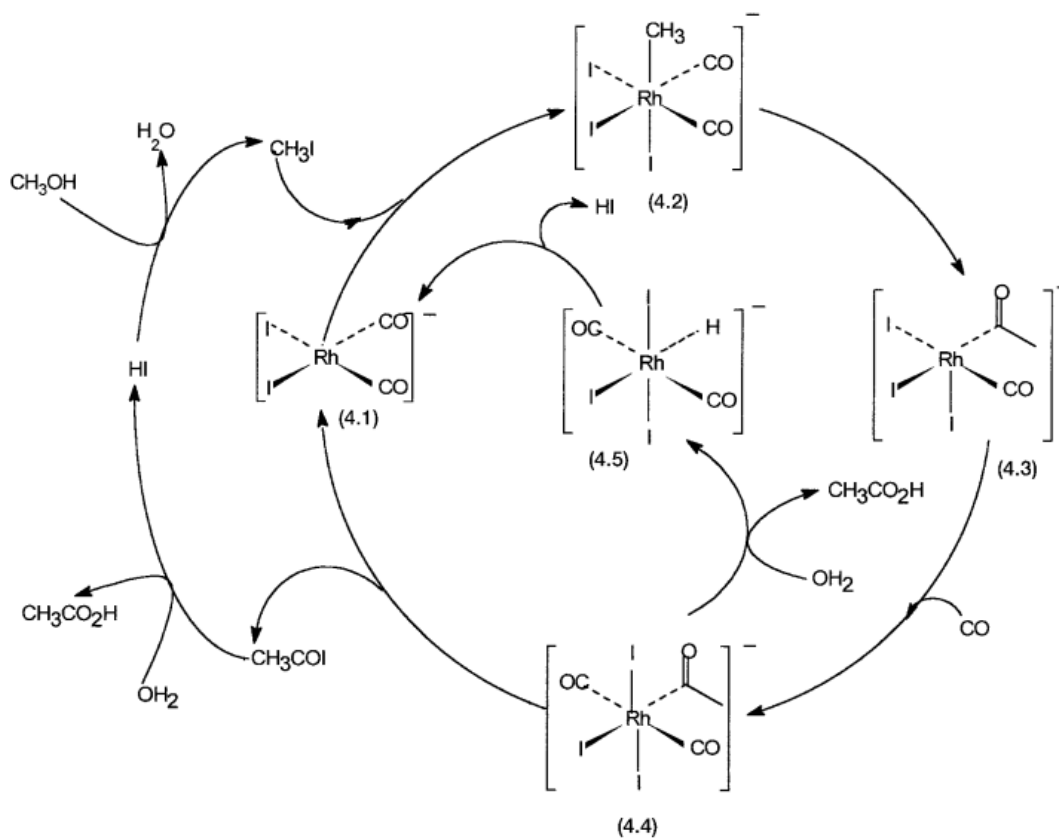


Figure Monsanto process

4.1-4.2 is an oxidative addition reaction, 4.2-4.3 is an incorporation reaction, and 4.4-4.1 is a reduction reaction to elimination. Third, the 16-electron complexes are 4.1 and 4.3, while the 18 electron numbers are 4.2, 4.4, and 4.5. The stoichiometry of the overall reaction is eventually that of reaction 4.1; methanol and CO are the only two reactants that join the loops irreversibly. The actual result of the primary catalytic process is acetyl iodide. Water, while essential for acetyl iodide hydrolysis, is produced in methanol reaction with HI. And the total stoichiometry does not include it. In the beginning small amounts of CH_3I and water are added to make the cycle operational. Methanol carbonylation rate exhibits zero-order dependency on methanol, carbon monoxide, and acetic acid concentration. As shown, in relation to rhodium and methyl iodide concentrations, first order is:

$$\text{rate} = [\text{Rh}][\text{CH}_3\text{I}]$$

The rate-determining step in the catalytic cycle is the oxidative addition of CH_3I to 4.1. Oxidative alkyl halide additions are also considered to obey the $\text{S}_{\text{N}}2$ pathways. Which seems to be the case here too. The net negative charge on 4.1 increases its nucleophilicity and CH_3I reactivity.

The BASF process — the catalytic cycle

The basic steps of the catalytic cycle are shown in Fig with the cobalt catalyst.

4.3. That's right. Tetracarbonyl cobalt anion 4.7, by reactions 4.5–4.7, is formed from cobalt iodide.

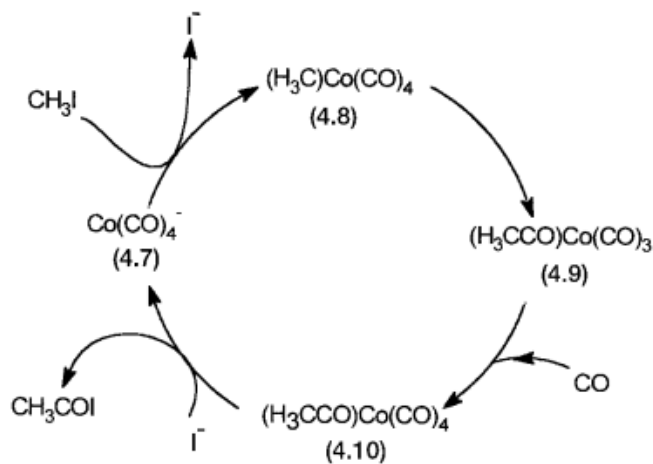
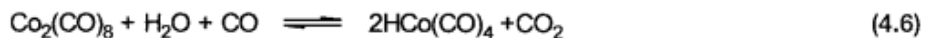
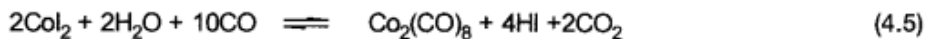


Figure. BASF process:

BASF process — Mechanistic studies

The cobalt-catalyzed carbonylation rate is heavily dependent on both carbon monoxide pressure and methanol concentration. Unlike 4.1, Complex 4.7 is a nucleophile with 18 electrons. Which makes the CH_3I attack by 4.7 a fairly slow reaction. High temperatures are required for the cobalt catalyst to reach appropriate levels. That in effect requires high CO pressures to stabilize 4.7 at high temperatures.

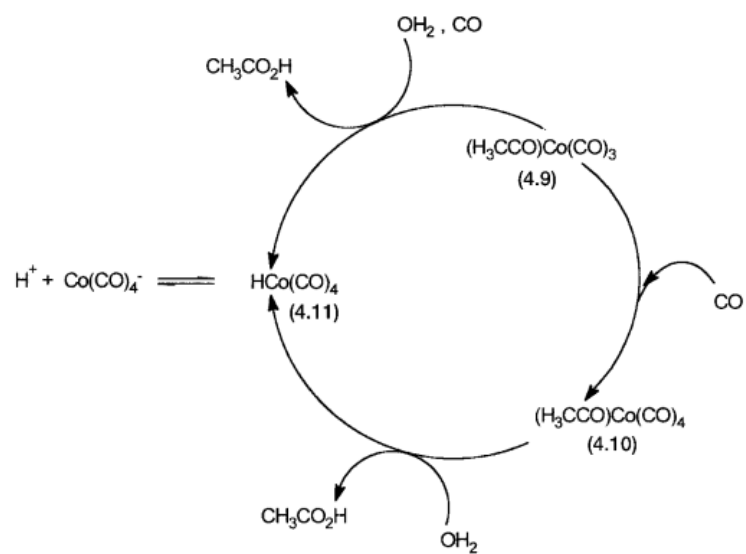


Figure 4.4 Pathways that lead to the generation of $\text{HCo}(\text{CO})_4$