

Pseudohalogens (Halogenoids)

A number of uninegative ions are known which show close resemblance to the halides, some of them may even be oxidised to a dimeric molecule corresponding to the oxidation of halides to the dihalogen molecules. These uninegative ions are called pseudohalides and the related molecules are called pseudohalogens.

Pseudohalide	Pseudohalogen	Hydroacid
① CN^- cyanide	cyanogen $(CN)_2$	HCN
② SCN^- thiocyanate	thiocyanogen $(SCN)_2$	$HSCN$
③ $SeCN^-$ selenocyanate	selenocyanogen $(SeCN)_2$	—
④ $SCSN_3^-$ azidodithiocarbonate	azidocarbonyl disulphide $(SCSN_3)_2$	—
⑤ $TeCN^-$ Telluro Tellurocyanate	—	—
⑥ OCN^- cyanate	—	$HOCN$
⑦ NCO^- isocyanate	—	$HNCO$
⑧ CNO^- fulminate	—	$HCNO$
⑨ N_3^- azide	—	N_3H

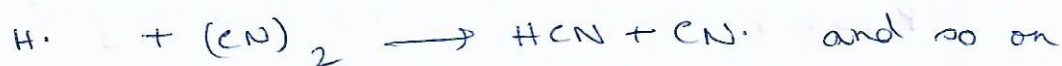
Similarities

The main points of similarity between pseudohalogens and halogens are:

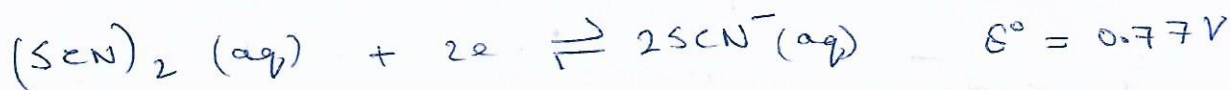
(i) Like the dihalogen molecules, the pseudohalogens undergo thermal & photochemical dissociation;



The reactions of these radicals are similar to those of halogens including chain reaction



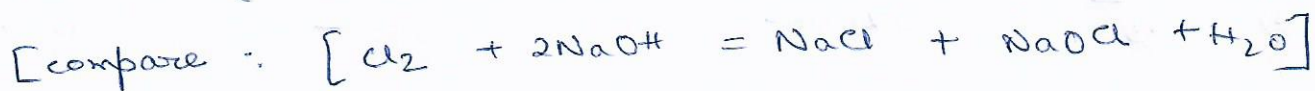
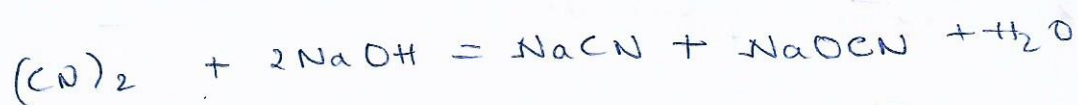
(ii) The pseudohalide anions may be oxidized easily to the pseudohalogen;



tricyanogen would oxidize iodide to I_2

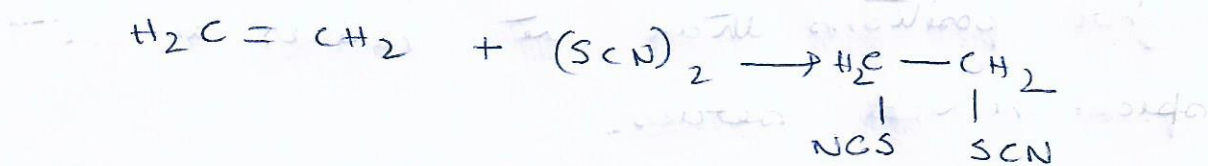


(iii) Pseudohalogens react with aqueous alkali similar to halogens:



(iv) Solubility of silver salts of pseudohalides in water resemble those of $\text{Ag}(I)$ salts of halides, i.e., AgCN is insoluble in water.

(V) Pseudohalogens can add to $C=C$ bonds eg,



(VI) Similar to halogen hydracids, there are hydracids corresponding to many pseudohalides. However these are considerably weak acids, eg - HCN $pK_a = 9.2$, N_3H $pK_a = 4.92$.

(VII) The pseudohalogens can also form interhalogens and interpseudohalogens, for eg. $ClCN$, ICN , CNN_3 .

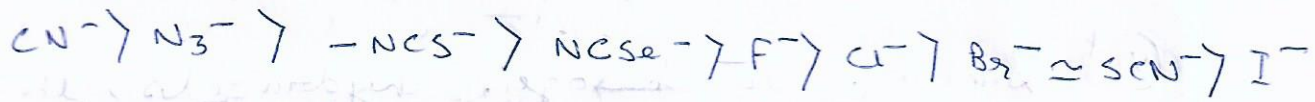
How Dissimilarities

There are some inherent differences between the halogens and pseudohalogens.

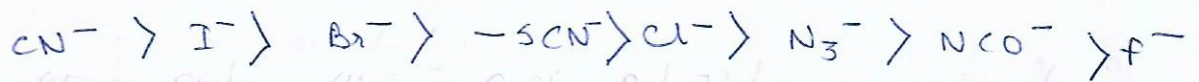
(i) Most pseudohalogens & pseudohalides are strong coordinating agents. In contrast the halides are weak ligands.

(ii) Many of them are ambident bases, having two alternating sites for coordination. In SCN^- , N is the hard base site & S is the soft base site.

(iii) The pseudohalides are good π -acids and occupy higher positions than the halides in the spectrochemical series.



(iv) Most halides are more polarizable than many of the pseudohalides, which is reflected in the nephelauxetic series



(v) The hydroacids formed by pseudohalide ions are all extremely weak.