[Contribution from Department of Chemistry, University of North Carolina.]

ZIRCONYL COMPOUNDS WITH THE OXY-HALOGEN ACIDS.[1]

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Received July 23, 1919.

Little is known of the zirconyl oxy-halogen salts though a chlorate, iodate, and periodate have been mentioned in the literature. The following investigation was undertaken to devise methods of preparation, to see if definite compounds could be obtained, and also to observe the effects of hydrolysis upon them. The salts prepared were those with iodic, perchloric, and chloric acids.

Zirconyl Iodate.

As zirconium hydroxide is insoluble in iodic acid this salt was prepared by precipitation. When a concentrated solution of iodic acid is added to one of zirconyl chloride a curdy, white precipitate forms immediately. As the solution is added gradually the precipitate first forms, redissolves on stirring, but soon becomes permanent. The precipitate settles readily and can be washed by decantation. A similar precipitate forms when an alkali iodate is substituted for iodic acid, which, according to Brinton and James,[2] is almost insoluble in nitric acid, provided a considerable excess of the iodate ion is present. Davis[3] states that the precipitation with an alkali iodate added in excess, is almost quantitative but, on account of the varying composition of the precipitate it could not be used analytically.

The precipitate formed was a white powder, insoluble in water, alcohol, and ether. It was decomposed by conc. hydrochloric acid with evolution of chlorine. It showed decomposition when heated to 100° and iodine vapors were distinctly visible at 125°. For analysis, therefore, samples partially dried at room temperature were used. Five preparations were made, care being taken to have neither compound in excess in the precipitation. In the first preparation both solutions were concentrated and the iodic acid added gradually to the zirconyl chloride. In the remaining preparations more dilute solutions were used to make handling the precipitates easier. In the first and second preparation no additional water was used for washing, but the water present, which should contain practically only hydrochloric acid, was removed so far as possible by suction. The third preparation was washed with 6 liters of water at room temperature in one-liter portions. The fourth preparation was treated with 20 liters of hot water in one-liter portions, and the fifth in the

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[1] Submitted to the Faculty of the University of North Carolina by I. W. Smithey as part of the requirement for the degree of Master of Science.

[2] This Journal, 41, 1080 (1919).

[3] *Am. Chem. J.*, 11, 26 (1889).

same way with 30 liters of hot water. It was thought that this change of conditions should give an approximate idea as to the progress of hydrolysis. The analyses were made by treating the sample with conc. hydrochloric acid and titrating the liberated chlorine with sodium thiosulfate. From the hydrochloric acid solutions thus obtained the zirconium hydroxide was precipitated by ammonium hydroxide, ignited, and weighed as zirconia.

In reporting the analyses and calculated formulas the following considerations have prevailed with us: The hydrolyzing of zirconium salts results in the formation of zirconyl compounds and the separation of the acid radical which, if soluble, is removable by water. The zirconyl salt is commonly hydrolyzable further, resulting in the separation of more of the acid radical and the formation of a basic zirconyl compound. In the case of the chloride this hydrolysis may proceed until comparatively little of the acid radical is left. The question then arises as to the composition of the basic radical. The normal hydroxide is quite unstable and the methods of preparation used in the investigation would seem to preclude its presence in the basic compounds. The facts of ionic dissociation give abundant evidence of the existence of the ZrO radical in such compounds and, according to some investigators, of the existence also of another radical, Zr_2O_3. We have been chiefly influenced by the fact that dialysis separates zirconyl hydroxide from strongly hydrolyzed solutions and prefer to regard these basic compounds as addition compounds with zirconyl hydroxide and the use of such formulas undoubtedly presents a better picture of the progress of the hydrolysis. There is evidence also that part of the water is more persistently retained.

Analyses of the compounds to be described in this paper were made in duplicate. Only one is reported unless there were noteworthy variations in the duplicates or other reasons make it advizable to give both.

1. Precipitate formed from concentrated solutions and unwashed so that the first stage of hydrolysis might undergo no change. The analyses on the water-free basis yielded the ratio $ZrO:IO_3::30.62:69.38$. The formula $ZrO(OH)_2.2ZrO(IO_3)_2$ gives the ratio 31.36:68.64.

2. Precipitated from more dilute solutions and unwashed to observe the effect, if any, of change in concentration. With more time at disposal a series of experiments with measured changes of concentration would have been carried out. From the analyses on water-free basis the ratio $ZrO:IO_3::33.14:66.86$ was obtained. The ratio calculated for $5ZrO(OH)_2.8ZrO(IO_3)_2$ is 33.11:66.89. The amount of water then in the solutions materially affects the degree of hydrolysis.

3. The preparation made as in No. 2 was washed with 6 liters of water at room temperature to observe the effect of cold water upon the precipitate already formed. The water was used in one-liter portions. The analyses (water-free) gave the ratio $ZrO:IO_3::34.73:65.27$. The formula $3ZrO(OH)_2.4ZrO(IO_3)_2$ would require $ZrO:IO_3::34.76:65.23$.

4. The preparation was washed with 20 liters of boiling water in one liter portions to test the effect of increased amount of water and raised temperature. The ratio

found here was $ZrO:IO_3::48.33:51.67$, and that required for the formula $2ZrO(OH)_2.ZrO(IO_3)_2$ is $47.75:52.25$.

5. The preparation was washed with 30 liters of boiling water in one-liter portions to magnify such effects as might be caused under the conditions in No. 4. The analytical results gave the ratio $ZrO:IO_3::55.38:44.62$. For the formula $3ZrO(OH)_2.ZrO(IO_3)_2$ the ratio is $54.92:45.08$. The hydrolysis, therefore, has progressed still further.

Whether the analyses are to be taken as representing definite compounds or not is not very material for our purposes. It might possibly be settled by repeating the experiments under identical conditions to see whether the same compounds were always obtained. The iodate offers many advantages on account of its insolubility and quantitative precipitation for studying this and other points, and such work may be done later. For the present it remains to sum up the results obtained under a few rather arbitrary, widely-varying conditions, as follows:

No.	Conditions of precipitation.	Formulas.		Mols. hydrolyzed per 1000.
		With H_2O.	Without H_2O.	
1	Pptd. from conc. sol.; unwashed..............	$ZrO(OH)_2.2ZrO(IO_3)_2$	$Zr_3O_4(IO_3)_4$	334
2	Pptd. from dil. sol.; unwashed..............	$5ZrO(OH)_2.8ZrO(IO_3)_2$	$Zr_{13}O_{18}(IO_3)_{16}$	385
3	Pptd. from dil. sol.; washed; cold H_2O....	$3ZrO(OH)_2.4ZrO(IO_3)_2$	$Zr_7O_{10}(IO_3)_8$	431
4	Pptd. from dil. sol.; washed; 20 liters boiling H_2O............	$2ZrO(OH)_2.ZrO(IO_3)_2$	$Zr_3O_7(IO_3)_2$	667
5	Pptd. from dil. sol.; washed; 30 liters boiling H_2O............	$3ZrO(OH)_2.ZrO(IO_3)_2$	$Zr_4O_7(IO_3)_2$	750

The normal zirconyl iodate $ZrO(IO_3)_2$ is not formed by this method but, if formed, is immediately more or less hydrolyzed. At some later time efforts will be made to prepare both this and the normal iodate.

Zirconyl Perchlorate.

This compound has not been previously prepared. The ordinary 60% perchloric acid showed little solvent power, but on diluting with an equal amount of water it dissolved zirconium hydroxide readily. Bearing in mind the influence of temperature upon hydrolysis two different methods of solution were used. In the first case cold diluted acid was allowed to stand in contact with an excess of the hydroxide for some weeks. The clear liquid was then separated from the undissolved hydroxide and allowed to evaporate over calcium chloride. Two large crystals and several smaller ones formed. The larger ones measured 15 × 14 × 11 mm. and 13 × 12 × 9 mm., respectively, and apparently belonged to the triclinic system. They weighed over 2.5 g. each after drying between filter paper, and were analyzed. The zirconium hydroxide was precipitated by ammonium hydroxide, washed and ignited for zirconia. The filtrate and washings, containing ammonium perchlorate, were evaporated on a water bath, dried, weighed, and analyzed on a water-free basis.

Calc. for $4ZrO(ClO_4)_2.ClO_4H$: ZrO, 32.20; ClO_4, 67.65. Found: ZrO_2 (1), 31.52; (2), 32.11; ClO_4 (1), 68.48; (2), 67.89.

The second method of preparation was by heating the perchloric acid with an excess of zirconium hydroxide on a water bath until no more hydroxide was dissolved. This saturated solution formed, on cooling, radiating clusters of crystals from which individual crystals could not be separated. The mother liquor was poured off, the crystals washed with a small amount of water and placed over sulfuric acid. They were very deliquescent and failed to dry completely. They were odorless, soluble in alcohol, ether, benzene, chloroform, and carbon tetrachloride, but no crystals were obtained from these solutions. A small portion heated quickly on platinum foil exploded with a sharp report, but when heated slowly it intumesced, leaving finally a white mass of zirconia. Decomposition was evident at 100°. Four different preparations were made and samples analyzed with the following results:

Water-free; ZrO, 37.79, 37.84, 37.82, 37.70; ClO_4, 62.21, 62.16, 62.18, 62.30

The reaction, then, may be represented by the equation

$$8ZrO(ClO_4)_2.ClO_4H + 2ZrO(OH)_2 = ZrO(OH)_2.9ZrO(ClO_4)_2 \ldots\ldots,$$

two molecules of the zirconyl perchloric acid dissolving two molecules of zirconyl hydroxide, this being the limit of saturation. The percentages required by the formula for this basic zirconyl perchlorate on the water-free basis are ZrO, 37.32 and ClO_4, 62.68. The crystalline character of the product and the uniformity of the results from several different preparations would go to show that the compound is a definite one. We have in these two compounds analogy with zirconyl sulfuric acid, $ZrOSO_4.SO_4H_2$.

In attempting to purify by recrystallization the crystalline crop obtained on saturating perchloric acid with zirconyl hydroxide it was found that, while crystals formed, they had returned to the composition of the original zirconyl perchloric acid, $4ZrO(ClO_4)_2.ClO_4H$. Part of preparation No. 1 was recrystallized 4 times and of preparation No. 2, 5 times, and the resulting crystals analyzed.

Found: ZrO_2 (1) 31.77; (2) 32.31; ClO_4, (1) 68.23, (2) 67.69.

These results agree with those required for the formula $4ZrO(ClO_4)_2.ClO_4H$.

This would appear to be the more stable form, two molecules of it having the power of forming a compound with one molecule of zirconyl hydroxide, this being dissociated on resolution.

Zirconyl Chlorate.

Weibull[1] has reported the preparation of this compound by the double

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[1] *Act. Univ. Lund.*, II, 18; V, 53 (1881).

decomposition of zirconium sulfate and barium chloride according to the equation

$$Zr(SO_4)_2 + 2Ba(ClO_3)_2 = BaSO_4 + Zr(ClO_3)_4,$$

assigning to the product the latter formula. Details and analyses are not given. Zirconium sulfate, however, is hydrolyzed in solution and the chlorate cannot well have the composition indicated as it also hydrolyzes.

Basic zirconyl chlorate was prepared by us by adding a solution of potassium chlorate to a cold concentrated solution of zirconyl perchlorate. An abundant crop of crystals formed immediately, consisting of potassium perchlorate and containing no zirconium. Additional crops of these crystals were separated as evaporation proceeded, the mother liquor becoming yellow, syrupy, and smelling of chlorine dioxide. Further concentration yielded larger, well-formed crystals, differing from the preceding crops. Only a faint test for potassium was obtained. The crystals were very deliquescent, soluble in alcohol but insoluble in ether. They had a slightly yellowish color and oxidized organic matter. Some of the crystals were washed and dried over phosphorus pentoxide. Neither calcium chloride nor sulfuric acid were effective as drying agents. In analyzing the chlorine was determined by dissolving a weighed amount in water in a small flask fitted with a separatory funnel for hydrochloric acid, a tube for admitting carbon dioxide, and a delivery tube connected with two U-tubes in series, containing potassium iodide solution. The liberated iodine was titrated with 0.1 *N* sodium thiosulfate. The zirconium hydroxide was precipitated from the hydrochloric acid solution, ignited, and weighed. Two preparations were analyzed on a water-free basis.

Calc. for $ZrO(OH)_2.3ZrO(ClO_3)_2$: ZrO, 45.99; ClO_3, 54.01. Found: ZrO_2, (1) 45.18; (2) 45.95; ClO_3, (1) 54.82, (2) 54.05.

The normal zirconyl chlorate was therefore not obtained. If formed, it was hydrolyzed under the conditions of the experiment. The hydrolysis is less far-reaching than in the case of the iodate, as only one out of four of the molecules are hydrolyzed compared with one out of three in the latter case. The definite nature of the hydrolyzed product is proved by the crystalline form. It is manifestly not very stable, as shown by the liberation and decomposition of chloric acid.

Summary.

1. Several basic zirconyl iodates were prepared and the stages of progressive hydrolysis indicated.

2. The perchlorate $4ZrO(ClO_4)_2.ClO_4H$ was obtained. This can be dissolved and recrystallized without further hydrolysis. Two molecules of it when warmed will dissolve two molecules of zirconyl hydroxide, forming $ZrO(OH)_2.9ZrO(ClO_4)_2$, which is also crystalline. On redissolv-

ing and crystallizing the acid perchlorate or zirconyl perchloric acid separates.

3. The basic zirconyl chlorate formed is crystalline and corresponds to the formula $ZrO(OH)_2.3ZrO(ClO_3)_2$. It is easily decomposed.

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STUDIES IN CONDUCTIVITY. V. NOTES ON THE MEASUREMENT OF THE CONDUCTIVITY OF SOLUTIONS.

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Received July 28, 1919.

During the past few years a series of very thorough and valuable papers by Washburn and his associates[2] on the methods and apparatus for measuring the conductivity of solutions has been published. ,Other papers by Acree and his students[3] have also added greatly to our knowledge of the subject. Nevertheless a number of difficulties which we have encountered in the measurements required for our work on formic acid solutions have either not been touched on at all or have received only very scant attention as will be pointed out below. Since we have developed simple criteria for detecting the difficulties in question and simple methods for overcoming them, it has been suggested to us that the publication of a résumé of these points would be of value to other workers in this field.

The resistance of the solutions was measured by the Wheatstone-Kohlrausch method, using a Siemens and Halske high frequency generator, a rotary bridge, and a standardized Curtis coil resistance box. The connections and the methods of shielding the apparatus are those recommended by Washburn and Bell.[4] In conjunction with the high frequency circuit we used a Leeds and Northrup condenser which permits of placing equal capacities in series with the two lines of the circuit; by means of a two-way switch this condenser could be eliminated and readings taken without any capacity in the high frequency circuit. It was observed that the introduction of the condenser, while it improved the sharpness of the minimum, decidedly shifted its position and that the shift thus produced depended on the type of resisting medium and the magnitude of

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[1] The work reported in this and the following paper of this series has been presented to the Faculty of the Ogden Graduate School of Science of the University of Chicago by F. H. Reed in part fulfillment of the requirements for the degree of Doctor of Philosophy. The work was completed in the fall of 1916.

[2] THIS JOURNAL, **38**, 2431 (1916); **39**, 235 (1917).

[3] Acree and Taylor, *Ibid.*, **38**, 2396 (1916).

[4] THIS JOURNAL, **35**, 177 (1913). An excellent résumé of the Washburn apparatus is given in the Leeds and Northrup *Catalog* **48** (1915).