7.5% sulfuric acid, the element will precipitate to some extent when as much as 0.2 g. is present, even in solutions containing 50% by volume of either acid.

Thorium.—The determination of thorium with phenylarsonic acid was accomplished by Rice, Fogg and James[1] only in solutions containing acetic acid and ammonium acetate. However, in the present work it was found that part of the thorium was precipitated, when 35 cc. of reagent was used, in a 5% solution of hydrochloric acid. This is the upper limit of acidity permissible for the determination of tin. A satisfactory separation of tin and thorium with this reagent does not seem possible.

Bismuth.—Due to the tendency of bismuth salts to hydrolyze it was necessary to precipitate in solution containing 5% by volume of hydrochloric acid. Results were not satisfactory in sulfuric acid solution. The volume of the solution was kept at approximately 200 cc. Precipitation was done in hot solution by the addition of 40–50 cc. of the reagent and the mixture was allowed to stand several hours before filtering. Reprecipitation was not necessary. The determination was completed in the manner already described. Taking amounts of stannic oxide between one and two tenths of a gram, in the presence of approximately equal amounts of Bi_2O_3, four determinations gave results with an average deviation of two parts per thousand.

Summary

A new gravimetric method for the determination of tin has been described, in which the tin is precipitated with phenylarsonic acid. This method separates tin quantitatively from a number of elements commonly occurring with it in alloys, but not from zirconium or thorium.

STATE COLLEGE, PENNSYLVANIA

RECEIVED MARCH 29, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Action of Hydriodic Acid on the Difficultly Soluble Sulfates[1]

BY EARLE R. CALEY

While a number of facts indicate that hydriodic acid is generally more reactive chemically than either hydrochloric acid or hydrobromic acid under like conditions, it has not been recognized that this difference is so great that a number of slightly soluble compounds, quite inert toward the latter acids, react easily with hydriodic acid, a striking example being stannic oxide.[2] In a preliminary note[3] it was stated that a number of other compounds highly resistant to hydrochloric acid, and even such active solvents as nitric acid and aqua regia, are more or less readily decomposed by hydriodic acid. This present paper contains a more detailed account of the action of the latter acid on certain of these compounds.

Materials and General Procedure.—The hydriodic acid used in the experiments was principally the constant boiling acid of specific gravity

---

(1) Abstracted from a paper presented at the 85th meeting of the American Chemical Society, Washington, D. C., March, 1933.

(2) Caley, THIS JOURNAL, **54**, 3240 (1932).

(3) Caley, *ibid.*, **54**, 4112 (1932).

1.70, although for certain experiments acids of lower concentration were prepared from this by dilution. The several reactions were tried through repeatedly with a pure acid prepared by the interaction of iodine and hydrogen sulfide, and also with a commercial constant boiling acid stabilized by the addition of 1–2% of hypophosphorous acid. Since the use of the stabilized acid is so much more convenient from a practical manipulative viewpoint, duplicate experiments using this mixture were performed in view of the possible applications of these reactions in chemical analysis. Qualitatively, and to a large extent quantitatively, practically no differences were observed in the behavior of the two acids except in respect to ease of air oxidation and amount of free iodine liberated in the reactions. The several sulfates used in these experiments were prepared by the writer from pure chemicals.

In the following experiments the general procedure was to treat weighed samples of the finely divided solids with definite volumes of acid of known concentration at various temperatures, noting evidences of a reaction or lack of reaction and, in the case of a reaction taking place, collecting and examining the gaseous or solid products by the usual qualitative or quantitative methods, usually both. In cases where pure hydriodic acid was employed the reactions were studied under a carbon dioxide atmosphere, while the corresponding experiments with the stabilized acid were performed in air.

Alkaline Earth Sulfates.—At room temperature the sulfates of barium, strontium and calcium are somewhat less soluble in concentrated solutions of hydriodic acid than in solutions of hydrochloric or hydrobromic acids of like normality, as found by a series of solubility determinations. On the other hand, these compounds have a much higher apparent solubility in hot solutions of concentrated hydriodic acid than in similar solutions of hydrochloric and hydrobromic acids due to an oxidation–reduction reaction progressively occurring between the dissolved salt and the acid, that results in the formation of hydrogen sulfide, iodine, water, and the corresponding metallic iodides. The onset of this reaction is dependent on acid concentration, temperature, and the sulfate-ion concentration as furnished by a particular salt, varying for the salts in the order of their solubility as shown in Table I. The following results are illustrative of the speed with which constant boiling hydriodic acid effects the decomposition of these sulfates at the boiling point in an open vessel. With the quantities given in the footnote to the table, complete decomposition of calcium sulfate occurs in about one minute, that of strontium sulfate in from seven to eight minutes, while barium sulfate decomposes only to the extent of about 60% in twenty minutes. Complete decomposition of the latter cannot be effected under these conditions due principally to the adverse effect of the progressive increase in barium-ion concentration on the solubility of

TABLE I

INFLUENCE OF ACID CONCENTRATION AND TEMPERATURE ON THRESHOLD APPEARANCE OF THE REACTION BETWEEN ALKALINE EARTH SULFATES AND HYDRIODIC ACID[a]

Effect sought	Acid normality	Barium sulfate	Strontium sulfate	Calcium sulfate
Apparent rate of decomposition in boiling acid of medium concentration	1.0	Nil	Nil	Very slow
	2.0	Nil	Very slow	Slow
	3.0	Very slow	Slow	Mod. slow
Apparent rate of decomposition in constant boiling acid at the boiling point	7.6	Slow	Mod.	Rapid
Approximate temperature of beginning reaction in constant boiling acid, °C.	7.6	85	60	50

[a] In each of these experiments a 100-mg. sample of the powdered (100-mesh) sulfate was suspended in 10 cc. of acid in a tube containing a strip of lead acetate paper suspended above the liquid. Evolution of hydrogen sulfide was used as an indication of the start of the reaction and length of paper stained in a given time an indication of the rate of decomposition.

the sulfate and hence on the concentration of dissolved salt available for further reaction. By using successive fresh portions of acid, however, small samples of barium sulfate can be transposed completely. That this decomposition is not due to a direct surface action of the hydriodic acid on these sulfates was indicated by experiments in which a soluble sulfate was first dissolved in cold constant boiling acid in an amount just sufficient to reproduce the initial concentration of sulfate ion furnished by the previously-measured slight solubility of a given alkaline earth sulfate, and then the resulting homogeneous solution was heated. Under these conditions it was observed that the action started at about the same temperature and gave the same reduction products as though the particular alkaline earth sulfate were present. The decomposition of alkaline earth sulfates by hot concentrated hydriodic acid apparently takes place then in two principal stages. First, the salts dissolve to a limited extent in the acid, furnishing the usual ions to the solution, after which the oxidation–reduction reaction takes place between the sulfate ions and the acid. The two stages follow each other progressively and the total rate of decomposition with a given salt depends primarily on the velocity with which sulfate ions are furnished to the solution, which is governed by the specific solubility of the salt, its particle size and the degree of agitation. Second, the rate is determined by the velocity of the oxidation–reduction reaction itself, which is practically imperceptible at room temperature, quite rapid at the boiling point of the acid, and dependent on both sulfate ion and hydrogen iodide concentration, the latter having been found to be of greater influence.

In formulating suitable equations to represent the decomposition of alkaline earth sulfates by hot concentrated hydriodic acid, the following facts must be considered. The essential chemical change consists in the reduction of sulfate ion by the acid with the formation of hydrogen sulfide, iodine, water, and iodide ions as the only discernible products of the primary reaction. To a limited extent secondary reactions also occur between these products, such as that between the hydrogen sulfide and the free iodine to form hydrogen iodide and free sulfur, with some oxidation of the latter, when air is present, to form sulfur dioxide. These latter reactions were found, however, to occur largely in the gas phase above the solution. This reaction has a marked temperature coefficient and a measurable rate of speed, so that it is probably not wholly ionic. Hence it seems most likely that it is largely molecular hydrogen iodide that engages in the reaction with the sulfate ion. On these bases one may write: $SO_4^{=} + 10HI \longrightarrow H_2S + 4H_2O + 4I_2 + 2I^-$. In a given case the total stoichiometric change can be represented by the equation: $SrSO_4 + 10HI \longrightarrow SrI_2 + H_2S + 4H_2O + 4I_2$.

Chromic Dihydroheptasulfate.—The peculiar compound formed by fuming a mixture of chromic hydroxide, or a soluble chromic salt, with an excess of concentrated sulfuric acid for several hours is remarkable for its high resistance to the action of nearly all acids, acid mixtures, and fused salts. Some recent writers have considered this compound to be normal anhydrous chromic sulfate in spite of the considerable evidence existing in the literature respecting its complex nature. By reason of this element of doubt, the compound prepared for use in these experiments from chromium nitrate was checked as to composition and the empirical formula $Cr_4H_2(SO_4)_7$ was again confirmed.

It has been shown by Noyes and Bray[4] that chromic dihydroheptasulfate is attacked slowly by hot concentrated hydrochloric or hydrobromic acid, the latter being more effective. Complete decomposition by these acids requires, however, an excessive number of hours even with small samples. On the other hand, hot concentrated hydriodic acid not only attacks this compound at a higher initial rate, but complete decomposition and solution can be effected in a reasonable time. By using constant boiling acid this substance is decomposed in boiling solution more rapidly than barium sulfate, but not nearly as rapidly as strontium sulfate. Apparently when chromic dihydroheptasulfate is decomposed by the action of hydrochloric or hydrobromic acid, the action involves only the slow initial breakdown of the complex, furnishing chromic and sulfate ions to the solution, and as the concentration of these increases the system tends to reach a state of equilibrium. With hot hydriodic acid, however, equilibrium is not reached due to the continuous destruction of the sulfate ions by the hydrogen iodide with the formation of hydrogen sulfide, iodine, water and iodide ions. This is believed to explain, in some measure, the greater effectiveness of this acid in decomposing the compound.

(4) "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1927, pp. 315, 319.

The total stoichiometric change involved in the reaction can be represented by the equation: $Cr_4H_2(SO_4)_7 + 68HI \longrightarrow 4CrI_3 + 7H_2S + 28H_2O + 28I_2$. This equation is admittedly unusual by reason of the large coefficients before some of the quantities, but it is thought to represent the facts. It explains why, in accordance with experiment, such a large proportion of hydriodic acid is required for the complete decomposition of a given quantity of chromic dihydroheptasulfate.

Lead Sulfate.—It has long been known that an iodide solution placed in contact with lead sulfate causes the partial transformation of the latter into lead iodide, but it does not seem to have been previously observed that a comparatively small volume of cold concentrated hydriodic acid completely transforms the salt into the iodide due to the progressive solution of this in the acid with complex formation, leaving free sulfuric acid in the resulting homogeneous golden-yellow liquid. For example, it was found that at 23° only 4.00 cc. of constant boiling acid is required for the solution of 1.000 g. of lead sulfate. This effect falls off rapidly with decrease in acid concentration, so that slight or extended dilution of a solution obtained in this manner results in a copious precipitation of lead iodide.

The nature of the complex formed when hydriodic acid reacts with lead iodide was briefly investigated by Berthelot,[5] who isolated from the solution an unstable compound $PbI_2 \cdot HI \cdot 5H_2O$ which he termed lead hydriodide. This formula, however, rests on a single partial analysis, so by way of confirmation a quantity of the compound was prepared and analyzed with the following results.

Anal. Calcd. for $PbI_2 \cdot HI \cdot 5H_2O$: Pb, 30.51; I, 56.07; H_2O, 13.27. Found: Pb, 30.80; I, 55.66; H_2O, 13.40.

In migration experiments performed on concentrated lead iodide–hydriodic acid solutions, movement of lead to the anode was observed, indicating the existence of the metal in the negative ion. For this reason it seems probable that in such solutions the complex is largely iodoplumbous acid with the formula $HPbI_3$, assuming that it exists in solution with the same molecular ratio between constituents as in the above solid compound, which can be considered as being a hydrated form of this acid.

The total change, then, involved in the solution of lead sulfate by cold concentrated hydriodic acid can be represented by the equation: $PbSO_4 + 3HI \longrightarrow HPbI_3 + H_2SO_4$.

When a solution obtained in the above manner is heated, or when lead sulfate is treated with the hot concentrated acid, the oxidation–reduction reaction between sulfate ions and hydrogen iodide then ensues as with the other slightly soluble sulfates, except that in this case the decomposition is very rapid due to the speed with which all the possible sulfate ion becomes available for the reaction.

(5) Berthelot, *Compt. rend.*, **91**, 1024 (1880); *Ann. chim. phys.*, [5] **23**, 85 (1881).

Applications.—The above means of decomposing difficultly soluble sulfates has been found to be of considerable practical value in analysis. For example, the presence of such sulfates in the acid insoluble residue obtained in the usual qualitative scheme can be detected readily by heating a sample of the dried residue with stabilized constant boiling acid and testing for the evolution of hydrogen sulfide by means of lead acetate paper. After proper treatment of the resulting solution, the metals can then be detected by the usual reactions. Rapid identification of natural alkaline earth sulfates can be made in this manner as shown by tests on minerals of known character. In quantitative analysis also, hydriodic acid can be used for difficult separations involving these sulfates. As a test of its value in this respect a series of experiments were made on the separation of mixtures of quartz and alkaline earth sulfates. In these analyses each mixture was boiled for a sufficient period with a small volume, or successive small volumes, of the concentrated acid, after which the unattacked silica was transferred to a filtering crucible, washed a few times with water, dried and weighed. Good quantitative separation was obtained. In general, the use of finely-divided samples is essential for the most certain and rapid analytical application of this method of decomposition, especially in dealing with barium sulfate. It is planned to work out in a more detailed manner these uses of hydriodic acid in analytical chemistry.

Summary

All the difficultly soluble sulfates can be decomposed by the action of hot concentrated hydriodic acid. The apparent mechanism involves the reduction by hydrogen iodide of the sulfate ions continuously furnished to the acid solution by these salts with the resulting formation of hydrogen sulfide, iodine, and water, leaving the corresponding metallic iodides in solution. Lead sulfate is also quite soluble in hydriodic acid of high concentration at room temperature. The value of these reactions in chemical analysis has been indicated.

PRINCETON, NEW JERSEY

RECEIVED APRIL 8, 1933
PUBLISHED OCTOBER 6, 1933