

Study Notes On Interhalogens and Pseudohalogens



Interhalogens and Pseudohalogens

The interhalogens:

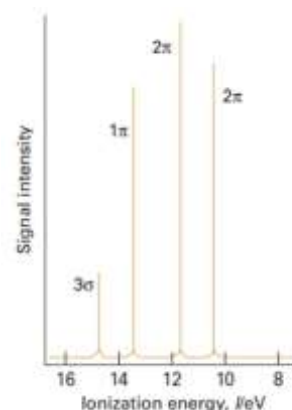
All the halogens tend to form compounds with other members of the group. The interhalogens are formed between Group 17 elements. The binary interhalogens are molecular compounds having formulas XY , XY_3 , XY_5 , and XY_7 , while the heavier, less electronegative halogen X is the central atom. They also form ternary interhalogens of the type XY_2Z and XYZ_2 , where Z is also a halogen atom.

Halogen oxoanions:

Oxidation number	Formula	Name*	Point group	Shape	Remarks
+1	ClO^-	Hypochlorite [monoxidochlorate(I)]	$C_{\infty v}$	Linear	Good oxidizing agent
+2	ClO_2^-	Chlorite [dioxidochlorate(III)]	C_{2v}	Angular	Strong oxidizing agent, disproportionates
+5	ClO_3^-	Chlorate [trioxidochlorate (V)]	C_{3v}	Pyramidal	Oxidizing agent
+7	ClO_4^-	Perchlorate [tetraoxidochlorate(VII)]	T_d	Tetrahedral	Oxidizing agent, very weak ligand

* IUPAC names in square brackets.

Generally, all the F interhalogen compounds are exergonic. The least labile interhalogen is Cl, but ICl and IBr can also be obtained in pure crystalline form. Their physical properties are intermediate between those of their component elements. Photoelectron spectra indicate that the molecular orbital energy levels in the mixed dihalogen molecules lie in the order $3\sigma^2 < 1\pi < 2\pi^4$, which is the same as in the case of homonuclear dihalogen molecules. Most of the higher interhalogens are fluorides. The only neutral interhalogen with the central atom in a +7 oxidation state is IF_7 , but the cation ClF_6^+ , a compound of Cl(VII), is known. The absence of a neutral ClF_7 , reflects the destabilizing effect of non-bonding electron repulsions between F atoms. The lack of BrF_7 , might be rationalized in a similar way, but in addition, bromine is reluctant to achieve its maximum oxidation state.



The shapes of interhalogen molecules are largely in accord with the VSEPR model. For example, the XY_3 compounds (such as ClF_3) have five valence electron pairs around the X atom in a trigonal-bipyramidal arrangement. The Y atoms attach to the two axial pairs and one of the three equatorial pairs, and then the two axial bonding pairs move away from the two equatorial lone pairs. As a result, XY_3 molecules have a C_{2v} bent T shape. There are some discrepancies also like ICl_3 is a Cl-bridged dimer. The Lewis structure of XF_5 contains five bonding pairs and one lone pair on the central X atom and as expected from the VSEPR model, XF_5 molecules are square pyramidal in shape. As already mentioned, the only known XY_7 compound is IF_7 which is predicted to be pentagonal bipyramidal. As with other hypervalent molecules, the bonding in IF_7 can be explained without invoking d-orbital participation by adopting a molecular orbital model in which bonding and non-bonding orbitals are occupied but antibonding orbitals are not.

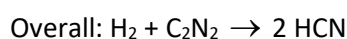
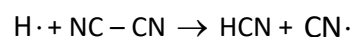
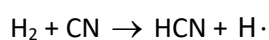
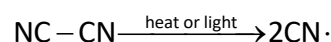
Polymeric interhalogens can also be formed and may be cationic or anionic. Examples of cationic polyhalides are I_3^+ (4) and I_5^+ (5). Anionic polyhalides are most numerous for iodine. The I_3^- ion is the most stable but others with the general formula $[(I_2)_n]^-$ are formed. Other anionic polyhalides include Cl_3^- and BrF_4^- .

XY	XY_3	XY_5	XY_7
ClF	ClF_3	ClF_5	
BrF^+	BrF_3	BrF_5	
IF	$(IF_3)_n$	IF_5	IF_7
BrCl			
ICl	I_3Cl_6		
IBr			
* very unstable			

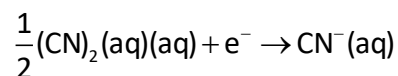
Pseudohalogens

Pseudohalogens and pseudohalides mimic halogens and halides, respectively; the Pseudohalogens generally exist as dimers and form molecular compounds with nonmetals and ionic compounds with alkali metals.

There are several compounds having properties so like those of the halogens that they are called Pseudohalogens. For example, like the dihalogens, cyanogen, $(CN)_2$, undergoes thermal and photochemical dissociation in the gas phase; the resulting CN radicals are isolobal with halogen atoms and undergo similar reactions, such as a chain reaction with hydrogen: The reactions can be represented as:



Another similarity is the reduction of a pseudohalogen:



The anion which is formally derived from a pseudohalogen is called a pseudohalide ion. An example is the cyanide anion, CN^- . Covalent pseudohalides that are similar to the covalent halides of the p-block elements are also common.

As with all analogies, the concepts of pseudohalogen and pseudohalide have many limitations. For example, pseudohalogen ions are not spherical, due to this, the structures of their ionic compounds often differ: NaCl is FCC, but NaCN is similar to CaC_2 . The pseudohalogens are generally less electronegative than the lighter halogen and some pseudohalides have more versatile donor properties. The thiocyanate ion, SCN^- , for instance, acts as an ambidentate ligand with a soft base site, S, and a hard base site, N.

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