

CARBONYLATION OF METHYL ACETATE

Conventional processing of acetic anhydride is based on the ketene ($\text{H}_2\text{C}=\text{C}=\text{O}$) reaction with acetic acid. Eastman Chemical Company, an Eastman Kodak subsidiary, developed facilities to produce 500 million lbs / yr of acetic anhydride and 165 million lbs / yr of acetic acid using coal as the feedstock in 1984. Coal is gasified in this process to give synthesis gas, which is then converted to methanol via a heterogeneous catalytic process. Methanol reaction with acetic acid gives methyl acetate, which is carbonylated to give anhydride to the acetate. About one billion lbs / yr of acetic anhydride is used by Eastman Kodak in the manufacture of cellulose esters used in the development of photographic films, plastics, coating chemicals etc. The major factors behind the spectacular success of this process are as follows. All the production facilities are located in the heart of Appalachian coalfields. That process is less energy-intensive than the process based on ketene. The carbonylation process recycles in the synthesis of methyl acetate the acetic acid, a coproduct in the manufacture of cellulose esters. Finally, conversions and rhodium metal recovery efficiencies of this process are sufficiently high to make the overall economics viable and attractive.

Mechanism and Catalytic Cycle

The acetic acid that forms part of the methanol carbonylation catalytic cycle consists of reactions between acetyl iodide and water to give acetic acid and HI. The hydroiodic acid binds to CH_3I and water with methanol to regenerate. A similar mechanism operates for the carbonylation of methyl acetate. Acetic acid and acetyl iodide react to give acetic anhydride and HI.

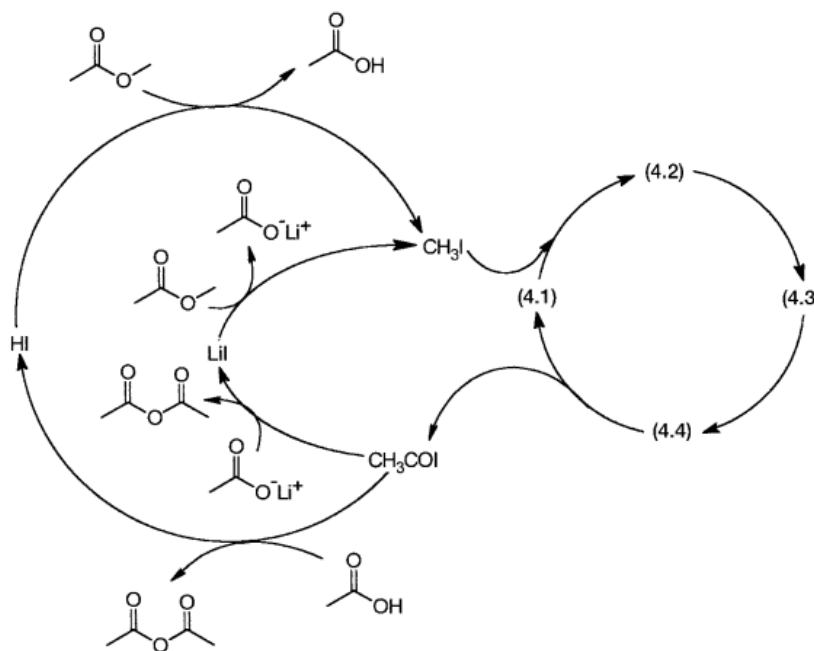


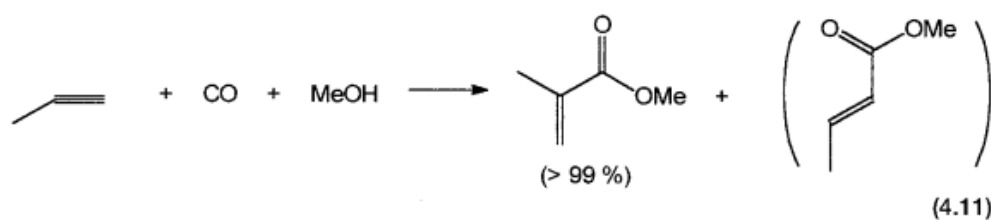
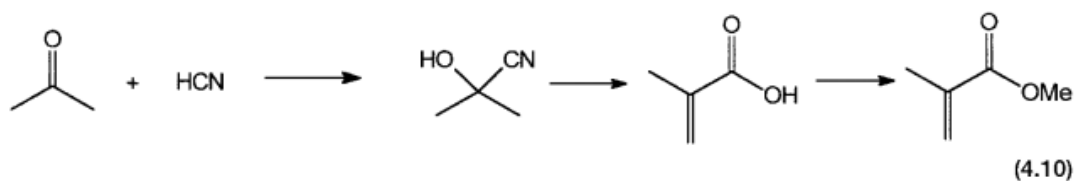
Figure. Carbonylation of methyl acetate to acetic anhydride

Additionally, there is another pathway promoted by lithium salt, which significantly contributes to product formation. Here the product-forming reaction between lithium acetate and acetyl

iodide is followed by the LiI-methyl acetate reaction. These reactions are shown by the inner loop on the left-hand side. Indeed, the inner loop is the primary pathway of product formation, and lithium salts play a crucial role in the overall catalysis. Note that the catalytic cycle loop on the right is exactly the same as in Fig.

CARBONYLATION OF ALKYNES; MANUFACTURE OF METHYL METHACRYLATE

Methyl methacrylate polymer (MMA) is known as "Perspex." It is a smooth, transparent glass-like material with high toughness, tear resistance and chemical stability. The traditional route involves the reaction between acetone and hydrocyanic acid, followed by concurrent hydrolysis, dehydration, and esterification, as shown by reaction 4.10. This process generates large quantities of solid wastes. An alternative route based on a homogeneous palladium catalyst has recently been developed by Shell. In this cycle a palladium complex catalyzes the propyne (methyl acetylene), methanol, and carbon monoxide reaction. This is expressed in reaction 4.11. The desired product is formed with a regioselectivity that could be as high as 99.95%.



This invention has its roots in Reppe chemistry. Reppe had developed a variety of manufacturing processes for bulk chemicals in Germany in the late 1930's, where acetylene was used as one of the basic building blocks. Even today BASF and Rohm Hass manufacture large quantities of acrylic acid and its esters by hydrocarboxylation of acetylene

A mixture of NiBr₂ and CuI catalyzes the reaction, 4.12. It requires high pressure (100 bar) and temperature (220 C) and is not fully understood mechanistically.



The Shell cycle for MMA, on the other hand, occurs under milder conditions (60 C, 10–60 bar), and the molecular mechanism is better known. The reaction is usually carried out in methanol,

which acts both as a solvent and as a reactant. The precatalyst is Pd(OAc)₂, which is mixed with an excess of phosphine ligand to generate the active catalytic intermediates in situ. An important requirement for efficient catalysis is the presence of an acid HX that acts as a co-catalyst.

A novel ligand, 4.31, a phosphine that also has a pyridine ring, is used in the Shell process. This ligand can act as a bidentate, as well as a monodentate ligand in the presence of an acid. This is because the acid protonates the nitrogen atom of the pyridine ring and an equilibrium, as shown by 4.13 is set up.

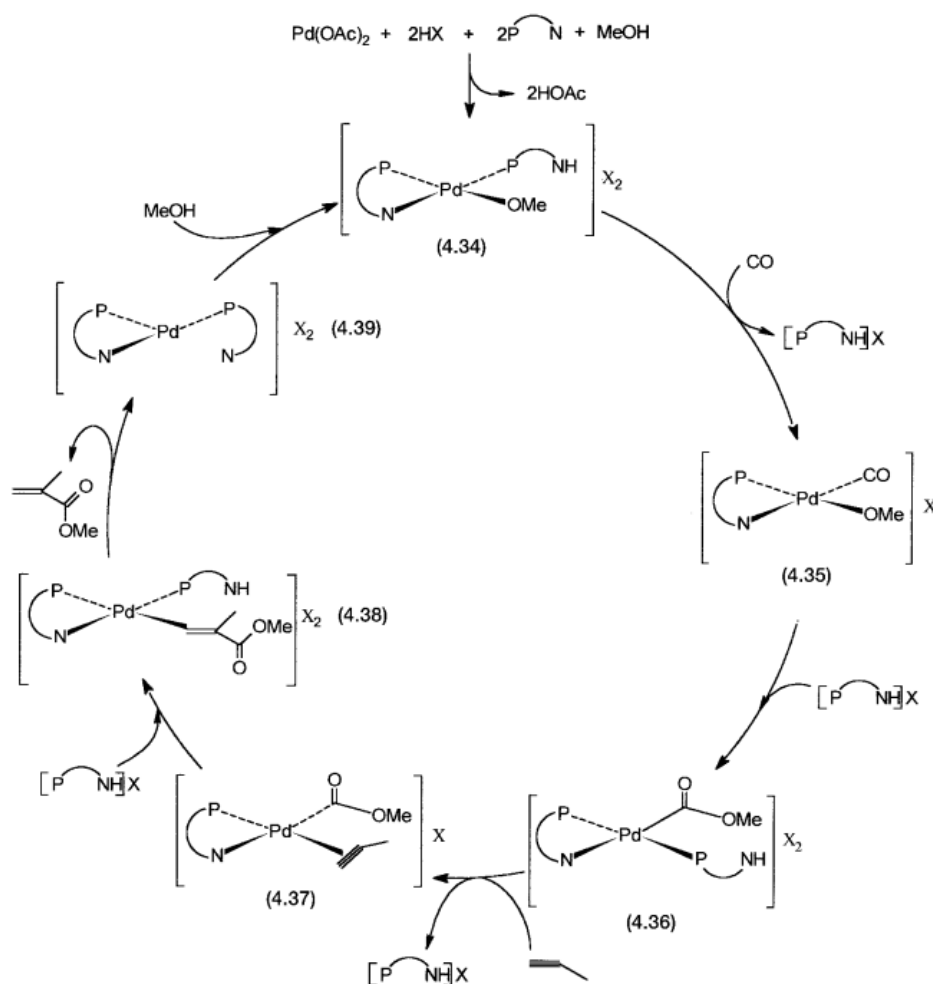
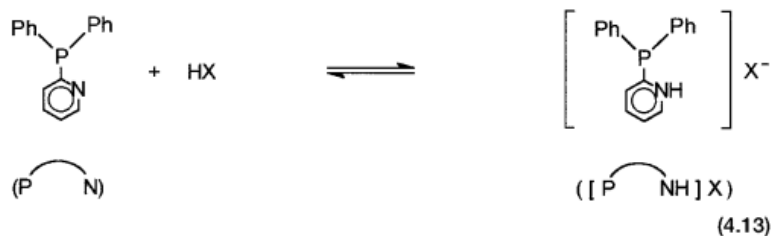


Figure. Shell process for the carbonylation of propyne (methyl acetylene) in methanol to give MMA