TDC Part I
Inorganic Chemistry

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TOPIC:- Oxoacids of Halogens

Oxoacids of Halogens

Four series of oxoacids of halogens are known (Table 27).

Table 27: Oxo acids of Halogens

	HOX	**HXO_2**	**HXO_3**	**HXO_4**
Oxidation State of Halogen	+1	+3	+5	+7
	HOF			
	HOCl	$HClO_2$	$HClO_3$	$HClO_4$
	HOBr	$HBrO_2$	$HBrO_3$	$HBrO_4$
	HOI		HIO_3	HIO_4

The structures of the ions formed are shown in fig 30.

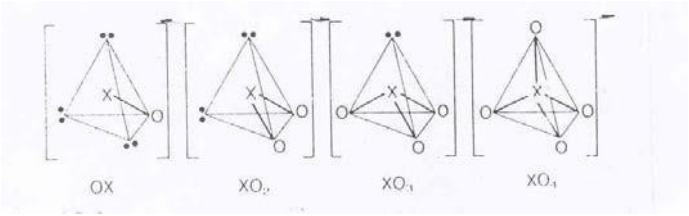


Fig.30: The Structures of Oxo anions

The halogen atom is sp^3 hybridized, there is significant pл – dл-bonding involving filled 2p orbital of oxygen and vacant d orbitals on halogens. Many of the oxoacids are known in solution, or in form of salts. Fluorine being more electronegative than oxygen does not form any oxoacid except the unstable HOF, which is obtained by passing F_2 over ice

$$F_2 + H_2O \xrightarrow{-50^0C} HOF + HF$$

It is difficult to prepare and isolate because of its reactivity towards H_2O and F_2

$HOF + H_2O \longrightarrow HF + H_2O_2$

$HOF + F_2 \longrightarrow HF + OF_2$

The oxoacids of chlorine are well known and arise from disproportionation of chlorine and related reactions:

$Cl_2 + 2H_2O \xrightarrow{\text{Cold}} HOCl + H_3O^+ + Cl^-$

$Cl_2 + HCO_3^- \xrightarrow{\text{Cold}} HOCl + CO_2 + Cl^-$

$3Cl_2 + 6OH^- \xrightarrow{\text{Hot}} ClO_3^- + 5\,Cl^- + 3H_2O$

$4KClO_3 \xrightarrow{\text{Heat}} 3KClO_4 + KCl$

In basic solution chlorine dioxide disproportionate to form chlorate and chlorite and the latter is used to form the free acid.

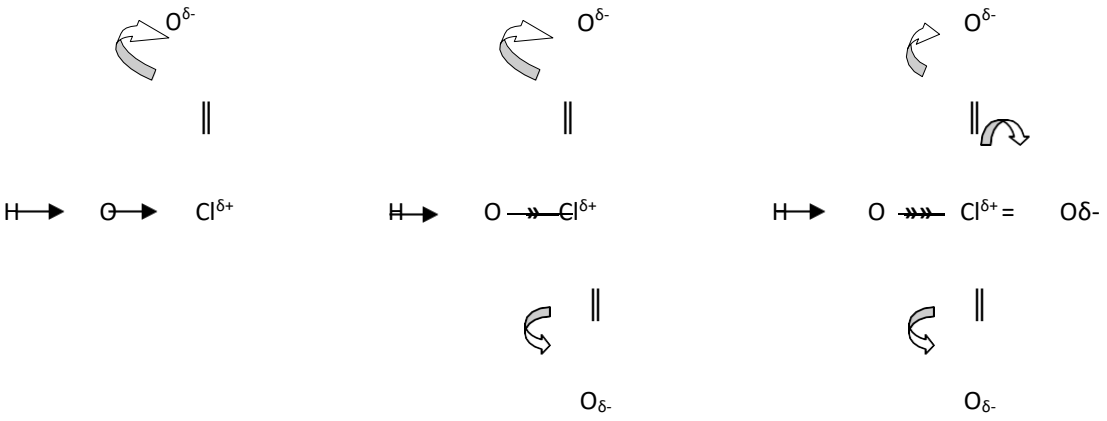
$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$

$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4\,(s)$

The acid strength of oxoacids increases with increase in oxidation number of the order of acid strength is

$HOCl < HOClO < HOClO_2 < HOClO_3$

As the oxidation state of the halogen increases, the number of oxygen atoms attached to the halogen increases. As oxygen is more electronegative, the halogen – oxygen bond is polarized leaving a small positive charge on the halogen. This now attracts the electrons of O- H bond towards itself, facilitating loss of hydrogen as proton. Greater the number of oxygen atoms, more is the acidity



Acid strength of oxoacids with halogen in the same oxidation state, decreases with decrease in electro-negativity of the halogen.

HOI < HOBr < HOCl

Sodium hypochlorite (NaOCl) is used in bleaching cotton fabrics, wood pulp and is a disinfectant. Anhydrous perchloric acid ($HClO_4$) is a very powerful oxidizing agent. Periodic acid (HIO_4) is used to oxidize alkenes to glycols.