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Mixed Halogen Acids of the Elements of the II and III Periodic Groups

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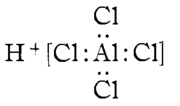
A general method of preparation and some properties are reported for the etherated complex mixed halogen acids of formula $H[Me^{III}X_3X']$ and $H[MeX_2X']$; the metals contained are Zn, Cd, Hg of group II and Al, Ga, In of group III.

Salts of the type $Me^I[Me^{II}X_3]$, $M^I[Me^{III}X_4]$, $Me^I_2[Me^{II}X_4]$ have been known for many years. Their methods of preparation and isolation and the study of their chemical properties present few difficulties. On the other hand the preparation of the corresponding free acids has until recently not been successful, although many experiments have been made in this direction. The preparation of the acids is of great interest, because they have been proposed by many authors as intermediates in the Friedel–Crafts reaction and in chain polymerization.

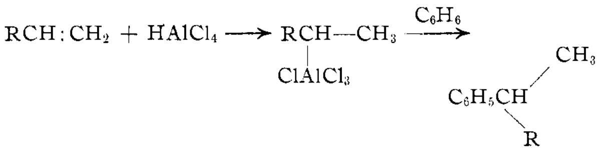
Some authors believe that HCl cannot combine with $AlCl_3$ to form the compound $H[AlCl_4]$ and Fontana and Harold[2a] believe that $H[AlCl_4]$ cannot exist at room temperature. The compound $Na[AlCl_4]$, as is known, can be prepared from NaCl and $AlCl_3$ and is a very useful catalyst. It is to be expected, therefore, that the analogous compound from HCl and $AlCl_3$ would be of electronic type



$H^+[Cl:\overset{Cl}{\ddot{Al}}:Cl]$ with $\ddot{Cl}$ below

and a strong acid with similar catalytic properties.[2]

Ipatieff[3] and co-workers accept the view that in the Friedel–Crafts reaction the not yet isolated compound $H[AlCl_4]$ forms addition-products with the reacting components which are like the esters of sulfuric acid. These esters react afterwards with aromatic hydrocarbons to give alkylated products.



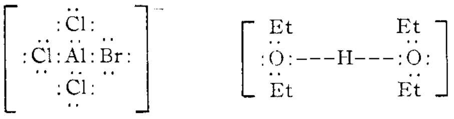
Brown and Pearsall[4] believe that, while the compound $H[AlCl_4]$ does not exist free, but only in the form of salts, it may be presumed to be involved in one of the steps of the Friedel–Crafts reaction. Sanderson[5] has come to the same conclusion by comparison of the electronegativity of the compounds HCl and $AlCl_3$, where the value of the stability ratio of the $AlCl_3$ is 3.91 in comparison to that of HCl, 4.19.

In 1954 employing a simple method,[6] we prepared the dietherated halogen acids of many metals and studied their properties.

Of theoretical interest is the study of the mixed complex halogen acids of formulas $H[Me^{III}X_3X']$, $H_2[Me^{II}X_2X_2']$, $H[Me^{II}X_2X']$ where X and X′ represent different halogen atoms. The only known compounds of this mixed type are the Li, Na, K, NH_4, Zn and Cd salts of bromotriiodoantimonic(III) acid prepared by A. Vournazos.[7]

The preparation of the etherated mixed halogen acids is analogous to that of the etherated complex simple halogen acids.[8] They are synthesized in ether medium by addition of dry hydrogen halide to the anhydrous metal salt.

The new compounds may be electronically formulated, for example, $HAlCl_3Br\cdot 2\ Et_2O$, as follows hypothetically. The symbol [---H---] represents a hydrogen bridge. The stability of these compounds may be ascribed to three types of bonds:



(a) homopolar bonds between the central ion of the complex and halogen ions, (b) heteropolar bond between the complex anions and the complex cation, (c) hydrogen bridging between the proton and the ether molecules, which significantly increases the volume of the cation, decreases the mobility of the proton and increases the stability of the molecule.

In all cases the monobasic complex halogen acids are formed with two molecules of ether. In the case of the dibasic complex halogen acids $[H_2MX_4]$ a third molecule of ether may be taken up.[9]

The time required for completion of the formation reactions of the different complex halogen acids varies from ten minutes up to some hours or days. It is to be expected that the tendency for the formation of the complex ions would vary from metal to metal and depend (a) upon the relations between volumes of the substituents, (b) upon the charge of the central ions and (c) upon the interactions of the central atom with the surroundings, etc. At the same time the preparation reactions of these acids are heterogeneous because they take place between a solid phase (metal halide) and a liquid phase (ether with HCl or HBr). For this reason the reaction velocity is strongly dependent on the active surface of the metal halide crystals which is a function of their lattice type and their fineness of subdivision.

The formation of complex metal halogen acids by the addition of molecules of hydrogen halides

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[2] (a) G. M. Fontana and R. J. Harold, THIS JOURNAL, **70**, 2881 (1948). (b) J. F. Norris and J. E. Wood, *ibid.*, **62**, 1428 (1940).

[3] V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

[4] H. C. Brown and H. Pearsall, THIS JOURNAL, **73**, 4681 (1951).

[5] R. T. Sanderson, *J. Chem. Education*, **31**, 238 (1954).

[6] E. Wiberg, M. Schmidt and A. G. Galinos, *Z. Angew. Chem.*, **66**, 443 (1954).

[7] A. Vournazos, *Compt. rend.*, **175**, 164 (1922).

[8] E. Wiberg, M. Schmidt and A. G. Galinos, *Z. Angew. Chem.*, **66**, 444 (1954).

[9] A. G. Galinos, *ibid.*, **69**, 507 (1957).

and ether to the metal halides we call "etherohydrohalogenosis." The velocity of etherohydrohalogenosis may be shown experimentally to be influenced not only by the nature of the metal halide but also by the concentration of HCl or HBr in the ether.

General Properties.—All the newly prepared mixed halogen acids are colored, their color varying according to the nature of the metal and halogen. They are oily liquids, freezing at low temperatures, from 8 to −80°.

Their freezing points are not sharp. Due to hydrolysis to form HCl or HBr, they fume in the air. They are soluble in many polar solvents (nitrobenzene, chloroform and liquid sulfur dioxide) and insoluble in non-polar solvents (ether, benzene, etc.). They also react very vigorously with water and give acid solutions containing all the ions of the halides used. The solutions in polar media (nitrobenzene) conduct the electrical current, the acids dissociating into ions.

This type of compound can be used as catalyst for the esterification of alcohols, and for the polymerization of styrene and α-pinene, with vigorous reaction.[10-12]

General Method of Preparation.—For the preparation of the mixed complex halogen acids we used chemically pure anhydrous salts. These were added to an excess of absolute ether which was already saturated with dry hydrogen chloride or hydrogen bromide.

The products in the form of heavy oily phases were separated from the ether phase. Excess ether then was pumped off and the final products dried in a vacuum desiccator. Precautions were always taken to use freshly prepared solutions of HX in absolute ether.

All these compounds can be obtained as crystals by freezing to temperatures as low as −80°, filtering quickly and washing with cold ether, with the exclusion of moisture.

The compounds were analyzed by addition of samples to water yielding a solution containing hydrogen, halide and metal ions and ether.

The halogen ion was determined by titration and the metal ion by standard methods of analysis. The chloride content in the presence of bromide was obtained by the method of Bugarszy–Andrews,[13] while the analysis of iodide in the presence of chloride and bromide was carried out with the use of $PdCl_2$. The ether content of the compounds was estimated by difference. Results are given in Table I.

TABLE I

PREPARED COMPOUNDS

Compound	Analysis	Description
$HZnCl_2Br\cdot 2Et_2O$	H, 1:Zn, 1:Cl, 2:Br, 1:Et_2O, 2.08	Yellow
$HZnBr_2Cl\cdot 2Et_2O$	H, 1:Zn, 1.1:Br, 2:Cl, 1:Et_2O, 2.1	Pale yellow
$HZnI_2Cl\cdot 2Et_2O$	H, 1:Zn, 1:I, 2:Cl, 1:Et_2O, 1.9	Carmine red
$HZnI_2Br\cdot 2Et_2O$	H, 1:Zn, 1:I, 2:Br, 1:Et_2O, 2.06	Carmine red
$HCdCl_2Br\cdot 2Et_2O$	H, 1:Cd, 1.06:Cl, 1.98:Br, 0.925:Et_2O, 1.89	Reddish yellow
$HCdBr_2Cl\cdot 2Et_2O$	H, 1:Cd,1:Br, 2:Cl, 1:Et_2O, 2	Orange
$HCdI_2Cl\cdot 2Et_2O$	H, 1:Cd, 1:I, 2:Cl, 1:Et_2O, 2.1	Pink
$HCdI_2Br\cdot 2Et_2O$	H, 1:Cd,1:I, 2.1:Br, 1:Et_2O, 2.2	Carmine red
$HHgI_2Cl\cdot 2Et_2O$	H, 1:HgI_2, 1.03:Cl, 1.07:Et_2O, 2.03	Yellow
$HHgI_2Br\cdot 2Et_2O$	H, 1:HgI_2, 1.06:Br, 0.98:Et_2O, 2.1	Deep yellow
$HAlCl_3Br\cdot 2Et_2O$	H, 1:Al, 1:Cl, 3:Br, 1:Et_2O, 2	Coffee brown
$HAlBr_3Cl\cdot 2Et_2O$	H, 1:Al, 1:Br, 2.96:Cl, 1:Et_2O, 1.85	Brownish yellow
$HAlI_3Cl\cdot 2Et_2O$	H, 1.09:Al, 1:I, 3.1:Cl, 1:Et_2O, 2.09	Deep red
$HAlI_3Br\cdot 2Et_2O$	H, 0.93:Al, 1:I, 2.95:Br, 1:Et_2O, 1.87	Dark red
$HGaCl_3Br\cdot 2Et_2O$	H, 0.98:Ga, 1:Cl, 2.92:Br, 1:Et_2O, 1.89	Yellow
$HGaBr_3Cl\cdot 2Et_2O$	H, 0.96:Ga, 1:Br, 3.1:Cl, 1.02:Et_2O, 2.1	Pale yellow
$HInCl_3Br\cdot 2Et_2O$	H, 0.98:In, 1:Cl, 2.98:Br, 0.98:Et_2O, 2.04	Yellow
$HInBr_3Cl\cdot 2Et_2O$	H, 0.97:In, 1:Br, 2.94:Cl, 0.97:Et_2O, 2	Brownish yellow
$HInI_3Cl\cdot 2Et_2O$	H, 1:In, 1:I, 3.03:Cl, 1.1:Et_2O, 1.92	Yellow
$HInI_3Br\cdot 2Et_2O$	H, 1.05:In, 1:I, 3.02:Br, 1:Et_2O, 2	Deep red

TABLE II

Compound	Theor.	Found	Average
$HZnBr_2Cl\cdot 2Et_2O$	409.9	201, 199, 196	198.6
$HHgI_2Cl\cdot 2Et_2O$	639.1	332, 337, 335	334.6
$HAlCl_3Br\cdot 2Et_2O$	362.5	205, 198, 196	199.9
$HInI_3Cl\cdot 2Et_2O$	539.3	282, 277, 276	278.3

The molecular weights of some of these acids in nitrobenzene were determined cryoscopically. The values we found are about one-half of the theoretical formula weights as shown in Table II.

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(10) A. G. Galinos and I. M. Tsangaris, *Prak. Akad. Athenone*, **32**, 393 (1957).

(11) A. G. Galinos and I. M. Tsangaris, *Z. Angew. Chem.*, **70**, 24 (1958).

(12) A. G. Galinos and I. M. Tsangaris, *Prakt. Akad. Athenone*, **34**, 113 (1959).

(13) Scott's "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 1939, p. 194.