

Physical and Chemical Properties of Metal Carbonyls

PHYSICAL PROPERTIES

State:

Majority of the metallic carbonyls are liquids or volatile solids.

Colour:

Most of the mononuclear carbonyls are colourless to pale yellow. $V(CO)_6$ is a bluish-black solid.

Polynuclear carbonyls exhibit are dark in colour.

Solubility:

Metal carbonyls are soluble in organic solvents like glacial acetic acid, acetone, benzene, carbon tetrachloride and ether.

Toxicity:

Due to low melting points and poor thermal stability, they show toxicity related to the corresponding metal and carbon monoxide. Exposure to these compounds can cause damage to lungs, liver, brain and kidneys. Nickel tetracarbonyl exhibits strongest inhalation toxicity. These compounds are carcinogenic over long-term exposure.

Magnetic Property:

All the metal carbonyls other than vanadium hexacarbonyl are diamagnetic. The metals with even atomic number form mononuclear carbonyls. Thus, all the electrons in the metal atoms are paired. In case of dinuclear metal carbonyls formed by metals with odd atomic number, the unpaired electrons are utilized for the formation of metal-metal bonds.

Thermal Stability:

Most of the metal carbonyls melt or decompose at low temperatures. Solid carbonyls sublime in vacuum but they undergo some degree of degradation.

Thermodynamic Stability:

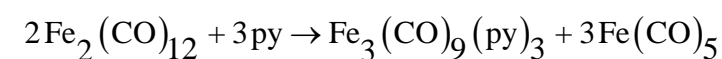
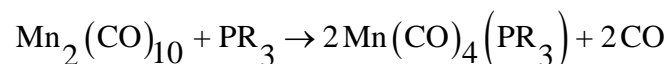
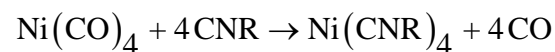
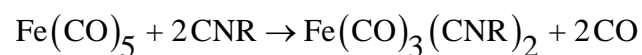
Metal carbonyls are thermodynamically unstable. They undergo aerial oxidation with different rates. $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$ are oxidized by air at room temperature while chromium and molybdenum hexacarbonyls are oxidized in air when heated.

CHEMICAL PROPERTIES

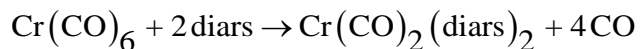
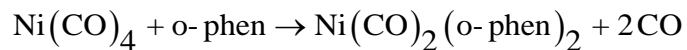
The metal carbonyls give a variety of chemical reactions.

Ligand substitution reactions:

Substitution of carbon monoxide ligand by various mono dentate and bidentate ligands can be carried out using thermal and photochemical reactions. Monodentate ligands like isocyanides (CNR), cyanide (CN⁻), phosphine (PR₃) and ethers can partially or completely replace the carbonyl group.

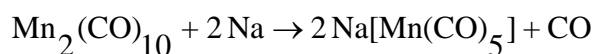
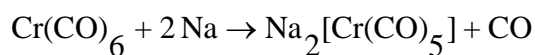


Bidentate ligands like o-phenylene-bis(dimethyl arsine) (diars) and o-phenanthroline(o-phen) can replace carbonyl groups in the multiple of two.



Reaction with metallic sodium:

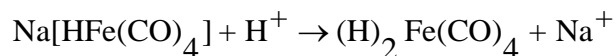
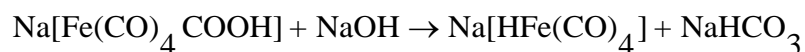
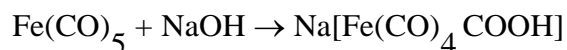
Metallic sodium and its amalgam can be used to reduce the metal carbonyls.



In the above two reactions, the Cr and Mn atoms in their zero oxidation states are reduced to -2 and -1 oxidation states respectively.

Reaction with sodium hydroxide:

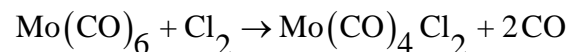
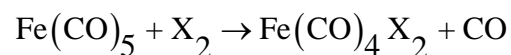
The reaction of sodium hydroxide with metal carbonyls results in nucleophilic attack by hydroxide ion on the carbonyl group to give a metal carboxylic acid complex. Upon further action with sodium hydroxide, the carboxylic acid gives up carbon dioxide to form a hydrido anion. The protonation of this anion results in the formation of iron tetracarbonyl hydride as shown below:



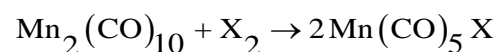
The above reaction is known as Heiber base reaction.

Reaction with halogens:

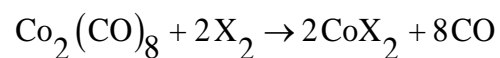
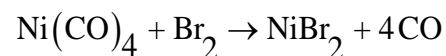
Most of the metal carbonyls react with halogens to give carbonyl halides



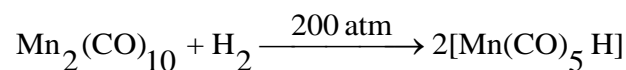
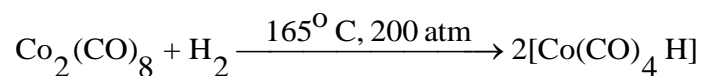
Halogens can cause cleavage in the metal-metal bonds in case of polynuclear carbonyls



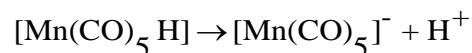
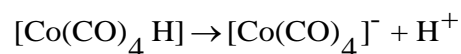
Some carbonyls undergo decomposition upon reaction with halogens

**Reaction with hydrogen:**

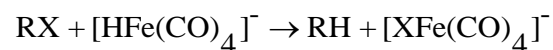
Some of the carbonyls can be reduced by hydrogen to give carbonyl hydrides



Even though, these compounds are named as hydrides, they are known to behave as proton donors. The neutral hydrides like $[\text{Co}(\text{CO})_4\text{H}]$ and $[\text{Mn}(\text{CO})_5\text{H}]$ behave as acids as shown below:

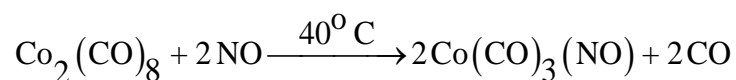
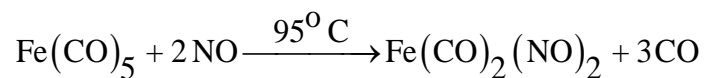


The anionic hydrides like $[\text{HFe}(\text{CO})_4]^-$ are true hydrides and behave as reducing agents for alkyl halides as shown below:



Reaction with nitric oxide:

A good number of metal carbonyls react with nitric oxide to give carbonyl nitrosyls.



The reaction between iron pentacarbonyl and nitric oxide involves replacement of three carbonyl groups by two nitric oxide molecules. Electronically, this is equivalent as nitric oxide is a three electron donor ligand whereas carbon monoxide is a two electron donor.

Source :

<http://nptel.ac.in/courses/104106064/3>