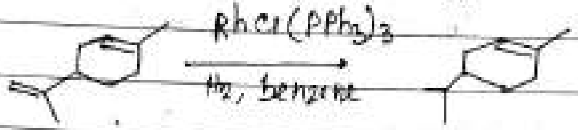
Dr. Manoj Majumder, MTSC

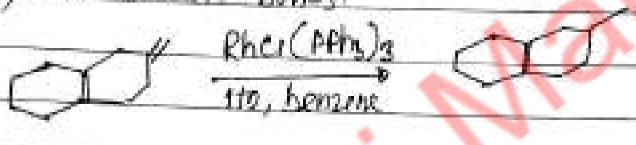
Examples of selective hydrogenation by wilkinson Catalyst — Specially for CSIR NET, GATE, JAM.

Wilkinson catalyst can be used to achive selective hydrogenations.

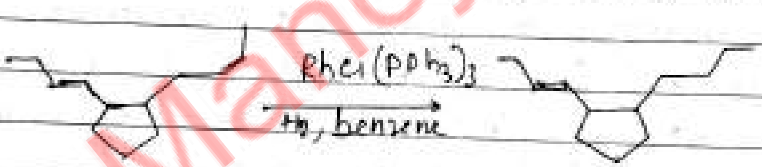
(i) Less substitution and sterically less hindered double bonds are selectively hydrogenated.



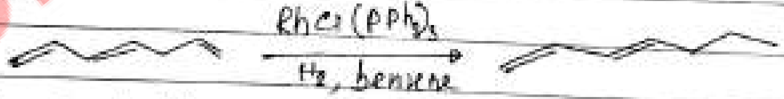
(ii) Exocyclic double bonds are selectively hydrogenated over endocyclic double bonds.



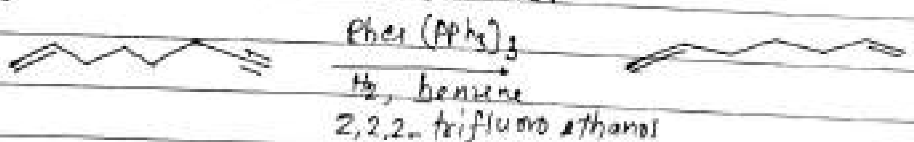
(iii) Cis alkenes are reduced rapidly than trans alkenes.



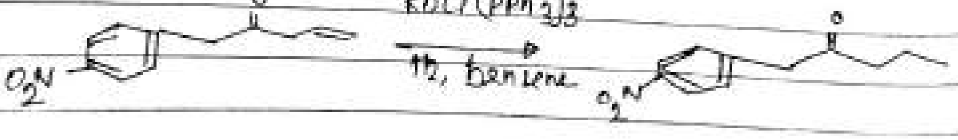
(iv) Isolated double bonds are rapidly hydrogenated over Conjugated dienes.



(v) Terminal alkynes are hydrogenated more rapidly than terminal alkenes. The selectivity can be enhanced by using acidic alcohalic co-solvents.

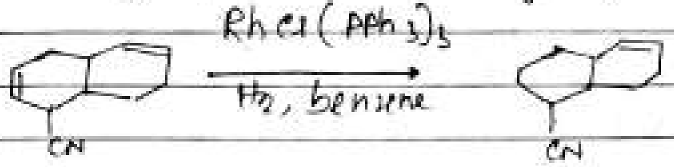


(vi) Functional groups like $>C=O$, $>C=N$, $-NO_2$, Aryl, $-CO_2R$ etc. are uneffected. The compatibility of Wilkinson's catalyst with polar multiple bonds indicates the metal hydride bond is primarily covalent in nature.



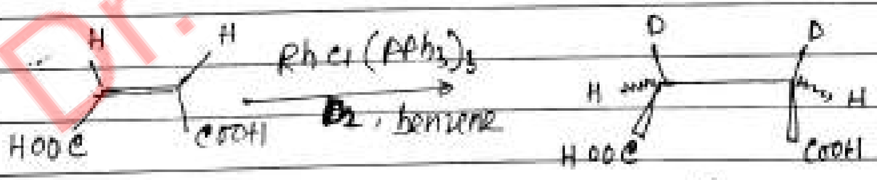
But sterically unhindered aldehyde groups are susceptable to decarbonylation

(vii) Unsaturated substrates containing polar functionality are hydrogenated more rapidly. It may be due to easy co-ordination of olefin to the catalyst that is assisted by polar functional group.



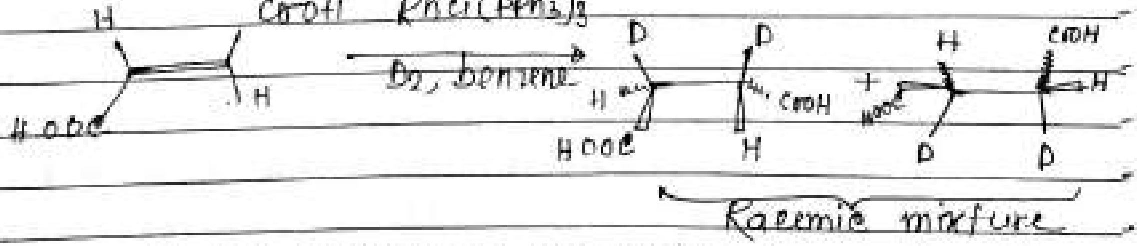
Stereochemistry of wilkinson hydrogenation :—
Hydrogenations catalyzed by wilkinson's catalyst involve stereospecific syn hydrometallation of multiple bond followed by stereospecific reductive elimination. Hence the hydrogenation of olefins or alkynes result in syn addition products.

Eg.- Hydrogenation of Maleic acid or fumaric acid with D_2 in presence of wilkinson catalyst is diastereoselective. Hydrogenation of Maleic acid with D_2 give meso compound exclusively.



Meso

whereas with fumaric acid, a racemic mixture is formed.



Hence wilkinson's ~~catalyst~~ hydrogenation is both stereospecific as well as stereoselective.

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Substitution in planar complexes :- Most of the Kinetic work in square planar complexes has been done on derivatives of d^8- Configurations viz Pt(II), Ni(II), Pd(II) and Au(III). Compared to octahedral complexes, the square planar complexes are considerably less subject to steric factors. An associative mechanism has been suggested for substitution in planar complexes, since the rate constants for the replacement of Cl by H_2O in the complexes $PtCl_4^{2-}$, $Pt(NH_3)Cl_3^-$, $Pt(NH_3)_2Cl_2$ and $Pt(NH_3)_3Cl^+$ are nearly the same and for a dissociative process, the rate of substitution should depend on the charge on the complex.

A five co-ordinate transition state has been proposed, associative mechanism and this is quite reasonable since five co-ordinate d^8 complex are known.

For substitution reactions of the general type

$$L_nPtCl_{4-n} + Y \longrightarrow L_nPtCl_{3-n} + Cl^-,$$

the usual form of the rate law is :-

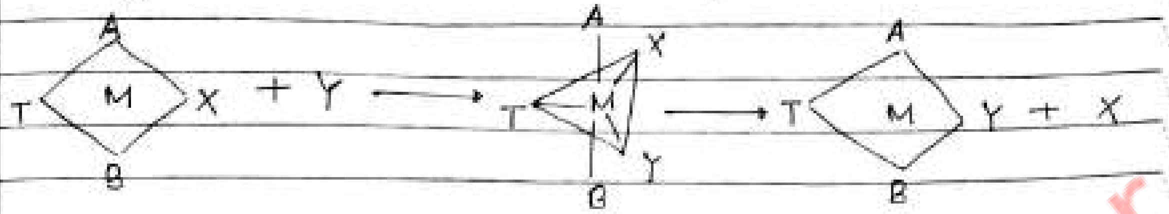
$$-\frac{d}{dt}[L_nPtCl_{4-n}] = k_1[L_nPtCl_{4-n}] + k_2[L_nPtCl_{4-n}][Y]$$

The above expression indicates that the reaction proceeds simultaneously by two different mechanisms. The 2nd term on the right hand side corresponds to S_N2 mechanism. The first term shows a first order dependence on the substrate and it appear in the rate eqn, only when the solvent (eg. water) is a potential ligand. This corresponds to a two stage process, in which Cl^- is replaced by the solvent (water) initially in a slow S_N2 ~~type~~ step, which is followed by a rapid displacement of H_2O by the incoming ligand Y.

In most of the reactions, with Pt(II), substitution takes place with retention of geometrical isomerism. This is interpreted as follows -

The entering ligand (Y) attacks the complex from one side of the plane with the formation of a trigonal bipyramidal transition state as shown in the following scheme where M is the central metal ion, Dr M. Majumder, MTBC

T, A, B and X are four ligands and Y is the entering ligand (the ligand 'trans' to T is replaced by Y)



Again for many reactions of substitution at Pt(II), K_2 is the rate expression written earlier is found to increase in the sequence

$F^- \sim H_2O < NH_3 \sim Cl^- < Br^- < Py < I^- < CN^-$

which is called the nucleophilicity sequence for the reaction series.

'Trans' effect in square planar complexes : for CSIR-NET

This is an effect which gives the relationship between the reaction rate and the nature of the ligand trans with respect to the departing species. The general order of 'trans' effect ie the trans directing influence of the 'spectator' ligand is in the increasing order →

$H_2O \sim OH^- \sim NH_3 \sim Py < Cl^- < Br^- < I^- \sim NO_2^- < C_6H_5^-$
$< CH_3^- < PR_3 \sim H^- << CO \sim CN^- \sim C_2H_4$

The trans effect is illustrated by studying reaction of the type.

$$LPtX_3 + Y \longrightarrow LPtX_2Y + X.$$

Thus we observe the following characteristics of two similar reactions.

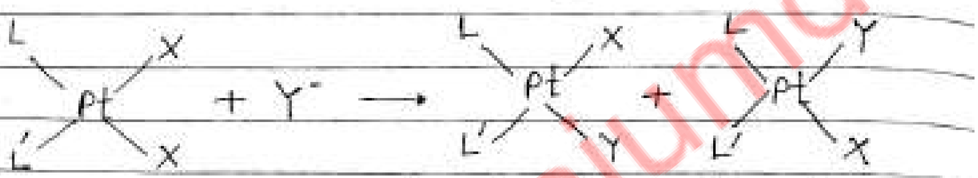
$$PtCl_4^{2-} \xrightarrow{NH_3} Pt(NH_3)Cl_3^- \xrightarrow{NH_3} cis\text{-}Pt(NH_3)_2Cl_2$$

$$Pt(NH_3)_4^{2+} \xrightarrow{Cl^-} Pt(NH_3)_3Cl^+ \xrightarrow{Cl^-} trans\text{-}Pt(NH_3)_2Cl_2$$

It is seen from the second step of the above reactions that a chloride ion in the complex directs the entering ligand into a position trans to itself more strongly than an ammonia molecule does

What we observe in the above case is actualy the relative magnitudes of the trans directing influence of Cl^- in the 1st case and NH_3 in the second case - it is more in the 1st case than in the 2nd case.

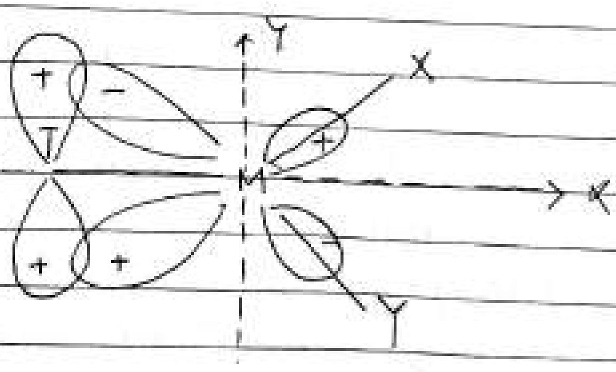
For a single general reaction of the type given below, the relative proportions of the products obtained give a method of finding the relative magnitudes of the trans effect of the ligands L and L'.



(Y is trans to L) (Y is trans to L')

The trans effect described above is the 'Kinetic trans effect', which is different from 'ground-state' or 'static trans effect', which affects physical properties such as bond length, vibrational frequency and chemical shift (in nmr)

Referring to the relative magnitudes of the trans effect of groups given earlier, the ligands CO, CN^- and C_2H_4 have relatively large trans directing influence. This is associated with their π-accepting charecter. In the following fig. the overlap of the d_{xy} orbital of the metal with π* orbital of the ligand T is represented to show that the electron density at the trans position is lowered to facilitate a bimolecular substitution. In the fig., X is the leaving group at the trans position (trans to T) and Y the entering ligand.



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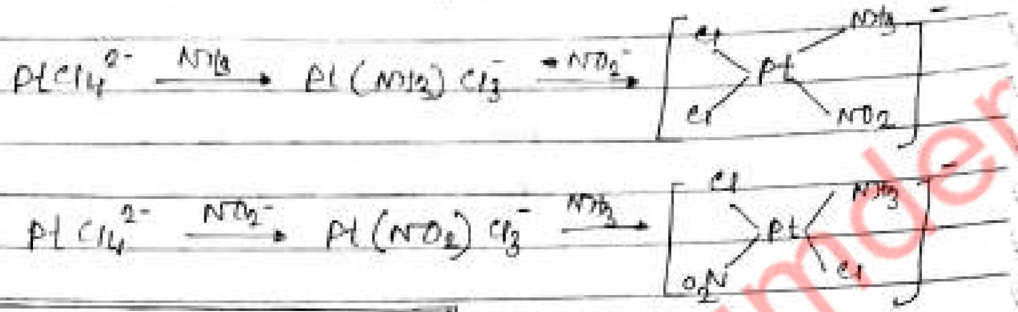
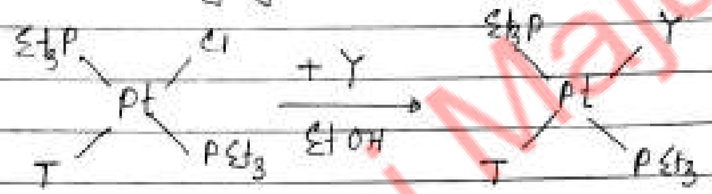
The trans effect is utilised in devising the synthesis of some Pt(II) complexes. e.g - preparation of cis and trans $Pt(NH_3)(NO_2)Cl_2^-$ from $PtCl_4^{2-}$. The order of substitution is varried as shown below—



Effect of the entering group— for CSIR NET

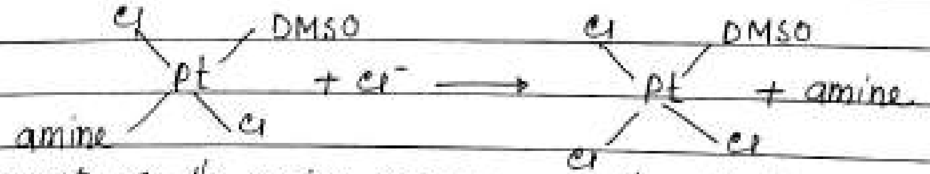


T = Cl^-, Me^- and Ph^-

when $Y = Br^-, N_3^-$ and NO_2^- or py (all relatively weak nucleophiles, the trans effect order is: $Me^- > Ph^- > Cl^-$, when the better nucleophile I^- is used, the trans effect order is changed: $Me^- > Cl^- > Ph^-$. Thus the influence of the trans director and the entering group cannot be considered in isolation.

Effect of leaving group—

In the reaction,



as the basicity of the amine increases, the displacement becomes more difficult. This shows that the bond-breaking is important in the rds.

X-ray crystallography measurements shows that the bond length of Pt–Cl bonds trans to Et_3P, C_2H_4, and Cl decrease in the order. bond strengths increase in the same order.