

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF
NORTH CAROLINA]

BEHAVIOR OF OXALATE AND TARTRATE SOLUTIONS OF COLUMBIUM AND TANTALUM OXIDES¹

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Introduction

The freshly precipitated oxides or hydroxides of columbium and tantalum are appreciably soluble in aqueous solutions of oxalic and tartaric acids. This paper is chiefly confined with the nature of the resulting solutions.

The solvent action of these acids on the freshly precipitated hydrated oxides may theoretically be due to a simple reaction of double decomposition with the formation of the corresponding salt; to peptization of the hydroxide by the oxalate and tartrate ions; and by the formation of a complex. Russ² claims to have prepared a columbium oxalate to which he assigned the formula $\text{Cb}(\text{HC}_2\text{O}_4)_5$. He did not make a thorough investigation of the nature of the aqueous solution of this compound. It appears very unlikely that the columbium exists here as the simple cation since columbium and tantalum ions are so very rare and unstable in aqueous solutions. One might as well write the above formula as $\text{H}_5\text{Cb}(\text{C}_2\text{O}_4)_5$. According to Werner,³ this compound may ionize into hydrogen ions and complex ions containing the metal. Evidence of this complex anion formation will be described in this paper.

Experimental

Preparation of the Pure Oxides.—The starting material consisted of a partially purified mixture of columbium and tantalum oxides containing some iron and silica. The iron was removed as follows: after grinding, the oxides were dissolved in a hot concentrated solution of oxalic acid and the solution was filtered while hot through a Büchner funnel to remove any undissolved particles of silica. After cooling, the filtrate was diluted to twice its former volume. The columbium and tantalum were precipitated from this solution as the white amorphous columbic and tantalic acids upon the addition of an equal volume of concentrated hydrochloric acid. The whole contents was allowed to stand overnight, when the supernatant liquid was carefully decanted from the sediment. A little water was added and the contents stirred and filtered through a Büchner funnel. The residue was washed five times with hot 3 *N* hydrochloric acid and finally with water. It consisted of a mixture of columbic and tantalic acids, the iron being dissolved in the hydrochloric acid and passing into the filtrate. Although this procedure is satisfactory for the removal of iron, it is not recommended for a quantitative

¹ The material in this paper is an abstract of a thesis submitted by G. G. Albritton to the Graduate school of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

² Russ, *Z. anorg. Chem.*, **31**, 42 (1902).

³ Werner, *J. Chem. Soc.*, **51**, 383 (1887).

recovery of the oxides of columbium and tantalum since some of these also dissolve in the hydrochloric acid.

Separation of Tantalum from Columbium.—The tannic acid method of Powell and Schoeller⁴ was used to separate tantalum from columbium. This method of separation is based on the fact that tantalum is precipitated from an oxalic acid solution with tannic acid at a hydrogen-ion concentration too high for a precipitation of the columbium. Although this method of obtaining pure tantalum from a mixture of the oxides is satisfactory, it is not desirable for a rapid quantitative separation. There is a certain range of the hydrogen-ion concentration where columbium always begins to fall out before all the tantalum has precipitated. The precipitate formed within this range of hydrogen-ion concentration was rejected since a quantitative separation was not the object here. The tannic acid precipitates were ignited to the snow-white pentoxides.

Behavior of the Oxalate Solution.—Since the ignited oxides are insoluble in oxalic acid they were fused in silica crucibles with potassium bisulfate to a clear melt, according to the method of Schoeller and Powell.⁴ After cooling, the fused mass was readily dissolved in a hot concentrated solution of sulfuric acid. Upon dilution and the addition of ammonia to neutralization, the white, gelatinous hydrated oxides of the metals precipitated. This unignited precipitate was readily and completely soluble in a boiling solution of oxalic acid.

The resulting solution behaved toward certain reagents as follows. Ammonia and the alkali hydroxides caused an incomplete precipitation of the metals as white amorphous precipitates. The tantalum being the least stable, is precipitated from this solution at a somewhat higher hydrogen-ion concentration than columbium. However, a quantitative separation was not realized when a mixture of the two oxides in oxalic acid solution was treated in this manner. In the presence of each other, the metals lose their individualities and behave in an almost identical manner.

The oxalate solution showed no evidence of a reaction toward organic acids, as citric, malic, succinic, benzoic, phthalic, salicylic and picric. The reagent acid crystallized in every case upon standing.

All attempts to prepare double oxalates with the heavy metals proved unsuccessful when the solution was treated with salts of Fe^{++} , Fe^{+++} , Co^{++} , Ni^{++} , Hg^{++} , Ag^+ , Hg^+ , Cu^{++} , Al^{+++} and Cr^{+++} . In every case the oxalate of the reagent metal was precipitated.¹ [Russ claims to have prepared a double oxalate of columbium and barium to which he assigned the formula $\text{Cb}_2\text{O}_5 \cdot \text{BaO} \cdot 10\text{C}_2\text{O}_4$.]

Behavior of the Tartrate Solution.—Like oxalic acid and the alkali oxalates, tartaric acid and the alkali tartrates show appreciable solvent action on the freshly precipitated hydroxides of the two metals, which must be transferred to the tartrate solvent immediately after washing. The solubility of the hydroxides decreases rapidly when they are allowed to dry in the air. Furthermore the solvent action seems to be greatest if the solution is not heated to boiling but to a few degrees below. It may be mentioned here that solution takes place rather slowly as if dependent on an organic type of reaction rather than a reaction of the ionic type.

Differing from the oxalate solution, the metals are not precipitated in the least from the tartrate solution by ammonia and the alkali hydroxides. Strong mineral acids cause the metals to precipitate in the usual white amorphous form. Of the various salts of the heavy metals, only cobalt and calcium showed any evidence of forming complex tartrates with the metals. No activity was shown toward the above-mentioned organic acids. Acetone caused a quantitative precipitation of the metals in a fine white crystalline form, readily soluble in warm water. The resulting solution likewise proved to be inactive toward the various reagents.

⁴ Powell and Schoeller, *Analyst*, 50, 485 (1925).

Since the tartrate solution of the two metals showed very little activity, its exact nature became a question of interest. Experiments were carried out in an attempt to gain some knowledge of the manner in which the metals are held in solution.

An aqueous solution of tartaric acid was saturated with freshly precipitated columbium hydroxide and allowed to stand over sulfuric acid. The solution became viscous after a few days, and finally fine white tetrahedral crystals made their appearance. These crystals were found not to be tartaric acid. Upon prolonged standing they set to a hard crystalline mass which was very soluble in warm water. The resulting solution was inactive toward ammonia and the alkali hydroxides. This inactivity toward bases together with the formation of a viscous solution and a subsequent crystallization of microscopic crystals indicates the formation of tartrate complexes.

Other Evidence of Complex Tartrate Formation.—The change in the total hydrogen equivalent of the solvent, tartaric acid, was determined by saturating an aqueous solution of 9.5356 g. of tartaric acid with the hydroxide and the subsequent titration with sodium hydroxide, using phenolphthalein as indicator. The tartaric acid solution was diluted to 250 cc. and aliquots of 25 cc. were titrated against 0.3826 *N* sodium hydroxide.

RESULTS		
Tartrate solution, cc.	25	25
Base, cc.	33.3	33.2
Total hydrogen equiv. calcd. as free tartaric acid, g.	9.5550	9.527

These results clearly show that there is no change in the total hydrogen equivalent of the tartaric acid. The dissolving of the hydroxide evidently does not involve a reaction of double decomposition in which hydrogen ions take part with formation of simple salt, or else if such a salt is formed it must be less stable than phenolphthalein, which seems improbable.⁵

The presence of a negative ion was determined electrolytically. Pure tartaric acid solution was placed in an anode compartment and the tartaric acid solution of the columbium pentoxide in the cathode compartment. The two compartments were connected by means of a salt bridge containing pure tartaric acid solution, the ends of which were plugged with cotton to prevent mechanical diffusion. The two platinum electrodes were connected to ten dry cells arranged in series. Three hours after closing the circuit the anode solution gave a decided test for columbium, and in twenty hours all the columbium had migrated to the anode.

Similar experiments were performed using tantallic acid instead of columbic. The behavior was the same.

These results indicate either a complex anion or an adsorption complex in which the metal is attached to the acid other than by the carboxyl group. Practically there is little difference between the two concepts.

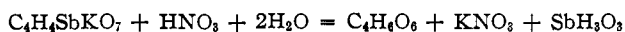
Preparation and Analysis of Tartra-columbic Acid.—An aqueous solution of tartaric acid was saturated with $\text{Cb}(\text{OH})_5$ by warming and stirring with an excess of the hydroxide for six hours. The undissolved hydroxide was filtered off and the filtrate allowed to stand over sulfuric acid. Fine white tetrahedral crystals formed after two days. Analysis showed the composition to be: Cb, 22.05%; $\text{C}_4\text{H}_4\text{O}_6$, 73.25%; H_2O (crystallization), none. The results of this analysis give a ratio of two moles of tartrate to one mole of columbium and a total percentage of 95.33. Now if it be assumed that one OH group is attached to the columbium as in the compound $(\text{C}_4\text{H}_4\text{O}_6)_2\text{CbOH}$, the metal will then have a normal valence of five and the total percentage would be 99.51.

This formation of a compound of definite composition proves that the metal is not

⁵ Mellor, "Modern Inorganic Chemistry," Longmans, Green and Co., 1930, p. 286.

present in a dispersed condition. Evidently the hydroxide is acted upon by tartrates in a manner analogous to antimony, aluminum, arsenic, vanadium and other acidic oxides forming a class of compounds of the tartar emetic type.

Comparison with Other Acidic Oxides.—Clarke and Stallo,⁶ in an investigation into the nature of the tartrates of antimony, came to the conclusion that tartar emetic ($\text{KC}_4\text{H}_4\text{O}_6\text{SbO}$) is a salt of the acid, $\text{Sb}(\text{C}_4\text{H}_4\text{O}_6)$. This acid, which he named tartra-antimonious acid, interacts, so he said, with the strong mineral acids with the precipitation of H_3SbO_3 according to the equation

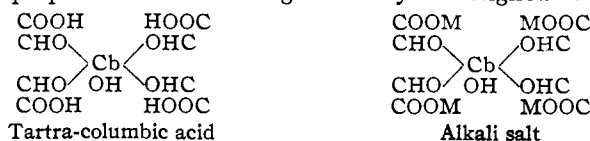


Henderson,⁷ in a study of the action of certain acidic oxides on salts of hydroxy acids, prepared a sodium tartrarsenite by dissolving arsenious oxide in a hot solution of sodium hydrogen tartrate. Analysis showed the empirical formula to be $\text{AsONaC}_4\text{H}_4\text{O}_6 \cdot 2.5\text{H}_2\text{O}$. It appeared probable that this compound was the salt of tartrarsenious acid. This led him to the conclusion that the oxide enters into reaction with part or all of the alcoholic groups. According to this view the formula (A) was assigned to the so-called tartrar-senious acid. He failed to show, however, that the arsenic was tied up in a complex anion. No ion migration tests were made.

Discussion of Results

As regards the constitution of the compounds formed by the action of tartaric acid on the hydroxides of columbium and tantalum, in the first place, it may be considered certain that they are not salts in which the radicals (HCbO) and (HTaO), play the part of metallic elements in replacing the hydrogen of one or more carboxyl groups. Moreover, the formation of these compounds by the action of hot aqueous solutions of the alkali tartrates and tartaric acid proceed very slowly. This mode of formation has a much closer resemblance to the organic type of reaction than to the production of metallic salts by the action of an acid on a basic oxide.

The structure of these compounds which agrees with the slow process of formation, composition and properties, is that the radicals (HCbO) and (HTaO) replace the hydrogen of the alcoholic hydroxyl groups, forming substances comparable to the acetyl and benzoyl derivatives of the hydroxy acids. If this view is accepted the following constitutional formulas for the compounds prepared in this investigation may be assigned as follows



⁶ Clarke and Stallo, *Am. Chem. J.*, **2**, 319 (1880).

⁷ Henderson, *J. Chem. Soc.*, **67**, 102 (1895).

where M represents the alkali metal. This conclusion is in accord with that of Henderson, concerning the action of the tartrates on arsenious oxide.

Ion migration test of the oxalate solution also showed that the metals migrate as anions. According to Russ² the oxides dissolve in oxalic acid forming definite compounds to which he assigned formulas. He did not test for the complex nature of these compounds. Since this investigation revealed the fact that the metals migrate as anions, it must be concluded that they are joined with the oxalate ions, forming complexes. It may be that columbium and tantalum form complexes with oxalic acid similar to chromium. According to Werner,³ chromium forms with oxalic acid the complex chromo-oxalic acid, $H_6Cr_2(C_2O_4)_6$, where the chromium is united with the oxalate ion forming a complex anion. In agreement with this theory, columbium and tantalum would form the compound, $H_5M(C_2O_4)_5$, where M represents the metal.

Summary

The freshly precipitated hydrated oxides of columbium and tantalum were found to be appreciably soluble in a hot aqueous solution of tartaric acid, forming compounds of the tartar emetic type.

Also it was found that the compounds formed when the oxides were dissolved in oxalic acid were not simple salts, but instead there were formed complexes. Ion migration tests showed that the metals united with the oxalate ion to form complex anions.

The oxalate and tartrate solutions of columbium and tantalum showed no activity toward various organic acids.

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE PREPARATION OF IODINE-FREE BROMINE

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The purification of most of the reagents used in the preparation of large samples for analysis for small amounts of iodine has been discussed at length by von Fellenberg¹ and Reith.^{2,3,4} Some of the reagents used in smaller amounts, however, have not been dealt with so completely by these or other authors. Bromine, which is used as an oxidizing agent in one titrimetric method for the final determination, offers considerable chance for the introduction of iodine into the blank, *c. p.* bromine being frequently listed as containing 0.1% of that element. Saturated bromine water

¹ Von Fellenberg, *Ergebnisse Physiol.*, **25**, 194 (1926).

² Reith, Dissertation, Utrecht, July, 1929.

³ Reith, *Biochem. Z.*, **216**, 250 (1929).

⁴ Reith, *ibid.*, **224**, 223 (1930).