PSEUDOHALOGENS

Pseudohalides are certain uni-negative groups (CN^- , OCN^- , N_3^- etc.) which are made up of two or more electronegative atoms and resemble halide ions in some respects. Examples of some important pseudohalide ions are : cyanide ion(CN^-) ; cyanate ion(OCN^-) ; isocyanide ion(NC^-) ; fulminate ion (ONC^-) ; isocyanate ion(NCO^-) ; selenocyanate ion ($SeCN^-$) ; isoselenocyanate ($NCSe^-$) ; azide ion (N_3^-) etc.

As the dimers of halide ions are called halogens, the covalent dimmers of the pseudohalide ions are called pseudohalogens. Example of some pseudohalogens are cyanogen $(CN)_2$, oxycyanogen $(OCN)_2$; thiocyanogen $(SCN)_2$; selenocyanogen $(SeCN)_2$; azidocarbon disulphide$(SCSN_3)_2$ etc.

The pseudohalides does not forms pseudohalogens. Example: azide (N_3^-).

PREPARATIONS:

1. Reaction of copper sulphate with potassium cyanide gives cyanogens at 60°C
   $2CuSO_4 + 4KCN \rightarrow (CN)_2 \uparrow + 2CuCN + 2K_2SO_4$
   Cyanogen is a colourless poisonous gas.
2. Thiocyanogen may be prepared by suspending AgSCN in diethyl ether or SO_2(liquid) and oxidising the anion SCN^- at low temperature with Br_2 or I_2 . $(SCN)_2$ melts at ~ -7°C to an orange suspension which rapidly polymerise to the brick-red $(SCN)_x$.

DISSIMILARITY BETWEEN HALOGENS AND PSEUDO HALOGENS

Pseudohalogens undergo polymerisation and form polymerised species. For example:

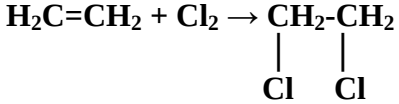
$n(CN)_2$ [500°C]→ $2(CN)_n$

$n(SCN)_2$ [Room temp.]→ $2(SCN)_n$

Halogens have no tendency to undergo polymerisation.

Similarities between halogens and pseudohalogens:

1. Like halogens, pseudohalogens are also dimeric and fairly volatile in the free state.
2. Pseudohalogens are isomorphous to halogens when in the free or solid state. For example Cl_2 is isomorphous to $(CN)_2$ and similarly Br_2 is isomorphous with $(SCN)_2$.
3. Like halogens, pseudohalogens also add to ethylenic double bond linkage.



$$H_2C=CH_2 + (SCN)_2 \rightarrow \underset{\underset{SCN}{|}}{CH_2}\text{-}\underset{\underset{SCN}{|}}{CH_2}$$

4. **Reaction with alkalies :** Like halogens, pseudohalogens also react with alkalies.

Cl_2 + 2KOH (cold, dilute) → KCl + KOCl + H_2O
$(SCN)_2$ + 2KOH (cold, dilute) → KSCN + KOSCN + H_2O

$3Cl_2$ + 6KOH (Hot, concentrated) → 5KCl + $KClO_3$ + $3H_2O$
$3(SCN)_2$ + 6KOH (Hot, concentrated) → 5KSCN + $KSCNO_3$ + $3H_2O$

5. Like halogens, pseudohalogens also combine with hydrogen to form monobasic hydracids. (Ex. HCN, HSCN, HSeCN etc.)

SIMILARITIES BETWEEN HALIDE IONS AND PSEUDOHALIDES:

The main points of similarity between the pseudohalogens and the halogens are that they may be reduced to corresponding uni-negative anions of similar chemical behaviour.

1. Like the dihalogen molecules, the pseudohalogens undergo thermal and photochemical dissociation.
   Cl_2 -hν→ 2Cl• ; $(CN)_2$ -hν→ 2CN•
2. The pseudohalide anions like halides may be oxidised to the corresponding pseudohalogens.
   $I_2 + 2e \rightarrow 2I^-$ **E° = + 0.54 V**
   $(SCN)_2 + 2e \rightarrow 2SCN^-$ **E° = +0.77 V**

3. Like halide ions, pseudohalide ions also form complex ions with transition metal ions. Complex ions given by halide ions: FeF_6^{3-} ; $CoCl_4^{2-}$; HgI_4^{2-}
   Analogous complex ions given by pseudohalide ions: $Fe(CN)_6^{3-}$; $Co(SCN)_4^{2-}$; $Hg(CN)_4^{2-}$

4. With hydrogen ion pseudohalides may form hydracids, eg. HCN, HSCN, N_3H, which are however very weak acids compared to halogen acids like HCl, HBr and HI.

5. Like halide ions, pseudohalide ions give insoluble salts with Ag+, Pb^{2+} and Hg+ cations. Like AgCl, AgCN is also white, insoluble in water but soluble in ammonia. **$Ag^+ + +Cl^- \rightarrow AgCl\downarrow$**
   $Ag^+ + +CN^- \rightarrow AgCN\downarrow$

   $2Hg^+ + 2Cl^- \rightarrow Hg_2Cl_2\downarrow$
   $2Hg^+ + 2SCN^- \rightarrow Hg_2(NCS)_2\downarrow$

   $Pb^{+2} + 2Cl^- \rightarrow PbCl_2\downarrow$
   $Pb^{+2} + 2CNS^- \rightarrow Pb(CNS)_2\downarrow$

6. Behaviour of Pb(IV) chloride and Pb(IV) pseudohalide towards heat is similar.

$$PbCl_4 + \text{-HEAT} \rightarrow PbCl_2 + Cl_2 \uparrow$$
$$Pb(SCN)_4 + \text{-HEAT} \rightarrow Pb(SCN)_2 + (SCN)_2 \uparrow$$

7. Like halide ions, pseudohalide ions also behave as a bridging ligands.