TDC Part I
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Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR
B. R. A. BIHAR UNIVERSITY
Dr. Priyanka

TOPIC:-GROUP -14

Oxidation states and Bond Type

Catenation and multiple bond formation

Intercalation compounds

Chemical properties

Oxidation states and Bond Type

The commonly observed oxidation states in this group are +4 and +2. Carbon and silicon are generally tetravalent but on descending the group the stability of the +4 oxidation state decreases due to inert pair effect. The +2 oxidation state becomes important progressively and lead is predominantly divalent. Therefore Pb(IV) compounds like $PbCl_4$ and PbO_2 are highly oxidizing and PbO_2 may oxidize hydrochloric acid to chlorine.

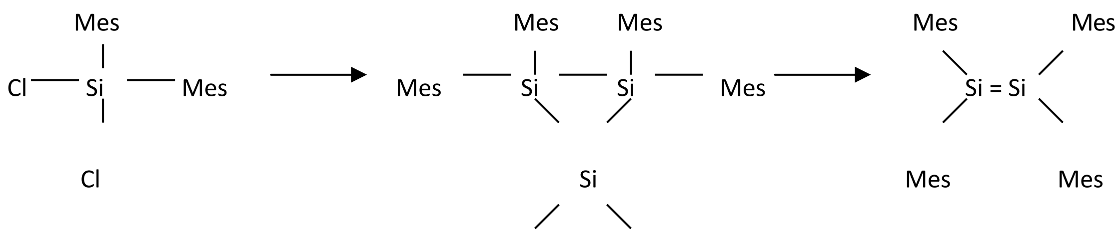
$$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$$

The lower oxidation state is more ionic as M^{4+} is smaller than M^{2+} and covalence is favored by large charge on cations and small size. In tetravalent compounds the Group 14 element is sp^3 hybridized. Carbon has greater electronegativity and may form carbide ion, C^{4-} and C_2^{2-}

Catenation and multiple bond formation

Carbon has a remarkable property of forming long chains and rings when bound to itself. This is called catenation and is attributed to the strength of the C-C bond, The M – M bond strength decreases down the group and tendency for catenation also decreases. Carbon also forms pл – pл bonds with itself and other electronegative elements e.g. C=C, C≡C, C=O, C=S and C≡N linkages are known. The other elements do not form such bonds. The reluctance of the silicon atom to form multiple bonds is revealed by the fact that silicon adopts a diamond – like structure and not graphite – like structure; CO_2 is a gas comprising of discrete stable O=C=O units whilst SiO_2 is a high-melting solid having a net-work three- dimensional structure of Si-O-Si linkage.

Chemists have been exploring the tendency of the silicon atom to form multiple bonds. Transient reaction species containing the Si = C bond have been known since 1966 and the first such species, $Me_2Si = CHMe$ was isolated a decade later. In view of the extensive chemistry of alkenes it was natural to search for analogous compounds containing the > Si = Si < bond. The first such compound, tetramesityldisilene, was isolated in 1981 as orange crystals following photolysis of cyclotrisilane.



where, Mes =Mesityl

Mes Mes

The Si = Si distance in such compounds lies in the range 214 to 216pm considerably shorter than the normal single bonded Si—Si distance. Disilenes are chemically very reactive and it is possible to add reagents like halogens, HX and EtOH across the Si = Si double bond. The 3p orbitals of Si are larger and more diffused than the 2p orbitals of C; therefore the π-bond formed between the Si atoms is weaker than that between the C atoms.

<u>Intercalation compounds</u>

The structure of graphite indicates loosely bound layers separated by a large distance. Many molecules can be inserted in the space between the layers forming intercalation compounds of varying composition. The interlayer distance increases in these compounds. If the graphite sheets remain flat, then the new compound retains the structure and conductivity of graphite. If the attacking species add electrons, the conductivity increases.

Heating graphite 300^0 C in presence of vapors of K, Rb and Cs gives bronze coloured compounds C_8M, on heating further at reduced pressure, some of the metal is lost and intercalation compounds are formed which vary in colour, depending on the number of layers invaded by the metal.

C_8M ⟶ $C_{24}M$ ⟶ $C_{36}M$ ⟶ $C_{48}M$

C_8M: Bronze (every layer is occupied)

$C_{24}M$: steel blue (every second layer is occupied)

$C_{36}M$: blue (every third layer is occupied)

$C_{48}M$: Black (every fourth layer Is occupied)

Intercalation compounds of graphite are known with $FeCl_3$, chlorine, bromine, some metal oxides and sulphides. The intercalated compounds exhibit interesting properties.

Chemical properties

The chemical reactivity increases down the group. Some reactions of Group 14 elements are shown in table 1

Table 1 : Some Reactions of Group 14 Elements

HCl (hot, concentrated)	$M + 2\,HCl \longrightarrow MCl_2 + H_2$	M = Sn, Pb
H_2SO_4 (hot, concentrated)	$M + 2H_2SO_4 \longrightarrow MO_2 + 2SO_2 + 2H_2O$	M = Sn, Pb, C slow for Ge
HNO_3 conc.	$3\,M + 4HNO_3 \longrightarrow 3MO_2 + 4\,NO + 2H_2O$ $3\,Pb + 2HNO_3 \longrightarrow 3PbO + 2NO + 4H_2O$	M=Ge, Sn
NaOH (aq)	$Si + 2NaOH + H_2O \quad Na_2SiO_3 + 2H_2$	-
O_2 / air (heat)	$M + O_2 \quad MO_2$ $2Pb + O_2 \quad 2PbO$	M=C, Si, Ge, Sn
Cl_2 (heat)	$M + 2Cl_2 \quad MCl_4$ $Pb + Cl_2 \quad Pb\,Cl_2$	M=C, Si , Ge, Sn