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Reduction of Antimonic Acid in Hydrochloric Acid Solution with Mercury

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CCAY and Anderson (2) have shown that ferric salts and vanadic acid are completely reduced, the former to the ferrous, the latter to the vanadyl condition, when their hydrochloric acid solutions are shaken for 5 minutes in the presence of mercury. They have also shown that chromic, molybdic, and antimonic acids in dilute hydrochloric acid solution are more or less reduced when subjected to a similar treatment.

Especially interesting is the behavior of solutions of antimonic acid in the presence of mercury. The author has made a long and detailed study of this reaction, and has succeeded in establishing the conditions under which the reduction of the element from the quinquivalent to the trivalent state can in all cases be made quantitative.

STUDY OF THE REACTION

When a solution of antimonic acid, prepared by oxidizing one of antimonious chloride or sulfate with potassium bromate, and containing one-fourth or one-third its volume of concentrated hydrochloric acid (sp. gr. 1.19) is shaken violently for 5 minutes in the presence of mercury, all the antimonic is reduced to antimonious acid:

 $Sb^{+++++} + 2Cl^{-} + 2Hg = Sb^{+++} + 2HgCl$

Owing to the air present a small amount of mercuric chloride is also formed:

$2HgCl + 2HCl + O = 2HgCl_2 + H_2O$

If, however, the solution be one of dihydrogen potassium pyroantimoniate, the reduction of the antimony to the trivalent state is, in the circumstances, never complete. Even when such a solution is heated on the water bath for 15 to 20 minutes, and shaken violently off and on for one hour, quinquivalent antimony can be detected in the filtrate from the mercurous chloride and finely divided mercury. Better results may be obtained by placing the well-stoppered bottle containing the solution and the mercury in a powerful shaking machine and agitating it for one hour. While the reduction here is generally complete, sometimes it is not, for in some instances over a milligram of antimony may remain in the higher state of oxidation. Three very pure samples of the pyro-salt from three well-known houses were used in this work. Their solutions all behaved in an analogous manner. The qualitative test for minute amounts of quinquivalent in the presence of relatively large amounts of trivalent antimony, according to the method of Bunsen, as ordinarily carried out, is apt to prove misleading (5), for not only does boiled and cooled water acidified with hydrochloric acid assume in a few minutes a pronounced vellow tint when potassium iodide, free from iodate, is added to it, but when antimonious chloride is also present the addition of the potassium iodide occasions the immediate formation of antimonious iodide, or oxyiodide which gives the solution a faint yellow color. Since, however, acid water alone when saturated with carbon dioxide and kept under an atmosphere of this gas and in the dark remains colorless or barely yellow for hours after the addition of potassium iodide, satisfactory results were obtained by proceeding as follows: The filtrate from the mercury and mercurous chloride was caught in a little bottle holding about 100 cc. and provided with a stopper ground so as to furnish an airtight joint (3). A brisk current of pure carbon dioxide was introduced, permitted to traverse the liquid for ten minutes, a crystal of potassium iodide about the size of a pea was dropped in while the gas was still passing, the delivery tube was withdrawn, and the bottle was instantly stoppered. Since the amount of antimonious chloride in the filtrate was known within one or two milligrams, 100 cc. of a solution containing this amount of the pure chloride and the specified quantity of concentrated hydrochloric acid were subjected at the same time to the same treatment. After the bottles had stood for a few minutes in the dark and the colors of the two solutions were compared, that of the former appeared the darker if it contained quinquivalent antimony. In this way 0.1 mg. of Sb^v could be detected in the presence of relatively large amounts of Sb^{III}.

Practically no reaction occurs when water and pure mercury are shaken together; the water remains clear and the metal is barely tarnished. If hydrochloric acid be present the liquid remains perfectly clear for 5 minutes, and then becomes suddenly hazy owing to a separation of the highly characteristic silky needle form of mercurous chloride. The amount increases as the shaking is continued, and at the end of an hour it is comparatively large:

 $2Hg + O = Hg_2O$ and $Hg_2O + 2HCl = 2HgCl + H_2O$

In an atmosphere of pure carbon dioxide no change occurs,

even when the dilute hydrochloric acid and mercury are shaken together for hours.

The mercurous chloride equivalent to the antimonic acid reduced along with that formed by the interaction of the mercury and oxygen of the air may be the cause of the persistency with which solutions of the pyro-salt resist complete reduction. The globules into which the greater part of the mercury breaks, as well as the rest of the metal, get covered with a protecting skin of mercurous chloride. Of course during the shaking of the contents of the bottle some of these skins are occasionally knocked off, but they immediately reform. At all events the reductions in an atmosphere of carbon dioxide where no additional mercurous chloride can be formed are invariably complete at the end of an hour's shaking in the machine. Although this time may seem unnecessarily long it must be borne in mind that, in general, we have no means for knowing offhand the form in which the antimonic acid in a solution is present. We possess, indeed, no definite information in regard to the socalled ortho-, meta-, and pyro-antimonic acids, the methods for preparing them, the circumstances in which they may be converted into one another, and the tests for distinguishing between them. For this reason, in the quantitative work which follows, the author has always assumed that the solutions contained some or all of the acid in the form least easily reduced.

Arsenic and stannic acids in hydrochloric acid solutions undergo no change when shaken for hours in the presence of mercury.

QUANTITATIVE RESULTS

The bottle used in this work is cylindrical in shape, 12 cm. high from the bottom to the shoulder, 6 cm. in diameter, and holds about 150 cc. It is provided with a glass stopper which fits air-tight, and it is charged with 20 to 25 cc. of pure mercury. So charged it will be referred to as the reductor. The materials used in preparing the test solutions were the best grades furnished by the Kahlbaum house.

Solution A. 2.2063 grams of powdered antimony were treated in a covered dish with 50 cc. of concentrated sulfuric acid which was heated to gentle boiling. When solution was complete the flame of the burner was lowered and the acid allowed to fume strongly for about 15 minutes, so as to get rid of all traces of sulfur dioxide. Water was added, and the turbid liquid was cooled, transferred to a 500-cc. flask, and diluted with concentrated hydrochloric acid and water to the mark. So prepared the solution contained one-fourth its volume of concentrated hydrochloric acid. The antimony was determined in 25 cc. by the Györy method. Antimony found equaled 0.1103 gram, whereas the theory calls for 0.1103 gram.

Solution B. 8.6444 grams of dihydrogen potassium pyroantimoniate were dissolved in a liter flask on the water bath in 200 cc. of concentrated hydrochloric acid, water was added, the solution cooled and diluted to the mark with water and concentrated hydrochloric acid. The solution contained about one-third its volume of this acid. The large amount of acid is necessary to keep the solution clear indefinitely. The antimony in 25 cc. was determined by heating the strongly acidified solution with a large excess of sulfurous acid in a pressure bottle for one hour in the boiling water bath, evaporating the liquid to somewhat less than one-half its volume, cooling it, diluting to 200 cc., and titrating the antimony with 0.1 N potassium bromate. (The method is similar to that used for reducing arsenic acid solutions, 1.) A blank was made in the same way, using the same amount of sulfurous and hydrochloric acids. After correcting for the amount of bromate used in the blank (from 0.15 to 0.2 cc.), the antimony was calculated, and found to be (1) 0.1067 and (2) 0.1068 gram. As a check the antimony was also determined according to an indirect method highly recommended by Rose (4), and found to be 0.1067 gram. The element was calculated from the weight of potassium chloride obtained.

The 0.1 N potassium bromate used in the Györy method was standardized against the Bureau of Standards arsenious

oxide, which was also used in determining arsenic and antimony in the presence of each other.

The author has had over three years of experience with the Györy method, and has no hesitancy in pronouncing it the best of all methods for determining antimony. If plenty of hydrochloric acid be present, the same results are obtained when the volume of the solution to be titrated is 50. 100, or 200 cc. In the last case, however, the bromate should be run in at the rate of 90 to 100 drops a minute, with constant stirring, and, when the methyl orange begins to fade, a drop or two more of the dye added and the bromate from now on introduced a drop at a time followed by hard and thorough stirring. In this way the end point can be hit with great accuracy. If it be overstepped we can come back with the methyl orange (1 gram in a liter of water) which has been balanced against 1 or 2 drops of the bromate in 200 cc. of water containing one-fourth its volume of concentrated hydrochloric acid.

TABLE I. DETERMINATION OF ANTIMO

ANTIMONY	TAKEN
-	

AS DIHYDROGEN	
POTASSIUM PYRO-	ANTIMONY
ANTIMONIATE	Found
Gram	Gram
0.1067	0.1067
0.1067	0.1067
0.1067	0.1066
0.1067	0.1068
0.0854	0.0851
0,0854	0.0852
0.0427	0.0427

Convenient amounts of the standard solution were pipetted into the reductor, 15 to 20 cc. concentrated hydrochloric acid were added, and the liquid was diluted to about 75 cc. (scratch on the side of the bottle above the mercury to indicate this volume). The air in the reductor was displaced by introducing a brisk current of purified carbon dioxide gas for ten minutes, the delivery tube withdrawn, and the bottle instantly stoppered and agitated for an hour in the machine. After most of the mercurous chloride and finely divided mercury had settled (before filtering them some of the solutions stood overnight), the solution was poured on to a double filter paper (9 cm.), the filtrate being caught in a 400-cc. beaker. The slate-colored mass in the reductor was washed by letting a 10-cc. pipet full of dilute hydrochloric acid (10 cc. concentrated hydrochloric acid to 90 cc. water) flow down the inner neck and sides of the bottle, stoppering it, shaking well, decanting the liquid on to the paper, and repeating the operation five times. After rinsing off the stopper, the mouth of the reductor, and the glass rod with a little water, the mercurous chloride and mercury on the filter paper were washed until the washings were neutral. The solution was then diluted to 200 cc. and the antimony titrated. The filtration and washing require ordinarily about half an hour. The filtrates were always clear. The material on the filter paper was washed back into the reductor, the liquid, after a few minutes, poured off, and some concentrated hydrochloric acid and from 15 to 20 cc. of strong stannous chloride solution introduced. On stoppering and shaking the reductor violently for 2 or 3 minutes all the mercurous chloride is reduced to metallic mercury, which should be washed in the reductor by decantation until the washings are neutral. The reduction and washing are complete in 15 minutes. While washing the reduced mercury the author noticed a phenomenon of which he finds no mention. If, after washing is complete, the reductor be filled quite full with water, stoppered, and shaken vigorously up and down for about 15 seconds, the metal breaks up into a vast number of globules which form a foam completely filling the upper part of the bottle. The foam, however, rapidly subsides. A few milligrams of soap dissolved

in the water inhibit all tendency on the part of the metal to foam. It becomes gray in color, and must be treated again with stannous chloride to show the peculiar behavior. A little hydrochloric, sulfuric, or nitric acid in the water also precludes the mercury from foaming.

TABLE II. DETERMINATION OF ANTIMONY IN THE PRESENCE OF ARSENIC ACID

Antimony Taken as Dihydrogen Potassium Pyroantimoniate	Arsenic Taken as Dihydrogen Potassium Orthoarseniate	ANTIMONY FOUND
Gram	Gram	Gram
$\begin{array}{c} 0.1067 \\ 0.1067 \\ 0.0854 \\ 0.0427 \end{array}$	0.0625 0.0625 0.0625 0.0625	$0.1067 \\ 0.1068 \\ 0.0851 \\ 0.0426$

TABLE III. DETERMINATION OF ANTIMONY IN THE PRESENCE OF ARSENIC AND STANNIC ACIDS

Antimony Taken as Dihydrogen Potassium Pyroantimoniate	Arsenic Taken as Dihydrogen Potassium Orthoarseniate	Tin Taken as Stannic Ammonium Chloride	ANTIMONY Found
Gram	Gram	Gram	Gram
$\begin{array}{c} 0.1067 \\ 0.1067 \\ 0.1067 \\ 0.0854 \\ 0.0854 \\ 0.0427 \end{array}$	$\begin{array}{c} 0.0625\\ 0.0625\\ 0.0625\\ 0.0625\\ 0.0625\\ 0.0625\\ 0.0625\\ 0.0625\\ \end{array}$	0.1292 0.0969 0.0808 0.0869 0.0808 0.0808	$\begin{array}{c} 0.1073 \\ 0.1064 \\ 0.1065 \\ 0.0854 \\ 0.0852 \\ 0.0427 \end{array}$

If a solution contains antimonious and arsenious acids we may determine the amount of bromate required to oxidize both, then evaporate the liquid to about 50 cc., transfer it to the reductor, reduce the antimony to the trivalent state, filter, etc., and titrate the antimony. The difference between the amounts of bromate used in the two cases gives that used to oxidize the arsenic to the quinquivalent state. Standard solution A and a 0.1 N solution of arsenious acid were employed.

TABLE IV. DETERMINATION OF BOTH ANTIMONY AND ARSENIC

ANTIMONY Taken as Antimonious Chloride	Arsenious Oxide Taken	Antimony Found	Arsenious Oxide Found
Gram	Gram	Gram	Gram
$\begin{array}{c} 0.1103 \\ 0.1103 \\ 0.1103 \\ 0.1103^a \\ 0.0883 \\ 0.0883 \end{array}$	$\begin{array}{c} 0.1237\\ 0.0990\\ 0.0495\\ 0.0990\\ 0.0495\\ 0.0495\\ 0.0495\\ 0.0248\end{array}$	$\begin{array}{c} 0.1109\\ 0.1109\\ 0.1104\\ 0.1103\\ 0.0885\\ 0.0885\\ \end{array}$	$\begin{array}{c} 0.1233 \\ 0.0985 \\ 0.0493 \\ 0.0992 \\ 0.0495 \\ 0.0248 \end{array}$

^a Contained in addition 0.4 gram $(NH_4)_2SnCl_6 = 0.1292$ gram Sn.

The antimony (0.1067 gram) was determined in a solution containing roughly 0.083 gram Pb, 0.213 gram Bi, and 0.123 gram Cd, all as chlorides, and 0.1069 gram of antimony was found.

TABLE V. DETERMINATION OF ANTIMONY IN THE PRESENCE OF COPPER

Antimony Taken as Dihydrogen Potassium Pyroantimoniate	Copper Taken as Crystalline Cupric Sulfate	Antimony Found
Gram	Gram	Gram
0.1067	0.0656	0,1062
0,1067	0.0656	0.1062
0,1067	0.0525	0.1064
0.1067	0.0525	0.1062
0.1067	0.0394	0.1062
0.1067	0.0262	0.1061

Cupric salts are reduced by mercury to cuprous salts, the latter being completely reconverted into the former, when a brisk current of purified air is permitted to bubble through their solutions for half an hour. Since trivalent antimony alone undergoes no perceptible change when air is passed through its solution, attempts have been made to determine quinquivalent antimony in the presence of cupric salts by reducing both, oxidizing the cuprous to the cupric with air and titrating the antimony. The results are a trifle low, a fact which may be due to the oxidation of the cuprous inducing a slight oxidation of the antimonious chloride. The determination in Table V will indicate the extent to which the results differ from the true values.

A solution (75 cc.) containing 25 cc. of concentrated HCl, 0.1067 gram of Sb as the potassium pyro-salt, 0.0625 gram of As as H₂KAsO₄, 0.037 gram of Pb, 0.086 gram of Bi, 0.059 gram of Cd, 0.057 gram of Sn^{IV}, and 0.037 gram of Cu^{II}, the last five as chlorides, was shaken with mercury for an hour in the machine, in an atmosphere of carbon dioxide. The filtrate was slightly turbid but became perfectly clear when heated to steaming and stirred a few minutes. When cool, air was passed through it for half an hour and the antimony titrated. Antimony found equaled 0.1061 gram, a result which is practically identical with the average of those given above. If to the volume of 0.1 N bromate used in each of the above cases 0.1 cc. be added, the calculated results are very satisfactory. Experiments are being made to determine whether or not the low results are due to the oxidation of the cuprous to the cupric salt, inducing a slight oxidation of the trivalent antimony.

SUMMARY

Antimonic acid in hydrochloric acid solution is completely reduced to antimonious acid when the solution is shaken with mercury for an hour in an atmosphere of carbon dioxide.

Arsenic and stannic acids, as well as lead, cadmium, and bismuth, in hydrochloric solution, undergo no change when subjected to similar treatment.

In the same way cupric salts are reduced to cuprous salts, but the latter are selectively reoxidized when pure air is passed through their solutions for half an hour.

Use has been made of these facts in determining antimony in the presence of some or all the substances mentioned. In the case of copper the results are a trifle low.

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- (5) Zintl, E., and Wattenberg, H., Ber., 56, 1, 474 (1923).

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CORRECTION. In the article on "Apparatus for Reactions in Liquid Phase at Elevated Temperatures and Pressures" [IND. ENG. CHEM., Anal. Ed., 4, 342 (1932)], the length of the tubing for the steel spiral referred to in the thirteenth line from the bottom of the first column on page 343 should have been given as 4.3 meters or 14 feet. The external diameter of the steel tubing was 6.4 mm. (0.25 inch) and the internal diameter was 1.6 mm. (0.06 inch). HOMER ADKINS

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CORRECTION. In the paper on "Practical Vacuum-Tube Potentiometer for pH Measurement with Glass Electrodes" [IND. ENG. CHEM., Anal. Ed., 4, 398 (1932)] the values of certain resistors were omitted from Figure 1. R_1 is 2000 ohms, R_2 is 1000 ohms, R_3 is 50 ohms, R_4 is 500 ohms, and R_5 is 10,000 ohms. The resistor shown in the battery-charging circuit has a value of 1000 ohms; the lamp with which this resistor is in series may have a value of 10 to 75 watts (ordinary 110-volt type), depending upon individual tube-filament conditions. FRED ROSEBURY

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