TDC Part I
Inorganic Chemistry

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TOPIC:- Group 17,Basic properties of Halogens

Basic Properties of Halogens

Metallic character increases down the group and decreases across a period. It has been seen in Groups 14, 15 and 16 that the last member (Pb, Bi, Po) has metallic character. This is not very apparent in halogens as very little is known about the last element, astatine. However, there are certain evidences to show existence of halogen cations.

Fluorine is the most electronegative element; it has no tendency to display positive oxidation state. ClF ionizes to form Cl^+ and F^- Br^+ exist in complexes like $[Br(Pyridine)]^+ NO_3^-$. ICN on electrolysis liberates iodine at anode, indicating formation of I^+. Many pyridine complexes of I^+ are known eg. $[I(py)]^+ NO_3^-$, $[I(py)_2]^+ ClO_4^-$ and $[I(py)]^+ CH_3COO^-$, (py = pyridine).

Iodine dissolves in oleum to give a blue solution that contains I_2^+ and I_3^+

$$2I_2/3I_2 + 6H_2S_2O_7 \longrightarrow {}_2I^+/_3I^+ + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

Molten iodine conducts electricity and it has been shown that I_3^+ and I_3^- are present

$$3I_2 \rightleftharpoons {}_3I^+ + {}_3I^-$$

Many other compounds containing Cl_3^+, Br_3^+, I_3^+, I_5^+ have been prepared.

$$Cl_2 + ClF_3 + AsF_5 \longrightarrow [Cl_3]^+ [AsF_6]^- + F_2$$

$$Br_2 + BrF_3 + AsF_5 \longrightarrow [Br_3]^+ [AsF_6]^- + F_2$$

$$I_2 + ICl + AlCl_3 \longrightarrow [I_3]^+ [AlCl_4]^-$$

$2I_2 + ICl + AlCl_3 \longrightarrow [I_5]^+ [AlCl_4]^-$

ICl is an electrophilic iodinating agent, believed to contain I^+

When a solution of iodine in an inert solvent is passed through a cation-exchange resin, some iodine is retained by the resin, indicating the presence of I^+

$H^+ Resin^- + I_2 \longrightarrow I^+ Resin^- + HI$

The structures of the triatomic and penta-atomic cations are shown in Fig.28.

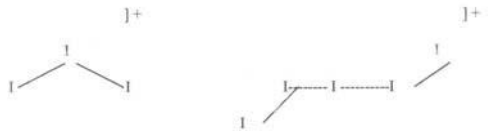

Fig.28: The structures of I_3 and I_5