

CHAPTER OVERVIEW

8: H- Wilkinson's Catalyst (Experiment)

[8.1: Part A- Synthesis of Wilkinson's Catalyst](#)

[8.2: Part B- Homogeneously-Catalyzed Hydrogenation of an Alkene](#)

Homogeneous Catalysis Introduction

A catalyst is "a substance which when added to a reaction mixture changes the rate of attainment of equilibrium in the system without itself undergoing a permanent chemical change." (Reference: Sharp "Penguin Dictionary of Chemistry" 1981) A catalyst increases the rate at which the system reaches equilibrium but it does not change the equilibrium itself, because it also increases the rate of the back reaction to an equal extent. The following related terms also need to be defined:

- catalyst precursor* = a compound or complex which undergoes a reaction to produce the active catalyst.
- autocatalyst* = a reaction product which is a catalyst for the same reaction
- inhibitor* = a compound which will slow down or stop a reaction
- substrate* = molecule upon which the catalyst acts
- % conversion = % of the substrate which has been converted to product
- turnover number* (TON) = moles of product per mole of catalyst (unitless)
- turnover frequency* (TOF) = moles of product per mole of catalyst per hour (units are h^{-1})

A *homogeneous catalyst* is a catalyst which is in the same phase as the substrate. A homogeneous catalyst could be an organic molecule, a salt, or a transition metal complex. The solution does not have to be homogeneous in order for the catalyst to be homogeneous. For example, homogeneous hydrogenation involves two phases; hydrogen is in the gas phase and the catalyst and substrate (an olefin) are in the liquid phase. Therefore, although the system is technically heterogeneous, the catalyst is a homogeneous catalyst.

Although heterogeneous catalysts have been the historical favorite in industry, homogeneous catalysts have a number of advantages (Table 1). They are used in many industrial processes.

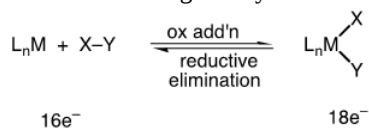
Table 1. Comparison of homogeneous and heterogeneous catalysis.

Heterogeneous	Homogeneous
Simple to prepare	Complicated synthesis
Very stable	Less stable
No solvent restrictions	Solvent restrictions
Easy to separate from products, solvents	Difficult to separate
Difficult to characterize	Simple to characterize (NMR, X-ray)
Only surface atoms used	All metal atoms used
Poisons easily	Somewhat more resistant
Low selectivity	High and tunable selectivity
Empirical matching of catalyst and substrate	Catalyst design

The mechanism of a homogeneously-catalyzed reaction is usually a cycle consisting of several steps, each of which can also occur as a stoichiometric reaction. For transition metal complexes, the most common primary steps are oxidative addition, reductive elimination and insertion.

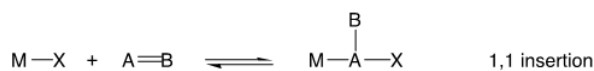
During the *oxidative addition* of a molecule X-Y (e.g. H_2 , HCl , RS-SR , Br_2 , R-I) to a metal fragment L_nM , the metal oxidation number is increased by two units, the X-Y bond is cleaved, and new M-X and M-Y bonds are formed. The electron count at the metal goes up by two units. Therefore oxidative addition is not possible if the metal already has 18 valence electrons or if it does

not have an energetically-accessible oxidation number two units above the present number.

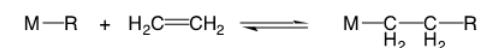
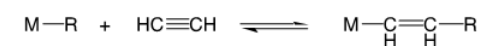
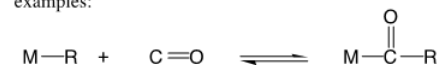


Reductive elimination is the opposite of oxidative addition. During the reductive elimination of a molecule X-Y from a metal fragment $L_nM(X)(Y)$, the metal oxidation number is decreased by two units, the M-X and M-Y bonds are cleaved, and a new X-Y bond is formed. The electron count at the metal goes down by two units. Therefore reductive elimination is not possible if the metal does not have an energetically-accessible oxidation number two units below the present number.

In an *insertion reaction*, an unsaturated molecule $A=B$ inserts into a metal-ligand bond M-X (where X is an anionic ligand). The bond order of the A-B bond decreases by one unit (i.e. a double bond goes to a single bond, a triple bond goes to a double bond). There are two possible geometries of insertion: 1,1-insertion and 1,2-insertion. You can predict which would happen by looking at how the molecule would bind to the metal as a ligand. 1,1-insertion usually happens if the molecule $A=B$ would bind end-on to the metal (for example, carbon monoxide). 1,2-insertion usually happens if the molecule $A=B$ would bind side-on to the metal (for example, an alkene).



examples:

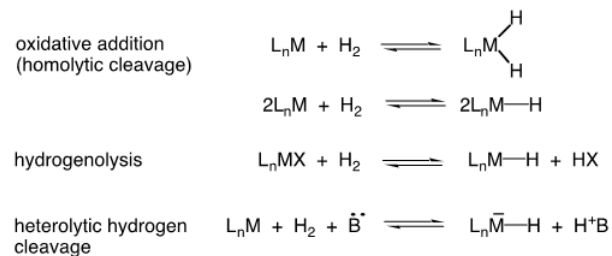


These simple steps (and a few others) are combined in a catalytic cycle. However, it can be extraordinarily difficult to figure out the catalytic cycle for a given catalytic reaction. A common technique is to try to observe the individual steps as stoichiometric reactions and then pose a catalytic cycle as a hypothesis; the mechanism must be consistent with the observed kinetics. However, even after all that work, the mechanism may only match the observations for one substrate, one temperature and one solvent. Changing to another substrate, temperature or solvent may cause an entirely different mechanism to take over.

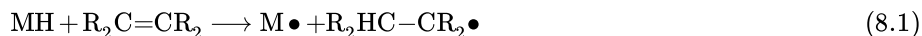
Another complication is the fact that any species which can be observed by spectroscopy during catalysis may actually be a species which is not in the catalytic cycle. If the species is so stable that it can be observed, it is probably so stable that it cannot be a part of a rapid catalytic cycle.

Homogeneous Hydrogenation

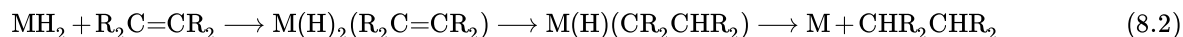
Hydride ligands are of paramount importance to homogeneous hydrogenation. Hydrogen gas (H_2) doesn't react with alkenes at room temperature without a catalyst. Metal complexes activate the hydrogen by forming hydride complexes, which then transfer hydrogen to the alkenes. The hydride complexes can be formed by oxidative addition of H_2 , hydrogenolysis, or heterolytic activation.



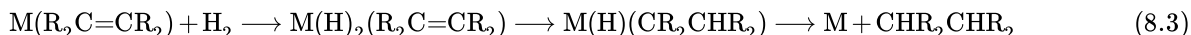
Another necessary step is transfer of the hydrogen from the metal to the alkene. This can happen in several ways, the most common of which are hydrogen atom transfer, the hydride pathway and the unsaturated pathway. The latter two routes differ only in the sequence of hydrogen and alkene binding to the metal.



H atom transfer (radical hydr.)

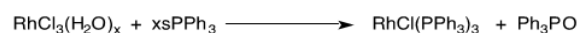


Hydride Pathway

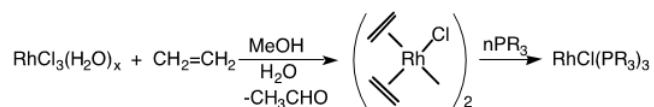


Unsaturated Pathway

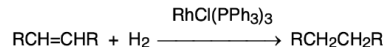
In 1964 Wilkinson and Coffey independently and nearly simultaneously discovered a remarkable homogeneous olefin hydrogenation catalyst, chlorotris(triphenylphosphine) rhodium(I), which is now commonly called "Wilkinson's catalyst". The simplest preparation of this complex is the direct reaction of rhodium chloride with triphenylphosphine, although with other phosphines this route does not work well.



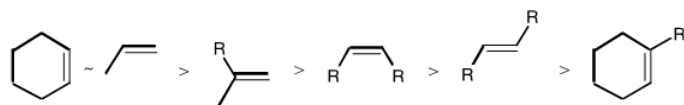
or:



This catalyst was the first to be able to rapidly hydrogenate unconjugated alkenes and alkynes at extremely mild conditions (1 atm of H_2 and at room temperature). The hydrogenation is usually performed in benzene with a polar cosolvent like ethanol. The polar solvent might facilitate migratory insertion, which is rate limiting.



The reactivity of olefins is primarily determined by steric factors, although some olefins like ethylene and 1,3 butadiene are very slowly reduced under ambient conditions and can act as powerful competitive inhibitors.

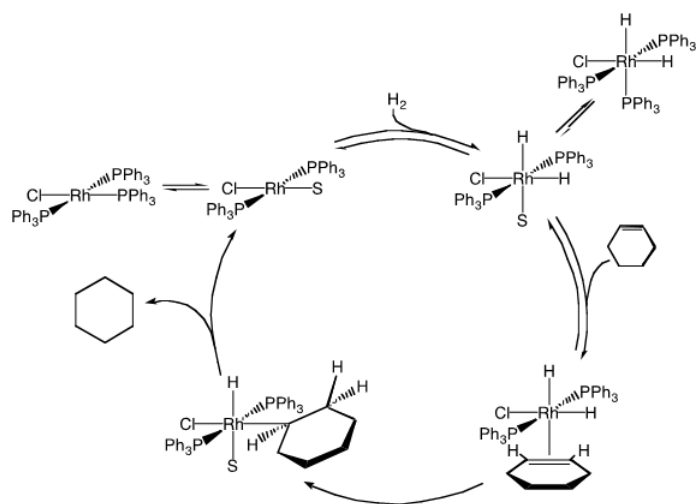


The complex slightly dissociates in solution, and this is thought to be important to the mechanism.



The mechanism for the hydrogenation of cyclohexene is shown below (S = solvent), but note that the mechanism for the hydrogenation of styrene is different, and yet another mechanism is involved in the hydrogenation of ethylene.

Note that according to this mechanism Wilkinson's catalyst should actually be called "Wilkinson's catalyst precursor".



Source: Szafran, Z.; Pike, R. M.; Singh, M. M. *Microscale Inorganic Laboratory*, John Wiley: 1991.

References:

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