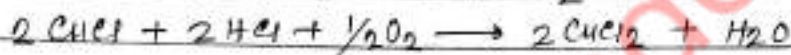


Organometallic Compounds

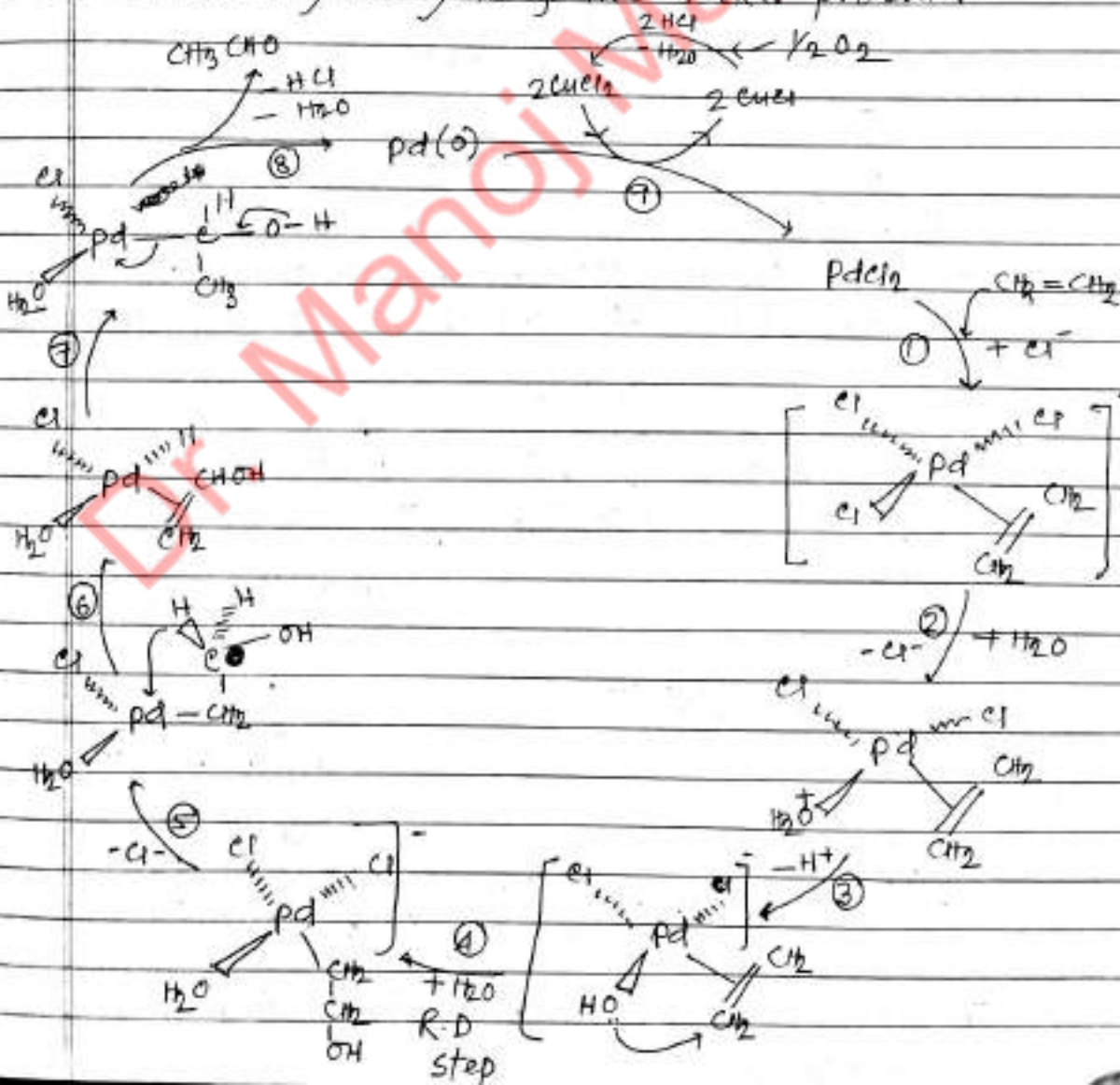
Olefin Oxidation (Wacker process) -

Ethylene and chloro complexes of Pd readily decompose in water to acetaldehyde and Pd-metal. The re-oxidation of Pd(0) to Pd(II) by O₂, mediated by the couple Cu⁺/Cu²⁺, led to a catalytic cycle: the Wacker process.



Here catalyst used is $CuCl \rightarrow CuCl_2$

The catalytic cycle of the Wacker process:

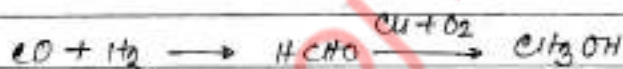
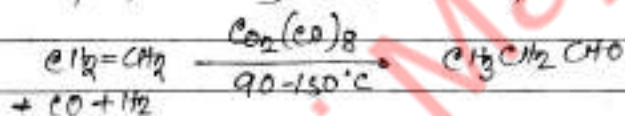


At Step ④ nucleophilic attack by OH^- occurs, this is the rate determining step. Acetaldehyde formed in the final step - 8 is from α -hydroxy ethyl σ -complex rather than from vinyl alcohol π -complex intermediate is supported by the fact that no deuterium is found in the product if the catalyst is performed in D_2O .

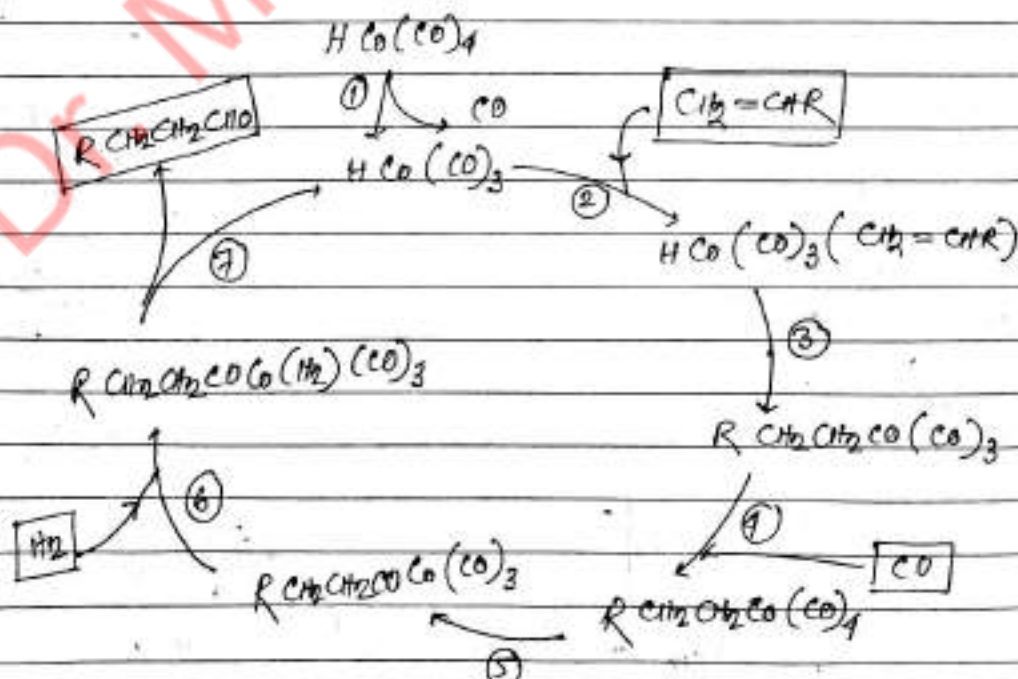
Alkenes of the type $\text{RCH}=\text{CHR}'$ and $\text{RCH}=\text{CH}_2$ are converted to ketones by this process.

Hydroformylation (oxo reaction):

The hydroformylation of olefins is a homogeneously catalysed process. The reaction of this type was first discovered by O. Roelen, in 1938, who prepared propionaldehyde from ethylene.



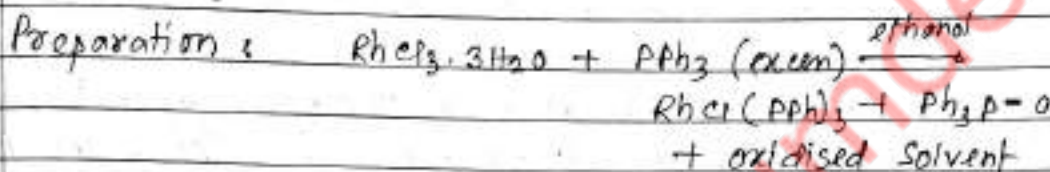
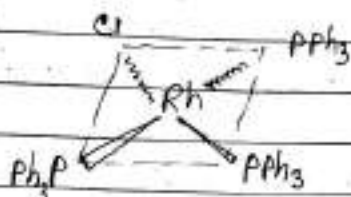
Hydroformylation is also known as oxo reaction. In oxo reaction, H and HCO are formally added across the double bond, it is thus referred to as 'hydroformylation'.



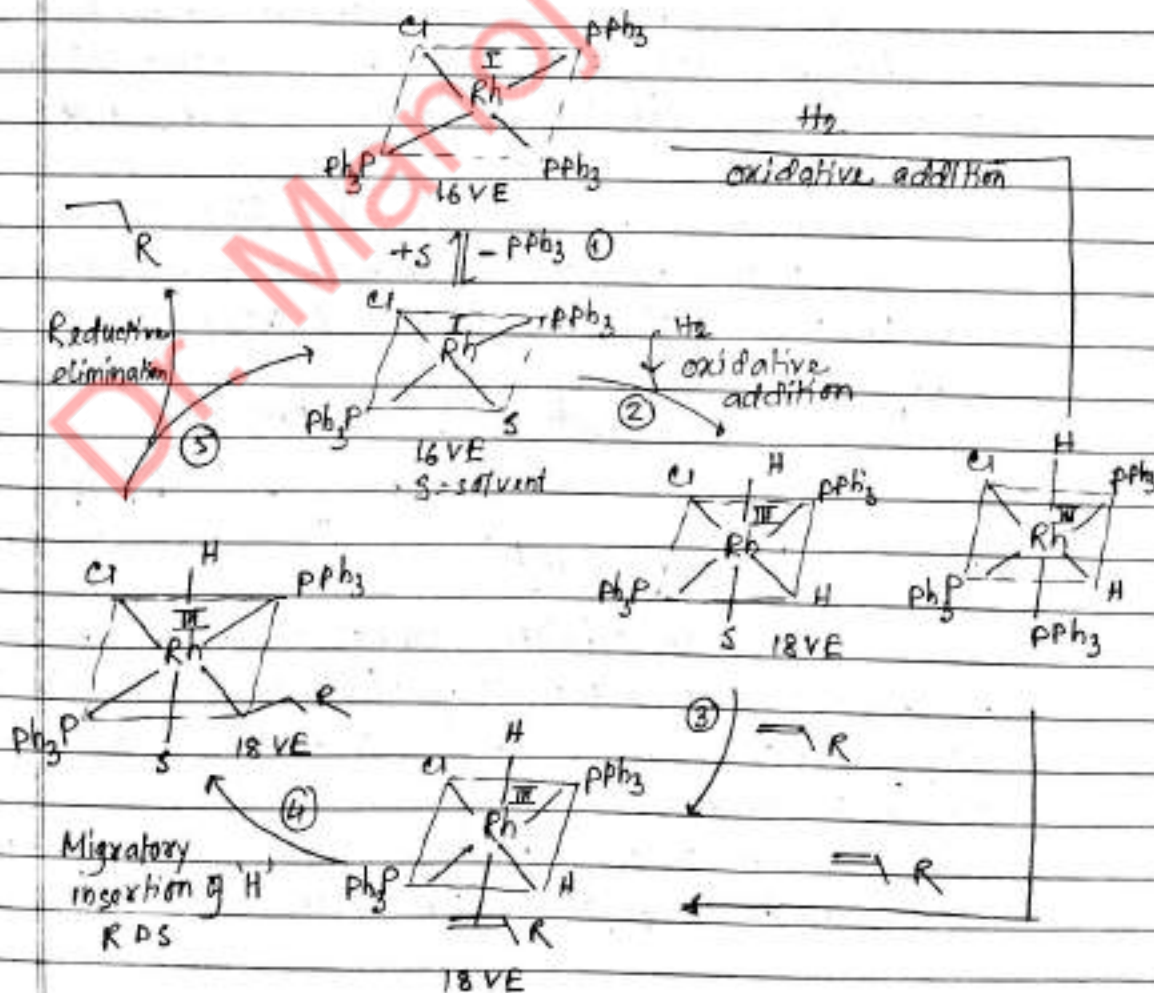
The oxidative addition of H_2 in step-6 is the rate determining step.

Hydrogenation of alkenes (Wilkinson's catalyst):

$RhCl(PPh_3)_3$; chlorotris(triphenylphosphine)rhodium(I), is known as Wilkinson catalyst. The complex is square planar, 16-electron complex, homogeneous catalyst.



Use: It is used for selective hydrogenation of alkenes and alkynes without affecting the functional groups eg - $>C=O$, $-CN$, $-NO_2$, $-COOR$ etc.

Mechanism:

In Step-1, Wilkinson catalyst is converted to active form by losing one PPh_3 group and solvent molecule fills the vacant site.

Step-2: Catalyst activates the molecular hydrogen by oxidative addition mechanism giving 1e valence electron complex and Rh expands its oxidation no to +3.

Step-3: The dihydride complex binds to the olefin with the concomitant loss of solvent or PPh_3 .

This path is referred as dihydride path.

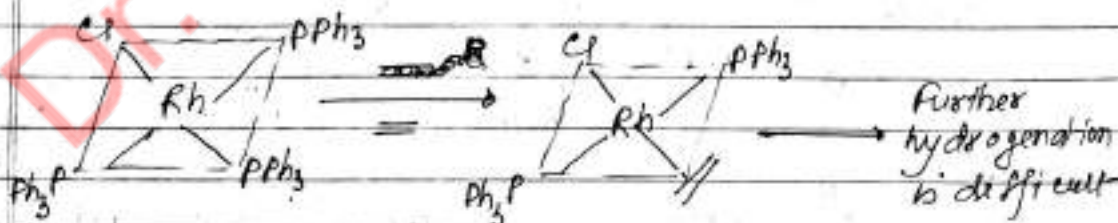
Step-4: One of the hydrogen undergoes migratory insertion of the double bond. This step is the RDS.

Step-5: Finally alkene is released rapidly by an irreversible reductive elimination step.

Important facts to support the mechanism -

1. The rate of the reaction decreases when excess of PPh_3 is added, indicating initial dissociation of one of the PPh_3 ligand before dihydrogen activation.

2. It is observed that strong π -acids like ethylene act as poisons by binding strongly with the electron rich Rh metal center and inhibit hydrogenation.

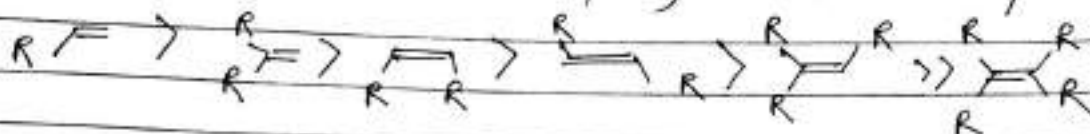


Though ethylene cannot be hydrogenated in presence of Wilkinson catalyst under normal condition, hydrogen transfer can be achieved with performed dihydride complex.

The rate of hydrogenations decreases with increase in the alkyl group substitution on double bond

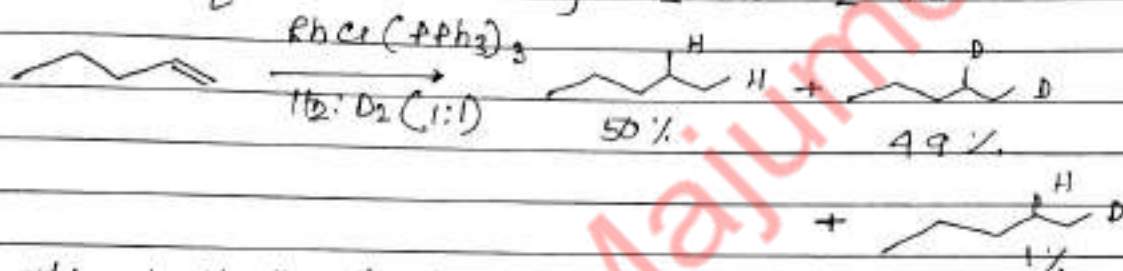
Dr. Manoj Majumdar, M.T.C.

probably due to mirroring their relative binding affinities to the metal center and also partly due to steric effect.



Therefore, for a successful hydrogenation, oxidative addition of dihydrogen polar to the binding of olefin is crucial.

3. There is minimal scrambling of H/D in the product, when an equimolar mixture of H_2 and D_2 are used.



This indicates the formation of dihydride complex that transfers both of its hydride ligands to the olefin and that the final reductive elimination step is very fast and irreversible.