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**Subject: Chemistry**  
**Class for which the note is prepared: Semester-6**  
**Paper: C13T (Inorganic Chemistry)**  
**Topic: Organometallic Chemistry**  
**Part 4**

**Comments-** Study the whole topic thoroughly.

**[N.B. - Acknowledgement of indebtedness to Mr.Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry]**

## Pentaaquanitrosonium iron (I) Sulphate $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^+\text{SO}_4^-$

### ● Preparation:

When freshly prepared sol<sup>n</sup> of  $\text{FeSO}_4$  is added to the water extract of a nitrate and conc.  $\text{H}_2\text{SO}_4$  is poured carefully along the sides of the test tube a brown-black ring is formed at the junction of the two layers. This brown black ring is a nitroferrous sulphate.

The formation of this complex takes place through the following steps

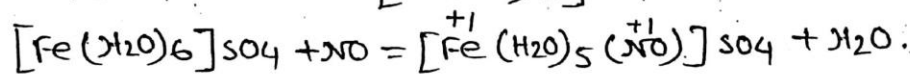
i) Nitrate reacts with conc  $\text{H}_2\text{SO}_4$  and produces  $\text{HNO}_3$

$$\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$$

ii)  $\text{HNO}_3$  produced as above oxidises  $\text{FeSO}_4$  to  $\text{Fe}_2(\text{SO}_4)_3$  in presence of  $\text{H}_2\text{SO}_4$  and is itself reduced to  $\text{NO}$

$$6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 = 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O}$$

iii)  $\text{NO}$  produced as above is absorbed by the aq. sol<sup>n</sup> of  $\text{FeSO}_4$  and brown black  $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^+\text{SO}_4^-$  is obtained

$$\text{FeSO}_4 + 6\text{H}_2\text{O} = [\text{Fe}(\text{H}_2\text{O})_6]^+\text{SO}_4^-$$


This brown black colour is due to the  $\text{Fe}^+ \rightarrow \text{NO}^+$  charge transfer bands occurring in the visible region.

### ● Properties:

$[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^+\text{SO}_4^-$  is stable only at low temp<sup>r</sup> and decomposes on heating with the evolution of  $\text{NO}$ .

$$[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^+\text{SO}_4^- \xrightarrow{\Delta} \text{FeSO}_4 + \text{NO} + 5\text{H}_2\text{O}$$

● Uses: i) The formation of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^+\text{SO}_4^-$  has been utilized in the identification of the  $\text{NO}_3^-$  ion in ring test.

ii) Decomposition of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is employed for the purification of NO and its separation from other gases.

• Structure :

The magnetic moment  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  has been found to be equal to 3.9 BM. This value shows that Fe has three unpaired electrons i.e., Fe is present as  $\text{Fe}^{\oplus}$  which has its valence shell configuration as  $3d^7 4s^0$ . The presence of unpaired electrons can be explained only when it is assumed as  $\text{Fe}^+$  is  $sp^3d^2$  hybridization in  $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$  ion.  $sp^3d^2$  hybridization of  $\text{Fe}^+$  has been explained by valence bond theory of complex compound.

According to CFT the valence shell configuration of  $\text{Fe}^{\oplus}$  is  $t_{2g}^5 e_g^2$  which gives three unpaired electrons.

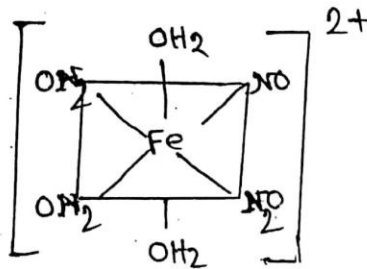


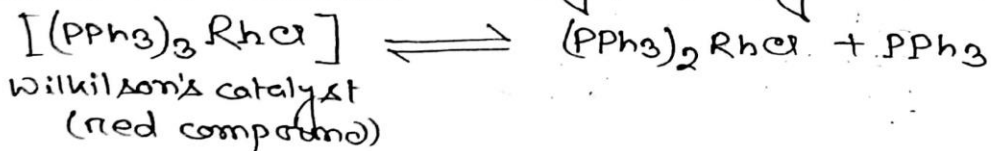
Fig: Octahedral structure (HS) of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  ion

## Alkyl Hydrogenation : [Wilkinson's Catalyst]

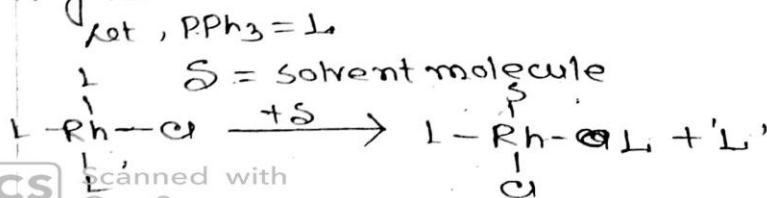
Although the react<sup>n</sup> of  $H_2$  gas with alkene [eg  $\rightarrow C_2H_4$ ] is thermodynamically favourable it does not take place at room temperature and pressure. That is the react<sup>n</sup>  $CH_2=CH_2 + H_2 \rightarrow CH_3-CH_3$  does not take place at room temperature and pressure.

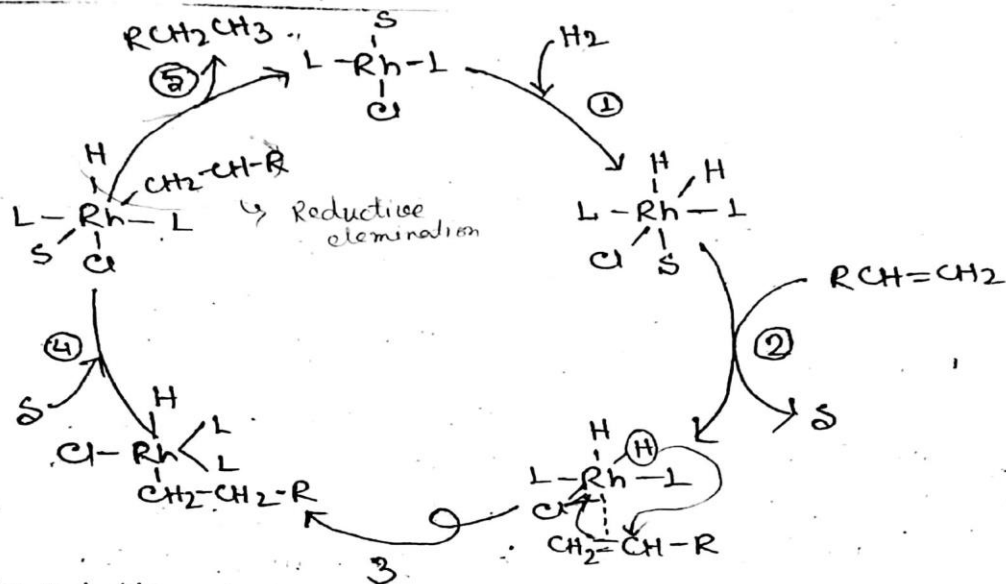
The 1st effective homogeneous catalyst to be discovered for hydrogenation was the square planar 16-e complex  $\Rightarrow$  chloro tri<sup>s</sup> (triphenyl phosphine) rhodium(I)  $(PPh_3)_3RhCl$ . It is known as Wilkinson's catalyst.

It may be prepared by refluxing  $RhCl_3$  with an alcoholic sol<sup>n</sup> of  $PPh_3$  in excess. The red compound undergoes very little dissociation in sol<sup>n</sup> in benzene.



The  $(PPh_3)_3RhCl$  molecule is solvated and can undergo oxidative addition with a molecule of  $H_2$ . An alkene can then coordinate and react with a coordinated  $H_2$ -ligand, to form an alkyl gr. This react<sup>n</sup> will result from migration of a  $H_2$  from the metal to a carbon in the coordinated alkene. Reductive elimination now gives back  $(PPh_3)_2RhCl$  solvated with the liberation of alkane. The process can be represented by the following cycle.

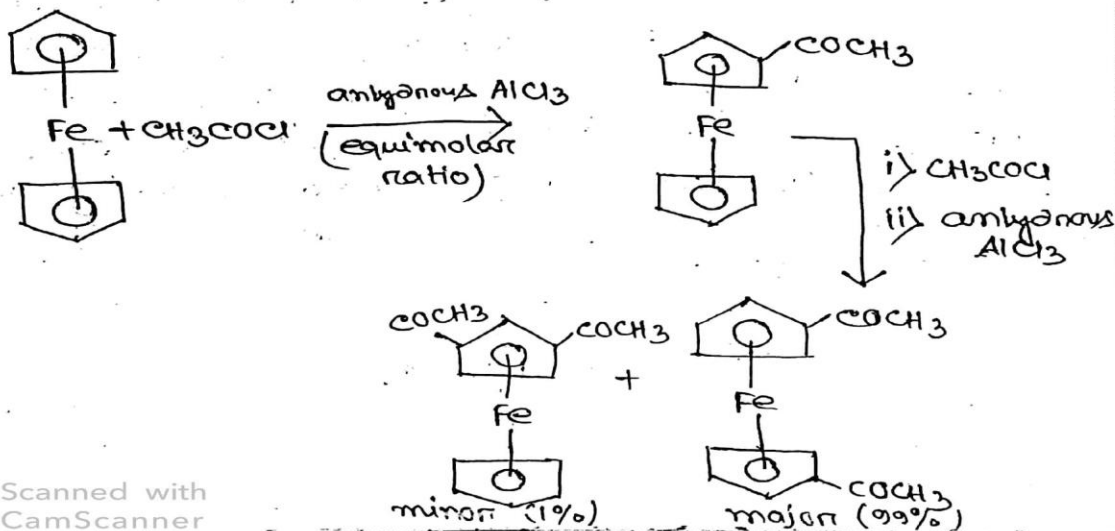




Catalytic cycle for the hydrogenation of alkenes

- 1) Oxidative Addition
- 2) co-ordination of alkene
- 3) Migratory insertion
- 4) Solvation
- 5) Reductive elimination.

How will you chemically show that the two cyclopentadiene rings in this compound (Ferrocene) freely rotate around the M-L axis.



Almost all the prod of this reac<sup>n</sup> is 1,1' isomer (ie, acetylo groups in the two different rings) with 1-2 isomer as a minor prod. This indicates the free rotation of the rings with respect to each other about the Cp-Fe-Cp axis.

Q Do you expect any rotation of the ethylene molecule in Zeise's salt without hampering the stability of the complex? — Explain.

Since the  $dxz$   $dzx$  orbitals are degenerate in the complex (Zeise's salt), the  $\pi$ -back bonding from metal to olefin will not be hampered if the C-C bond in ethylene remains in the plane of the  $PtCl_3$  portion. In other words the orientation of the ethylene molecule perpendicular to the  $PtCl_3$  plane is not essential for the stability of the molecule. The metal-olefin  $\sigma$ -bond (along the  $z$ -axis) offers no resistance to rotation of the alkene about the metal-olefin bond axis. The rotational barrier in the related complexes is only 40-70 kJ/mol.

Steric reason may be supposed to operate behind the perpendicular orientation of the ethylene molecule. Since this arrangement provides less congestion compared to the in plane orientation.

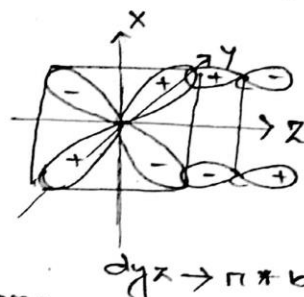
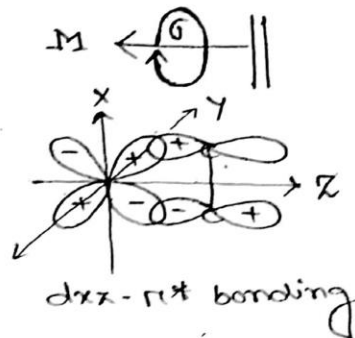


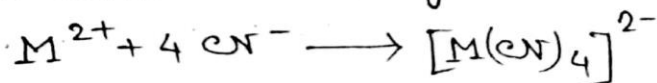
Fig: Rotation of the ethylene molecule around Pt-Et  $\sigma$ -bond axis

## Masking & Demasking agents

Masking may be defined as the process in which a substance without physical separation of it or its react products, is so transformed that it does not enter into a particular react. The species by which masking process takes place is known as masking agent.

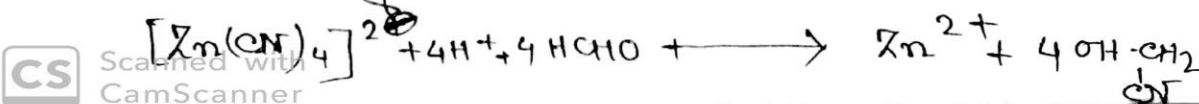
Demasking is the process in which the masked substance regains its ability to enter into a particular react. The species by which demasking process take place is known as demasking agent.

By the use of masking agents, some of the cations in a mixture can often be masked so that they can no longer react with EDTA or with the indicator. An effective masking agent is the  $CN^-$  ion. This ion forms stable cyanide complexes with the cations of Cd, Zn, Cu, Co, Ni, Ag, and Pt metals, but not with the alkaline earth metals, Mg and Pb.



Therefore it is possible to determine cation such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Pb^{2+}$  and  $Mn^{2+}$  in the presence of above mentioned metal by masking with an excess of KCN ~~and~~ NaCN.

The cyanide complexes of Zn and Cd may be demasked with  $HCHO$  or  $CH_3COOH$  sol<sup>n</sup> or with chloral hydrate.



The use of masking and demasking agents permits the successive titration of many metals. Thus a sol<sup>n</sup> containing Mg, Zn and Cu can be titrated as follows;

- i) Add excess of standard EDTA and back titrate with standard Mg sol<sup>n</sup> using EBT as indicator. This gives the sum of all the metals present.
- ii) Treat an aliquot portion with excess of KCN and titrate as before, this gives Mg only.
- iii) Add excess of chloral hydrate or formaldehyde - acetic <sup>acid</sup> sol<sup>n</sup> (3:1) to the titrated sol<sup>n</sup>, in order to liberate the Zn from the cyanide complex and titrate until the indicator turns blue. This gives Zn only. The Cu content may then be found by difference.

