Quadrant I - Notes

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Paper Code: CHC - 109

Paper Title: Inorganic chemistry (Section A)

Unit: Organometallic Chemistry

Module Name: Mononuclear Metal Carbonyl- Ni(CO)₄: Preparation, Properties, Structure and

Bonding

Module No: 5

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Metal carbonyl are complexes of CO ligand with transition metal in low oxidation state. Depending on the number of metal atoms they can be classified as mononuclear, binuclear or polynuclear carbonyls. The oxidation state of metal is zero, low positive or negative.

Tetracarbonylnickel - Ni(CO)₄

It is the first metallic carbonyls to be discovered and has found application in the metallurgy of nickel by Mond's process.

PREPARATION METHODS

i) Passing CO over finely divided metallic Ni below 100°C

$$Ni + 4CO \rightarrow Ni(CO)_4$$

ii) Passing CO through alkaline suspension of Ni(CN)₂ or NiS

$$Ni(CN)_2 + 4CO \rightarrow Ni(CO)_4 + C_2N_2$$

 $NiS + 4CO \rightarrow Ni(CO)_4 + S$

iii) By the action of CO on nickel (II) phenyl dithiocarbamate

 $2Ni(S.SC.NH.C_6H_5)_2 + 4CO \rightarrow Ni(CO)_4 + Ni(S.SC.NH.C_6H_5)_4$

PROPERTIES

i)

- a) Ni(CO)₄ is a colourless liquid boiling at 43°C and solidify at -25°C.
- b) It is Miscible with benzene and insoluble in water.
- c) No action of dilute acids or alkalies and highly poisonous
- ii) Action of H₂SO₄

$$Ni(CO)_4 + H_2SO_4 \rightarrow NiSO_4 + H_2 + 4CO$$

iii) Action of NO

$$2Ni(CO)_4 + 2NO + 2H_2O \rightarrow 2Ni(NO)$$

(OH) + H₂ + 4CO

iv) Substitution reactions

$$Ni(CO)_4 + 2NO_2 \rightarrow Ni(NO_2)_2 + 4CO$$

v) Action of heat

$$Ni(CO)_4 \rightarrow Ni + 4CO$$

vi) Oxidation reactions

$$Ni(CO)_4 + Br_2 \rightarrow NiBr_2 + 4CO$$

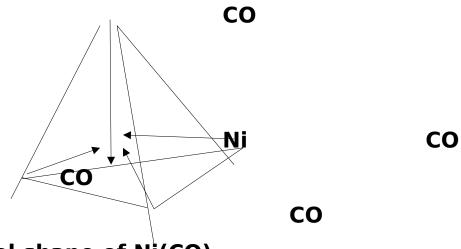
v) Reduction reaction : gets reduced by several reducing agents

$$4Ni(CO)_4 + 2Na \rightarrow Na_2[Ni_4(CO)_9] + 7CO$$

Bonding in Ni(CO)₄

Free Ni atom has electronic configuration of $3d^8$ $4s^2$. In this molecule Ni atom is sp^3 hybridised. Both the electrons of 4s orbital are shifted to 3d orbitals to vacate 4s orbital. Then 4s and 4p on mixing together give four sp^3 hybrid orbitals. The formation of four Ni \leftarrow CO σ bonds takes place. Due to sp^3 hybridization Ni(CO)₄ has tetrahedral shape.

STRUCTURE OF Ni(CO)₄



Tetrahedral shape of Ni(CO)₄