Oxides and oxoacids of halogens

Oxidation state of halogens:

All halogens show '- I' oxidation state as they are strongly electronegative in nature. Except fluorine, other halogens show +I, +III, +V and +VII oxidation states, due to the availability of d-orbitals.

So, this oxidation state becomes increasingly reducing on going down the group. Iodine anion is a moderate reducing agent, while chloride shows few reducing characteristics except with very strong oxidizing agents. For example, if we consider PbI_4 is a non-existent compound, because of the combination of highly oxidizing and highly reducing species. In contrast $PbCl_4$ and PbF_4 are moderately stable.

Oxides of halogen

Halogens form many oxides with oxygen but most of them are unstable.

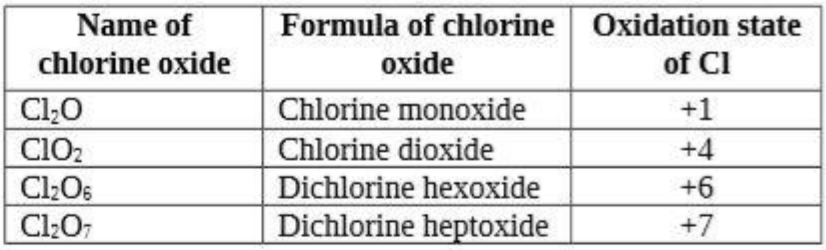
Fluorine combines with oxygen to form oxygen difluoride, OF_2 and oxygen monofluoride O_2F_2. These are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Only OF_2 is thermally stable at 298 K. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

$3O_2F_2 + Pu \rightarrow PuF_6 + 3O_2$.

The structure of OF_2 is similar to that of H_2O while that of O_2F_2 is similar to that of H_2O_2 involving sp^3 hybridisation of O atoms. The bond angle in OF_2 is lower than that of H_2O. The bond pair in OF_2 is closer to F atom and hence bond-pair –bond pair repulsion is decreased in OF_2 therefore decreasing the bond angle.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. Iodideoxygen bond is stable due to greater polarity of the bond while the stability of chlorineoxygen bond is due to multiple bond formation involving d-orbital of chlorine atom. Bromine being in between lacks both these characteristics. The higher oxides of halogens tend to be more stable than the lower ones.

Table 4.2 –Structure of various oxides of chlorine



Name of chlorine oxide	Formula of chlorine oxide	Oxidation state of Cl
Cl_2O	Chlorine monoxide	+1
ClO_2	Chlorine dioxide	+4
Cl_2O_6	Dichlorine hexoxide	+6
Cl_2O_7	Dichlorine heptoxide	+7

Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 (table 4.2) are highly reactive, strong oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents. The iodine oxides, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Structure of Oxides of Halogens:

Only the structures of OF_2, Cl_2O, Br_2O, Cl_2O_7 and I_2O_5 are definitely known. Structures of the monoxides can be illustrated on the basis of VSEPR theory. These oxides encompass tetrahedral structure having two lone pairs on oxygen. Therefore, the molecule is 'V' shaped or angular in shape. The bond angle EOE differs in the order FOF < ClOCl < BrOBr. This is due to electrons in case of OF_2 are closer to fluorine because of high electronegativity of F as compared to Cl or Br. The bonded electron pairs in Cl_2O and Br_2O are closer to oxygen making the repulsion between them more and thus reducing the lone pair-lone pair repulsion on oxygen to certain extent. As well due to the bulkiness of Cl and Br, the angles ClOC1 and BrOBr increase to such an extent which they are greater than 109°28', the tetrahedral angle. The figure shown below exhibits some of the structures of halogen oxides.

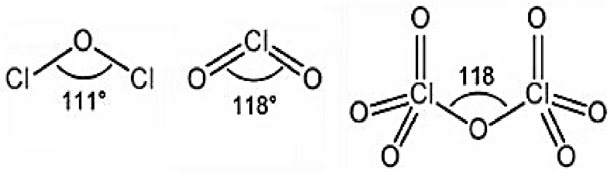
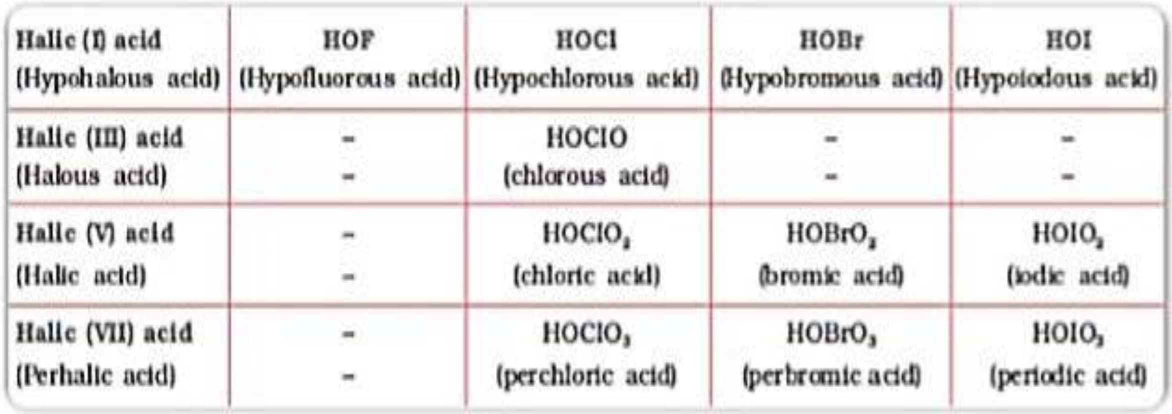


Fig: Structures of some Oxides of Halogens

Oxoacids of Halogens :

Being univalent and most electronegative atom, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens capable of displaying positive oxidation states form several oxoacids, Most of which exist only in aqueous solutions or in the form of their salts and are not isolable in pure state. The oxoacids of halogens are given in Table 4.3 and their structures are given in Fig. 4.1.

Table 4.3. Oxoacids of Halogens



Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	- -	HOClO (chlorous acid)	- -	- -
Halic (V) acid (Halic acid)	- -	$HOClO_2$ (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII) acid (Perhalic acid)	- -	$HOClO_3$ (perchloric acid)	$HOBrO_3$ (perbromic acid)	$HOIO_3$ (periodic acid)

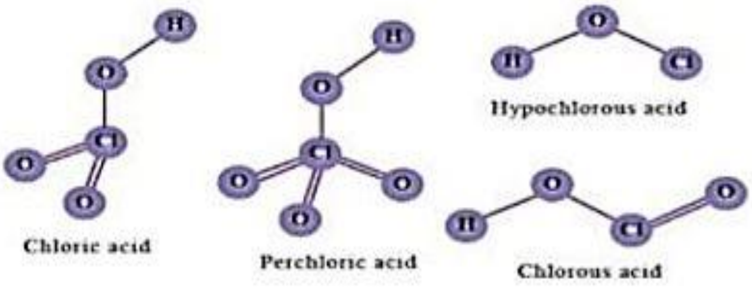


Fig 4.1 Structures of oxoacids of chlorine

Properties

These oxidation states of halogens in these acids are: +1 in HOX, +3 in HOXO, +5 in $HOXO_2$. +7 in $HOXO_3$. All are monobasic acid as one ionisable OH group is present in all the acids. For oxo acids of similar composition, the acid strength decreases with decrease in electronegativity of the halogen HOCl > HOBr > HOI.

The polarity of O-H bond is affected by attached halogen. As the electronegativity of the halogen decreases from Cl to I, electron withdrawal from O-X bond towards X decreases thus decreasing O-H bond polarity also. For same halogen, the strength of oxoacid increases with increase in oxidation state of halogen. $HClO_4 > HClO_3 > HClO_2 > HClO$. Higher positive oxidation state of the halogen leads to greater polarisation of attached O-H bond thus increasing its acidity.