# Microscopic Chemical Reactions of the acids of Chlorine, Bromine and Iodine.

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### II.

In Part I of the present work<sup>1</sup> the microscopic gualitative reactions of the halogen acids giving silver salts insoluble in  $HNO_3$  were discussed. According to the classification of Bunsen and Treadwell the next group to be considered comprises acids the silver salts of which are insoluble in water but soluble in dilute  $HNO_3$  (Group II).

Any division based on solublity is open to the objection that its limits cannot be sharply defined; e. g., it is possible for  $BrO_3^$ to appear in Group III, if the concentration of  $HNO_3$  is relatively high, for AgBrO<sub>3</sub> is appreciably soluble. However, this is not objectionably, since it will be recognized in Group II, and will not be confused with any member of Group III because of the specificity of its reaction with m-phenylenediamine. No other radical yields  $Br_2$  on reduction.

Periodate ion  $(IO_4^{-1})$  is the only other representative of the halogen acids falling in Group II. The physical chemistry of the silver periodates is somewhat in guestion<sup>2</sup>, and the acidity of the solution has a marked effect upon the nature of the precipitate obtained with Ag<sup>+</sup>. From neutral or very slightly acid solutions of IO<sub>4</sub><sup>--</sup> a precipitate is obtained which is satisfactory as a test, even though opinon is divided as to whether it consists of Ag<sub>8</sub>IO<sub>5</sub> or Ag<sub>5</sub>IO<sub>6</sub>. It is yellow to orange at first, fine grained, highly refractive, and probably owes its light color to its fine state of subdivision and high index of refraction. On standing, preferably on heating, the fine particles grow and their crystal form becomes apparent, while the color of the precipitate darkens nearly to black. No phase transformation seems to be involved, for the fine grains first formed, as far as can be observed, have a habit similar to the crystals developing later. These last are

<sup>&</sup>lt;sup>1</sup> Mikrochemie, 5, 85-101 (1927).

<sup>&</sup>lt;sup>2</sup> Mellor, Inorgan. and Theoret. Chem. Vol. II, p. 410, Longmans and Co., London (1922).

hexagonal and triangular plates and stars, which may change into snowflake forms. They are dark brown by transmitted light, or if finely enough divided, yellow. Birefringence is fairly strong. The precipitate may be dissolved in  $HNO_3$  and reprecipitated by NH<sub>4</sub>OH, but only fine crystalline grains are obtained by this procedure.

If the precipitation takes place in a solution containing an appreciable amount of  $HNO_3$  a different type of crystals appears. These have been given the formula  $Ag_2H_3IO_6$  (or  $Ag_4I_2O_9$ .  $3H_2O$ ). The crystals are pale straw-yellow, acute rhombohedral in habit, exhibiting symmetrical extinction and fairly strong birefringence. They are very soluble in  $HNO_3$ , and if more than a very small amount of the latter is present they will not be formed.

From solutions strongly acid with HNO<sub>3</sub>, or from HNO<sub>3</sub> solutions of either  $Ag_2H_3IO_6$  or  $Ag_5IO_6$  a third type of crystals may be obtained. These are highly soluble, and would not be likely to occur in a test. They are tetragonal bipyramidal in form, and are isomorphous with KIO<sub>4</sub>, so their formula must be  $AgIO_4$ . They are yellow in color, more soluble than KIO<sub>4</sub>, are highly refractive, and show strong birefringence. On the addition of water these crystals decompose to a fine grained mass, composed of tiny but typical crystals of  $Ag_2H_3IO_6$ .

Of all the above precipitates, only the first is insoluble enough for a gualitative test, and it is suitable only under the proper conditions, namely when the solution to be tested is neutral or only very slightly acid. Under these conditions a precipitate of Ag<sub>5</sub>IO<sub>6</sub> may be obtained with concentrations corresponding to about 0.0005 gram NaIO<sub>4</sub> per cc (20  $\mu$ g, IO<sub>4</sub><sup>-</sup> per drop). If more than a very small amount of acid is present, only very concentrated solutions of periodates are likely to give a precipitate. The color of the freshly precipitated, finely subdivided Ag<sub>5</sub>IO<sub>6</sub>, and its subsequent development of characteristic crystals, with darkening color, are typical, and in themselves would identify IO<sub>4</sub>-. The only other colored Ag precipitate likely to be confused with the  $Ag_{5}IO_{6}$  is  $Ag_{3}AsO_{4}$ , but since this is much less readily soluble in HNO<sub>3</sub>, forms crystals bristling with long slender needles, and may be identified by other tests,  $AsO_4^{---}$  is not likely to lead to error.  $Ag_2CrO_4$ , and  $Ag_2Cr_2O_7$  are also colored, but they do not exhibit any sequence of color changes, are of entirely different crystal habit, and unless so thick as to appear opague, are of a clearer, much more reddish hue by transmitted light. If these salts have been studied they need never be confused with the  $Ag_5IO_6$  precipitate.

As confirmatory tests for  $IO_4^-$  a number of reactions are available. K<sup>+</sup> gives with  $IO_4^-$  a characteristic precipitate of KIO<sub>4</sub>, acute tetragonal bipyramids, of fairly strong birefringence, not readily soluble in HNO<sub>3</sub>. These are obtained with concentrations greater than 0.001 gram NalO<sub>4</sub> per cc (40 µg IO<sub>4</sub><sup>-</sup> per drop). Rb<sup>+</sup> and Cs<sup>+</sup> give similar crystals, rather more soluble in water. This precipitation of KIO<sub>4</sub> is of the same order of sensitivity as that of KClO<sub>4</sub> as a test for ClO<sub>4</sub><sup>-</sup>, and is very distinctive, for acids giving potassium salts of very low solubility, are few indeed.

Periodates are reducible to iodine in much the same manner as are the iodates<sup>3</sup>. The iodine is identified by the starch reaction. It is possible thus to detect iodates in concentrations corresponding of 0.0005 gram NaIO<sub>4</sub> per cc (20  $\mu$ g. IO<sub>4</sub><sup>-</sup> per drop).

This reduction is also applicable to the  $Ag_5IO_6$  precipitate, which is dissolved in a very slight excess of  $HNO_3$  or  $H_2SO_4$ , and acted upon by the reducing agent (hydroxylamine sulphate, metallic Zn, etc.). A very fine white precipitate of AgI is formed. The reaction with starch does not take place, probably because of the precipitation of all the iodine in the form of very insoluble AgI.

The fact that  $Ba^{++}$  gives no precipitate with  $IO_4^-$  aids in distinguishing it from  $IO_3^-$ , or in separating  $Ba(IO_3)_2$  by precipitation so that the filtrate may be tested for  $IO_4^-$  with Ag<sup>+</sup>.

The non-halogen radicals of Group II include acetate, borate, carbonate, cyanate, oxalate, sulphate, sulphite, thiosulphate, and tartrate, giving colorless precipitates with Ag<sup>+</sup>, and arsenite, arsenate, chromate, permanganate, phosphate, and sulphide, giving colored precipitates. Most of these precipitates are recognizeable at once, and are not likely to be mistaken for those of the halogen acids. Identity tests are available for each of these radicals so that it is an easy matter to avoid confusing them with the halogen acids of this or other groups.

Group III of the Bunsen — Treadwell classification includes those acids which form no insoluble silver salts. Of the halogen radicals, perchlorate and chlorate fall in this group, which also contains the sulphate and nitrate radicals.

<sup>&</sup>lt;sup>3</sup> Mikrochemie, 5, 98 (1927).

Perchlorates. The most distinctive reaction of  $ClO_4^{-}$  is the formation of a characteristic precipitate with K+. Orthorhombic prisms and rhomb shaped forms are obtained in well crystallized habit. These are isomorphous with KMnO<sub>4</sub>, and are readily colored (solid solution) by the latter if a little is added th the test drop. The test is thus rendered more easily observable. Skeleton forms occur if the concentration of CIO<sub>4</sub><sup>-</sup> is high. Since the above test is only moderately sensitive, other members of the same isomorphous series were tested out, in the hope that a less soluble salt might be obtained. Rb+ is no more sensitive for ClO<sub>4</sub><sup>-</sup> than K+. Cs+ and TI+ are much less sensitive in practise. N(CH<sub>3</sub>)<sub>4</sub>ClO<sub>4</sub> is listed as having a solubility only about  $\frac{1}{4}$  that of KClO<sub>4</sub>; as a test it is distinctly less sensitive than the latter. Exposure to alcohol vapor was not found to hasten the appearance of KClO<sub>4</sub> crystals. The limit of sensitivity of the above test is about 0.001 gram HClO<sub>4</sub> per cc. (50 µg. per drop).

Strychnine sulphate gives a precipitate of simple rectangular, lath shaped forms with  $ClO_4^-$ . These have very weak birefrigence, parallel extinction, and tend to grow in parallel clusters, especially if the reagent is added as a solid. These crystals cross each other at right angles, overlying the fragment of strychnine sulphate, and giving an appearance similar to a frayed bit of cloth. The concentration of the reagent is best kept low. The sensitivity of this test is about 0.0005 gram HClO<sub>4</sub> per cc. (10 µg. per drop).

Other microscopic reactions of perchlorates are on record, but they are of guestionable specificity.

Chlorates are difficult to identify. The lack of insoluble salts eliminates any direct precipitation tests, though this negative evidence is not without value. Recourse must be had to some indirect procedure, either oxidation or reduction of  $ClO_3^-$ , and identification of the reaction products. Chlorates may be transformed to perchlorates by heating to dryness with H<sub>2</sub>SO<sub>4</sub>, but the HClO<sub>4</sub> formed is volatile, and may be lost. The H<sub>2</sub>SO<sub>4</sub> is supposed to serve as a preventive of overheating, as well as to facilitate the reaction, but neither function is performed perfectly enough to make the transformation even approximately guantitative. The  $ClO_4^$ formed is recognized by the precipitate it gives with K<sup>+</sup>, preferably in the presence of MnO<sub>4</sub><sup>--</sup>. In practise, the above method has many shortcomings, and is not always reliable on a micro scale.

The oxidation of  $ClO_3^-$  to  $ClO_4^-$  by persulphates, using Ag<sup>+</sup> as a catalyst, does not appear to yield results suitable for micro-

analysis. A more reliable method of identifying ClO<sub>3</sub><sup>-</sup> is by reducing it to Cl-. Hydroxylamine sulphate does not accomplish this though it does reduce  $BrO_3^-$  and  $IO_3^-$ ; but sulphites, ferrous salts, or metallic Zn in acid solution, are very effective. The Cl- formed is identified in the usual way, with Ag+, Pb++, etc. The Zn metal should be removed before the salts of the heavy metals are added, or these will be "plated out" and will not be available for the test. SO<sub>2</sub> is very useful for the reduction of ClO<sub>3</sub><sup>-</sup> to Cl<sup>-</sup>, when the introduction of a salt into the solution might be undesirable. It may be generated in a micro-crucible, and the drop to be tested exposed to the action of the gas, and then tested for Cl<sup>--</sup> with Ag<sup>+</sup>, or the Ag<sup>+</sup> may be put into the test drop before it is exposed to the SO2. In either case sufficient HNO3 must be present to prevent the precipitation of Ag<sub>2</sub>SO<sub>3</sub>, which might be confused with AgCl formed from ClO<sub>3</sub>-. Concentrations of KClO<sub>3</sub> greater than 0.001 gram per cc. (50 µg. per drop) give on reduction distinct precipitates of AgCl, and a faint precipitate is obtainable with about 0.0001 gram of KClO3 per cc.

 $KMnO_4$  is not decolorized by solutions of chlorates, though it is by chlorites, or by  $ClO_2$ .

Since AgBrO<sub>3</sub> is slightly soluble, especially in hot water, there is a possibility of BrO3- appearing in the group with ClO3- and ClO<sub>3</sub><sup>--</sup>, though unless a very small amount of BrO<sub>3</sub><sup>--</sup> is present, it will have been identified in the group of acids giving silver salts insoluble in HNO<sub>3</sub>. If there is any guestion as to a positive test for  $ClO_3^-$  (by reduction) being due to BrO3-, the reduction test using m-phenylene diamine may be applied to the solution of AgBrO<sub>3</sub>, and thus even a small amount of  $BrO_3^-$  may be detected in the presence of  $ClO_3^-$ . But, if a small amount of ClO<sub>3</sub> - is present with a large amount of BrO<sub>3</sub><sup>-</sup> the identification is less simple. The chromyl chloride test is applicable where no other compounds of chlorine are present. It is also possible to reduce the BrO<sub>3</sub><sup>-</sup> with hydroxylamine sulphate, which will not reduce the ClO<sub>3</sub>-; precipitate and filter off the AgBr, and test for  $CIO_3^-$  in the filtrate by reduction with metallic Zn, FeSO<sub>4</sub>, etc. This procedure is indirect, and is only moderately satisfactory on a micro scale.

The reaction of concentrated  $H_2SO_4$  with a dry chlorate forms chlorine dioxide as well as  $HClO_4$ , and the  $ClO_2$  may be made the basis of a useful test. The deep yellow color of the  $ClO_2$ , either as a gas, or better, dissolved in the  $H_2SO_4$ , is apparent when 1 drop of a solution of 0.001 gram  $KClO_3$  per cc. (30 µg.  $ClO_3^{-1}$ ) is evaporated to dryness, and a small amount of  $H_2SO_4$  added. The ClO<sub>2</sub> thus evolved may be distinguished from Cl<sub>2</sub> and Br<sub>2</sub> by the fact that it decolorizes KMnO<sub>4</sub>, causing a precipitate of light brown, amorphous flocculent MnO<sub>2</sub> in the test drop. This is best carried out in a micro-crucible, as a distillation test.

 $ClO_2$ , evolved in a micro-crucible, may also be recognized by means of a hanging-drop test with  $Pb(C_2H_3O_2)_2$  solution.  $Pb(ClO_2)_2$  is formed, as described below under the reactions of chlorites.

ACIDS NOT READILY CLASSIFIED.

## ClO<sup>-</sup>, BrO<sup>-</sup>, IO<sup>-</sup>: ClO<sub>2</sub><sup>-</sup>.

A number of acids of the halogens show somewhat anomalous behavior. Ideally, they give Ag salts of definite composition and solubility, but actually, under the conditions of microscopic analysis, these are not to be relied upon. The precipitate either does not form, owing to the absence of the particular conditions necessary, or it forms only to be immediately decomposed into some other compound, which may give a different precipitate. On account of this, such acids cannot be grouped definitely on the basis of their ideal Ag salts, but rather on the basis of those actually obtained, and on other properties.

Hypohalites. Strictly speaking, these salts belong with those of the acids whose silver salts are soluble in water, but this classification is of little use in analysis, for the instability of the hypohalites is such that they are in effect characterized more by their oxidizing power and by their decomposition products, than by the reactions of the theoretically pure compounds themselves. Hypohalites are present in any solution of a halogen in water, and conversely their solutions decompose readily on acidification to liberate the halogen. Heating a solution of a hypohalite causes it to be transformed to a mixture of the corresponding halide and halate; thus a hypochlorite will give a precipitate of AgCl with Ag<sup>+</sup>, and a hypoiodite, one of AgI and AgIO<sub>3</sub>. The identification of the decomposition products of the hypohalites is simple. But since these decomposition products alone do not identify the hypohalite, evidence of its oxidizing power is necessary.

Solutions of hypohalites ordinarily smell of the free halogen; even such a weak acid as  $H_2CO_3$  decomposes hypochlorites, forming HCIO, which is unstable and gives off  $Cl_2$ . Any tests employed for Seite 88

the identification of the free halogens are best carried out in test drops, exposed to the hypohalite contained in a micro-crucible.

Cl<sub>2</sub> from decomposition of hypochlorites may be identified by the precipitate of AgCl which it gives with a test drop of AgNO<sub>3</sub>, or by similar reactions with Pb<sup>++</sup> or Tl<sup>+</sup> salts. The fact that the chloride is the only substance precipitated (any chlorates formed being soluble) is distinctive, since Br<sub>2</sub> or I<sub>2</sub> will give precipitates of bromates or iodates, in addition to the insoluble halide, and these may be recognized by their anisotropic character.

If  $Br_2$  is known to be absent,  $Cl_2$  may be recognized by its oxidizing action on KBr; a test drop containing a little KBr and some m-phenylene diamine is exposed to the gas, and if  $Cl_2$  is present a test for  $Br_2$  will be obtained in the drop.

The fact that  $Cl_2$  does not decolorize KMnO<sub>4</sub> solution is worthy of note because it serves to distinguish between  $Cl_2$ and  $ClO_2$ .

Br<sub>2</sub> from hypobromites is identified by the m-phenylene diamine reaction. The fact that insoluble AgBrO<sub>3</sub> is formed, as well as AgBr, is also of value.

 $I_2$  from hypoiodites is recognized by the starch reaction; with AgNO<sub>3</sub>, AgIO<sub>3</sub> and AgI are precipitated. The other reactions for  $I^-$  may be applied, if desired, for confirmatory tests.

Clorites are of rare occurence, and are notably unstable, particularly in solution, so that they are not as likely to be present in an unknown as are the other halogen acids. Their decomposition to  $Cl^{-}$  and  $ClO_{3}^{-}$  is common, while their formation, generally from chlorine dioxide, is very likely to be accompanied by the formation of  $ClO_{3}^{-}$ .

All chlorites are soluble except those of lead and silver. Of these two,  $Pb(ClO_2)_2$  is the more useful in analysis for it may be precipitated in very weakly acid solution and is moderately stable; but if the solution is more than slightly acid this salt is readily soluble with the evolution of the gas  $ClO_2$  and the formation of  $Cl^-$  in solution.

Pb(ClO<sub>2</sub>)<sub>2</sub> forms very fine grained platelets and tiny prisms and crosses which are highly refractive and strongly birefringent.

AgClO<sub>2</sub> is formed only in alkaline solution and is moderately soluble; its habit appears to vary considerably with the conditions of precipitation and it is probable that the composition of the precipitate varies also; but since only anisotropic crystals are obtained, this serves definitely to distinguish AgClO<sub>2</sub> from AgCl. Since chlorites liberate  $ClO_2$  on heating, the reaction of this gas with KMnO<sub>4</sub> may be used in their identification.

## PRELIMINARY TESTS.

If a limited amount of the sample is available only a small portion should be expended upon the preliminary tests outlined below. The bulk of the sample should be reserved for whatever confirmatory tests are indicated by the group reactions.

The following outline is presented merely as a guide to possible procedure and is one which we have found useful; but it should not be followed slavishly if any other order or tests seem more appropriate to the particular problem in hand.

#### PROCEDURE.

To a drop of the neutral or only very slightly acid solution to be tested add  $AgNO_3$  solution in slight excess.

R. No precipitate is obtained. There may be present . . . . . . . . . . .  $ClO_3^-$ ,  $ClO_4^$ a) Reduce and test for CI-. b) Evaporate solution to dryness, add a drop concentrated H<sub>2</sub>SO<sub>1</sub>; there is evolution of  $\text{ClO}_2^-$  and formation of  $\text{ClO}_4^-$  on heating . . . . .  $\text{ClO}_3^$ c) Concentrate solution. Add K+ and a very little KMnO<sub>4</sub>. Characteristic crystals . . . . ClO<sub>4</sub> CIO<sup>--</sup>, BrO<sup>--</sup>, IO<sup>--</sup>, CIO<sub>2</sub><sup>--</sup> Note color and crystalline character of precipitate. Filter and wash ppt. Test filtrate as in A. I. Extract precipitate with dilute  $HNO_3$  (1:10). a) The precipitate dissolves . . . . . .  $IO_4^-$ Identify by reduction. b) The precipitate is insoluble in HNO3, Extract repeatedly with hot water. Concen-Confirm by reduction of original material. II. Extract the precipitate with  $NH_4OH$  (1:4). a) The precipitate is soluble. Allow the solution to evaporate at room temperature. Examine for crystals . . . . . . . Cl<sup>-</sup>, Br<sup>-</sup>, IO<sub>3</sub><sup>--</sup> Confirm 103 with reduction test: Br with oxidation test: CIT with Ag+ after removal of Br and I by oxidation. Confirm I with oxidation.

**C.** In all cases in which a ppt. has been obtained with AgNO<sub>3</sub>, test for the presence of . . . . CIO<sup>-</sup>, BrO<sup>-</sup>, IO<sup>-</sup>, CIO<sub>2</sub><sup>-</sup> by methods discussed under **Acids not** 

Readily Classified.

In the Bunsen-Treadwell classification of acids the customary grouping on the basis of the solubilities of barium salts, while not so directly applicable to the identification of the halogen acids should nevertheless be utilized in conjunction with the system outlined above.

Familiarity with the microscopic appearance of the precipitates formed by  $Ag^+$  and  $Ba^{++}$  with the various acids may enable the analyst to go at once to specific confirmatory tests and thus greatly shorten the time required for the analysis.

The solubilities of the barium salts of the halogen acids are as follows:

Readily soluble in water:  $BaCl_2$ ,  $BaBr_2$ ,  $BaI_2$ ,  $Ba(ClO_3)_2$ ,  $Ba(ClO_4)_2$ ,  $Ba(IO_4)_2$ .

Very slightly soluble in water: Ba(BrO<sub>3</sub>)<sub>2</sub>.

Very slightly soluble in water but soluble in dilute  $HNO_3$ :  $Ba(BrO_3)_2$ .

Not readily soluble in HNO<sub>3</sub>: Ba(IO<sub>3</sub>)<sub>2</sub>.

It is a basic principle in microscopic gualitative analysis that tests should be chosen for their certainty and their applicability in the presence of a great variety of possible substances. The circumstances, the history of the sample, the possible presence of interfering substances as well as the character of the information desired are all to be weighed in the planning of the method of attack and often justify marked deviation from any systematic scheme of analysis.

All these things the authors have had in mind in their discussion of the reactions and methods whereby an analyst may be enabled to differentiate between salts of the various halogen acids. If it has seemed to the reader that we have entered too fully into the chemistry of the reactions involved, we can say in justification that we have believed it to be essential if these tests are to be intelligently applied and interpreted, and are to be time and labor saving. For in time and labor saving lies the chief value of microscopic analysis, rather than in its adaptability to the detection of small amounts of material. CORRECTIONS to the previous articles of this series: Jahrg. IV, Seite 147:

0,5g.Br... should read ... 0,5µg.Br.

Jahrg. V, Seite 96:

The best reagent for revealing the presence of  $CrO_2Cl_2$  was found to be  $HgNO_3$ ... should read ... AgNO<sub>3</sub>.

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