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GLYCOLATES AND LACTATES OF
ZIRCONIUM AND HAFNIUM

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ZIRCONIUM GLYCOLATE

In investigating various substituted glycolic acids as analytical reagents for the determination of zirconium, Oesper and Klingenberg observed that a precipitate was formed when solutions containing high concentrations of zirconyl ions were treated with glycolic acid. (6). Quantitative precipitation was not obtained, hence, no further study was made. Blumenthal reported that sparingly soluble solids resulting from the interaction of zirconyl chloride and alpha-hydroxy aliphatic acids appear to have the general formula $H_2ZrO(O_2C \cdot CRHOH)_3$. No experimental data were cited; however, Mandl(5) reported the formation of a soluble compound $K_4Zr(C_2H_3O_3)_8 \cdot 3H_2O$ when a solution of potassium glycolate was treated with zirconium nitrate. Since no other mention of zirconium glycolate was found in the literature this investigation was undertaken to determine the exact composition and properties of the zirconium glycolate precipitate.

Experimental

A solution of zirconyl chloride was prepared by dissolving a known amount of chemically pure $ZrOCl_2 \cdot H_2O$ in 2M hydrochloric acid. Glycolic acid solutions were prepared by adding concentrated (12M) hydrochloric acid to glycolic acid (Eastman 70%) in an amount sufficient to make the mixture 2M in hydrochloric acid. The hydrochloric acid was added to prevent hydrolysis of the zirconyl chloride and the precipitate.

The zirconyl chloride solution was heated to $80^\circ C$ and a large excess of the above glycolic acid - hydrochloric acid solution was added dropwise from a burette. No precipitate formed in the hot solution but on cooling a finely divided white precipitate was formed. After standing for 48 hours the precipitate was filtered off, washed with successive portions of water, ethyl alcohol, and ether, then

dried at 110° for 4 hours. Analysis of the remaining solution showed that only 30 - 40 percent of the total zirconium was precipitated.

The above procedure was repeated for solutions which were 6M and 10M in hydrochloric acid. In these cases no precipitates were obtained at all, even after standing in the cold for several days. Upon dilution with ethyl alcohol, precipitates were obtained identical with those from the 2M solution.

In solutions less than 2M in hydrochloric acid, precipitates were obtained easily. These precipitates were identical in composition with those obtained from solutions of greater acidity, which indicated that no appreciable hydrolysis took place during precipitation.

Determination of the composition of the precipitate.

Known weights of the dried precipitate were ignited to constant weight and the weight of residue of zirconium oxide determined. From these data the empirical weight of the precipitate was determined. The values determined on four separate samples gave the following: 321.2, 332.7, 331.3, 332.5. These are in close agreement with the value of 333.4 from the formula, $\text{H ZrO}(\text{O}_2\text{C}\cdot\text{CH}_2\text{OH})_3$, postulated by Blumenthal. (2).

Carbon and hydrogen determinations also agreed.

C: (calculated) 21.62% (found) 21.48%

H: (calculated) 3.02 (found) 3.21

The solid zirconium glycolate was a finely divided hygroscopic powder, sparingly soluble in water and dilute mineral acids. It dissolved rapidly in ammonium hydroxide (dilute or concentrated) giving a clear solution. This indicated that a soluble complex was formed in basic solution. Dilute solutions of sodium hydroxide, however, produced a gelatinous precipitate of zirconium hydroxide indicating that the zirconium glycolate complex was not very stable.

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HAFNIUM GLYCOLATE

Experimental

Hafnium glycolate was prepared by treating hafnium chloride (HfOCl_2 99% pure) solutions with mixtures of glycolic acid and hydrochloric acid. The procedure followed was the same as that outlined previously for the preparation of zirconium glycolate. Precipitations were made from neutral, 2M, 4M, and 6M hydrochloric acid solution. These precipitates were identical in all cases. As the acidity was increased a smaller fraction of the hafnium was precipitated. In strongly acid solution, ethyl alcohol had to be added to obtain a precipitate. White finely divided precipitates were obtained as with zirconium.

Analysis of these precipitates gave the following results:

Empirical weight: 403.1, 401.4, 402.8

Calculated for $\text{H HfO}(\text{O}_2\text{C}\cdot\text{CH}_2\text{OH})_3$ 420.7

Carbon (observed) 18.5% (calculated) 17.1

Hydrogen (observed) 2.7 (calculated) 2.4

The calculated and observed results were not in as good agreement as with the zirconium glycolate. The lower empirical weight might be explained by partial hydrolysis, and the formation in part of a compound having the composition:

ZIRCONIUM LACTATE

Previous Work Behrens (1) reported the precipitation of zirconium by ammonium lactate in the presence of a little free lactic acid. Mandl (5) noted the formation of a temporary precipitate in a neutral solution containing zirconium nitrate and potassium lactate. De Boer (3) reported that zirconium formed a soluble complex with the lactate ion in alkaline solution. Oesper and Klingenberg (6) observed that a precipitate was formed when concentrated solutions of zirconyl

chloride were treated with lactic acid. Since none of the above investigators studied the composition and properties of the zirconium lactate precipitate, this investigation was made.

Experimental

Zirconium lactate was precipitated from neutral, and 2M, 4M, and 6M solutions of hydrochloric acid by the dropwise addition of lactic acid. Immediate precipitation was noted in the neutral and 2M acid solutions. A precipitate formed upon cooling the 4M acid solution, and ethyl alcohol had to be added to the 6M acid solution before a precipitate was obtained. About 650% of the zirconium was precipitated from the 2M acid while only 40% from the 6M acid.

The precipitates were filtered, washed with ethyl alcohol and ether, then dried at 110°. The zirconium lactate was obtained in the form of a white, finely divided, hygroscopic powder. This was sparingly soluble in water. Ammonium hydroxide dissolved the precipitate completely giving a clear solution. Sodium hydroxide solution reacted to form a precipitate of zirconium hydroxide.

The precipitate of zirconium lactate was analyzed, and like zirconium glycolate, was found to correspond to Blumenthal's formula:

Calculated: formula weight 375.4; C, 28.8; H, 4.30

Observed: formula weight (over) 372; C, 28.4; H, 4.5

HAFNIUM LACTATE

Experimental

Solutions containing hafnium chloride (99.9% pure) were treated with lactic acid under the same conditions described under the precipitation of zirconium lactate. Identical results were obtained. The hafnium lactate was a white hygroscopic powder, slightly soluble in water and soluble in ammonium hydroxide. It reacted with sodium hydroxide solution to give a gelatinous precipitate of hafnium hydroxide.

Analysis of the precipitate gave the following:

formula weight (aver) 473; C, 23.25; H, 3.68

Calculated for

formula weight 462.8 C, 23.35; H, 3.49

The fact that the observed empirical weight is greater than the calculated formula weight may be due to the formation of a small amount of $\text{Hf}(\text{O}_2\text{C}\cdot\text{CHOHCH}_3)_4$ by analogy with hafnium tetramandelate (4).

Summary:

Zirconium glycolate, hafnium glycolate zirconium lactate and hafnium lactate were prepared. These compounds are formed as white finely divided precipitates when zirconyl or hafnium chloride solutions are treated with glycolic, or lactic acids. The precipitates are sparingly soluble in water and in dilute hydrochloric acid. The composition approximates the general formula, $\text{H ZrO}(\text{O}_2\text{C}\cdot\text{CRHOH})_3$, as given by Blumenthal (2).

The solids dissolve in dilute or concentrated ammonia forming soluble ammonium compounds. Strong bases react to give a precipitate of insoluble zirconium (or hafnium) hydroxide.

Because of the hygroscopic nature and indefinite composition these compounds are not suitable for analytical purposes. (auth)

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