A COMPARISON OF HALOGENO AND OXYACIDS

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In a recent paper originating in this department and sent to one of the chemical journals for publication the term "fluo acid" was used to designate a flourine containing acid which could be considered as having been formed by substituting two flourine atoms for each oxygen atom in an oxyacid. Criticism of this term on the ground that it was novel and unusual resulted. The paper mentioned being essentially organic in its nature it was impossible to explain the matter sufficiently except as a separate discussion. The purpose of this paper is to make an attempt to establish the term "halogeno acid" as a general name for acids in which the halogens may be considered to replace the oxygen in oxyacids and to establish the terms, fluo, chloro, bromo, and iodo as the specific names of these acids where the halogen involved is flourine, chlorine, bromine, and iodine respectively. As a matter of fact these names have been used in several cases and are accepted terms for those cases, i.e., fluoboric acid, bromostannic acid, fluoplumbic acid, fluosilicic acid, etc.

When various molecular portions of water are added to the anhydrides of the acid forming elements, the several oxyacids are produced.

$$B_2O_3+H_2O\rightarrow 2HBO_2$$
$$B_2O_2+3H_2O\rightarrow 2H_3BO_3$$

In an analogous manner when the halogen acids are added to the halogen compounds corresponding to the anhydrides of the acid forming elements, the halogeno acids are formed.

$$2BF_3+H_2F_2\rightarrow 2HBF_4$$
$$2BF_3+3H_2F_2\rightarrow 2H_3BF_6$$

In Table 1 the anhydrides and oxyacids of several of the elements are given and with these the corresponding halogeno compounds and halogeno acids.

TABLE I

OXYGEN ACIDS			HALOGENO ACIDS		
ACID ANHYDRIDE	MOLECULE of WATER	ACID	ACID HALOGENIDE	MOLECULE of H_2F_2	ACID
Al_2O_3	1	$H_2(Al_2O_4)$	$2AlF_3$	1	$H_2(Al_2F_8)$*
Al_2O_3	2	$H_4(Al_2O_5)$	$2AlF_3$	2	$H_4(Al_2F_{10})$*
Al_2O_3	3	$2H_3(AlO_3)$	$2AlF_3$	3	$2(H_3AlF_6)$*
B_2O_3	1	$2H(BO_2)$	$2BF_3$	1	$2H(BF_4)$
B_2O_3	3	$2H_3(BO_3)$	$2BF_3$	3	$2H_3(BF_6)$
SiO_2	1	$H_2(SiO_3)$	SiF_4	1	$H_2(SiF_6)$
SiO_2	2	$H_4(SiO_4)$	SiF_4	2 Molecule of H_2Cl_2	$H_4(SiF_8)$†
Sb_2O_5	1 (Meta-)	$2H(SbO_3)$	$2SbCl_5$	1	$2H(SbCl_6)$
Sb_2O_5	2 (Pyro-)	$H_4(Sb_2O_7)$	$2SbCl_5$	2	$H_4(Sb_2Cl_{14})$‡
Sb_2O_5	3 (Ortho-)	$2H_3(SbO_4)$	$2SbCl_5$	3	$2H_3(SbCl_8)$¶
Bi_2O_3	1	$2H(BiO_2)$	$2BiI_3$	2HI	$2H(BiI_4)$
Bi_2O_3	2	$H_4(Bi_2O_5)$	$2BiBr_3$	4HBr	$H_4(Bi_2BR_{10})$
Bi_2O_3	3	$2H_3(BiO_3)$	$2BiF_3$	6HF	$2H_3(BiF_6)$
SnO_2	1	$H_2(SnO_3)$	$SnBr_4$	2HBr	$H_2(SnBr_6)$

*As NH: Salts.
†As Sn Salt.
‡As Mg Salt.
¶As Cr Salt.

Perhaps the greatest difficulty in the acceptance of this analogy lies in the attempt to write the halogeno acids structurally. When, however, one examines the formula of hydroflouric acid which conductivity measurements have shown to be H_2F_2 this difficulty disappears.

If the formula of H_2F_2 be written structurally it becomes $H-F=F-H$. In substituting two florine atoms for one oxygen atom this grouping has been assumed to hold. Thus where a double bonded oxygen atom is replaced the end valenceies of the $-F=F-$ group are assumed to be the ones involved and the group is written thus $\begin{matrix} F \\ \vdots \\ F \end{matrix}$. When a hydroxyl group is substituted it is replaced by the group, $-F=F-H$. The same arrangement of atoms and valenceies has been assumed to be true in the case of the other halogens.

One could continue this table and show the analogy of halogeno acids to oxyacids to hold for practically all of the acid forming elements.

In the table a few of the acids listed are not very stable and from this it might be assumed that the compounds, instead of being written as shown would probably more nearly represent the facts if they were written as a halogen compound of the element and the halogen acid constituting a molecular, that is, one would write $2AlF_3$-H_2F_2 in place of $H_2Al_2F_8$.

When, however, one examines such compounds as $(NH_4)_2(PbCl_6)$ and $(NH_4)_2(SnCl_6)$ the complex salts are more stable than either one of the molecular ingredients, in $2NH_4Cl$-$PbCl_4$ and $2(NH_4)Cl$-$SnCl_4$.

It is also worthy of note that in almost every case the halogeno acids are stronger acids than the corresponding oxyacids. This is to be expected from the periodic arrangement of the elements which places oxygen in group 6 and the halogens in group 7. Thus from the point of atomic structure the halogens are more electropositive than oxygen and would therefore form stronger acids.

While in several isolated cases the above given terminology has been used in chemical literature, so far as we have been able to ascertain the name halogeno acid has not been generally accepted for all acids where the oxygen may be considered to have been replaced by halogen in the ratio of one to two.

Conclusion. 1. We have pointed out the similarity of the halogen substituted oxyacids to the oxyacids themselves.

2. We have proposed the term halogeno acid as a general name for these substituted acids and more specifically the terms fluo, chloro, bromo, and iodo, as the names for these acids when flourine, chlorine, bromine, and iodine respectively are the halogens involved.