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ACTION OF BROMIC ACID ON METALS.

BY W. S. HENDRIXSON.

About two years ago I submitted to the Iowa Academy of Science* a communication on the action of chloric acid on metals, in which it was shown that in some cases the metals dissolved without the evolution of any gas, the action apparently being the oxidation of the metal and the immediate formation of salts from the oxides and the excess of chloric acid, and the hydrochloric acid produced by the reduction of chloric acid. In the cases of some metals there occurred at the same time oxidation of the metal and the evolution of free hydrogen. In fact, in the cases of the alkali metals and magnesium the latter action preponderated.

In the above series of experiments it was observed that there was no apparent reaction between the excess of chloric acid and the small amount of hydrochloric acid formed by reduction. Only a trace of free chlorine was observed in one or two cases. Later experiments in connection with the work on bromic acid showed that the action of chloric acid in concentrated solution, on hydrochloric acid of far greater concentration than could have been obtained by the reduction of chloric acid in the experiments cited, was very small. Though these experiments have not yet been carried as far as designed, a few results may be stated, for their own interest and to make clear the striking difference between the results obtained in the study of the action of chloric acid and of bromic acid on metals.

Hydrochloric acid and chloric acid were mixed so as to give them in the mixture the respective concentrations, twice normal and four-tenths normal, or as 5 to 1, which is the ratio in which they preponderantly react upon each other. The mixture was placed in a glass-stoppered distilling flask whose side arm was connected with a ten-bulb column containing potassium iodide. The flasks were filled with carbon dioxide and placed in the dark closet where the temperature was practically constant at 20°. At the end of definite periods the chlorine set free was aspirated over into the potassium iodide solution until all color disappeared from the first flask and the liberated iodine was titrated in the usual way. The amount of chlorine set free at the end of 2 hours was .0148 gram; at the end of 8 hours, .0256, and at the end of 17 hours, .0302 grams. These and other experiments showed that practical equilibrium was attained after a few hours, if allowance be made for the chlorine removed by diffusion into the second flask and absorption in the potassium iodide solution.

*Proceedings, 1904, p. 150.

It is evident that the interaction of chloric acid and the small amount of hydrochloric acid produced in the study of the action of chloric acid on metals, is insignificant. On the other hand the hydrochloric acid produced may itself be effective in dissolving small quantities of some metals, such as magnesium and zinc. In the action of bromic acid on metals the results were quite different, as anticipated. As is well known hydrobromic and bromic acid readily react upon each other in the proportion of five molecules of the former to one of the latter setting all the bromine free. The hydrobromic acid is, therefore, removed, as formed with the liberation of bromine, but the bromine may itself react upon the remaining metal.

The bromic acid used in the following experiments was made by Kahlbaum. It was as usual colored by bromine, which was aspirated off in a vacuum before use. It was free from sulphuric acid and its freedom from the acids of chlorine was tested by determining the ratio of silver to silver bromide, in which weighed amounts of pure silver were precipitated with hydrobromic acid made by reducing the bromic acid. Three experiments gave the following proportions:

1. Ag : AgBr :: 100 : 174.09
2. Ag : AgBr :: 100 : 174.01
3. Ag : AgBr :: 100 : 174.19

The average is 174.09 and the theory 174.08.

The concentration of the acid was found to be 1.25 normal, and in most of the experiments it was used undiluted. In the experiments the apparatus was such as to permit the reaction of the acid and metal to take place in carbon dioxide, in order to avoid any oxidizing action of the air. The acid was placed in a glass-stoppered distilling flask whose side tube entered the neck of another distilling flask and its tip was placed just under the surface of a solution of potassium iodide. To the side arm of the second flask was connected a bulb column to absorb the last traces of bromine, in the dilute potassium iodide which it contained. The whole apparatus was filled with carbon dioxide, the stopper removed, the metal dropped in. It was placed in a dark closet and allowed to remain, usually several hours or till the metal was all dissolved. The bromine was then all aspirated over into the potassium iodide with a stream of air under about 50 mm. pressure. The free iodine was titrated with sodium thiosulphate and the corresponding bromine calculated.

In the experiments described below the bromine is usually a little smaller than required by theory, on the supposition that the hydrobromic acid produced in the oxidation of the metal reacts with bromic acid thus: $5\text{HBr} + \text{HBrO}_3 = 3\text{H}_2\text{O} + 6\text{Br}$. The deficiency amounts on the average to about 5 per cent. and may be due to one of two causes or both. The bromine set free may act directly upon the remaining metal forming a bromide which would again react with bromic acid, or there may result the formation of some hypobromous acid, which would not distil over under the conditions. I regret that I have not been able to pursue the subject farther and hope to return to the study in the near future.

Action of Bromic Acid on Zinc. The zinc was of excellent quality, of the same lot described in the paper on chloric acid. Any adherent oxide was removed with emery paper. Pure zinc and bromic acid give off no hydrogen. The zinc simply goes into solution rapidly and at ordinary room temperatures. The liberated bromine was aspirated into potassium iodide solution as described and the free iodine was titrated.

1. .6010 grams of zinc gave .2792 grams of bromine. Calculated .2979.
2. .5131 grams zinc gave .2371 grams of bromine. Calculated .2512.
3. .5808 grams zinc gave .2664 grams bromine. Calculated .2841
4. .4252 grams zinc gave .2048 grams bromine. Calculated .2093.

Action of Bromic Acid on Aluminum. Unlike zinc aluminum dissolves in bromic acid with the liberation of considerable quantities of hydrogen. It was not deemed practicable to determine the hydrogen and the bromine set free in the same experiment. In one experiment in which .2082 gram of aluminum and 23 c. c. of bromic acid of sp. gr. 1.25 were taken the hydrogen began to come off at the rate of about one bubble to five seconds, increased to one bubble a second and then gradually decreased, practically ceasing after several hours, when 0.1578 gram of the metal had dissolved. The hydrogen collected corresponded to .0225 gram or about 15 per cent of the metal dissolved.

Two other experiments in which the bromine alone was determined resulted as follows:

1. .3113 grams aluminum gave .4632 grams bromine.
2. .3278 grams aluminum gave .4836 grams bromine.

If the hydrogen was given off in the same proportion as in the above experiment the theoretical amount of bromine corresponding to the metal used in reducing the bromic acid are 4753 and 4994.

Action of Bromic Acid on Magnesium. Bromic acid acts upon magnesium with the rapid evolution of hydrogen at first, but soon free bromine begins to appear and the hydrogen then slackens as in the case of the solution of aluminum. In one experiment .1315 grams of magnesium wholly dissolved and gave off a volume of hydrogen corresponding to 37.6 per cent. of the metal.

Action of Bromic Acid on Iron. Iron rapidly dissolved in bromic acid, going as might be expected into the ferric condition. Apparently in the beginning of the reaction there is a trace of hydrogen set free, but it is entirely too small to admit of measurement.

1. .2469 grams of iron gave .2132 grams of bromine. Calculated .2116.
2. .2479 grams of iron gave .2088 grams bromine. Calculated .2125.

Action of Bromic Acid on Sodium. As stated in a former paper chloric acid is only very slightly reduced by sodium or potassium amalgam. Bromic acid on the other hand is very readily reduced. In two experiments in each of which 5 c. c. of 1.25 normal acid were diluted to 20 c. c. and treated with 20 grams of 2 per cent amalgam, very little hydrogen appeared at first and no bromine. After about an hour the hydrobromic acid produced was determined by weighing as silver bromide. The amounts of bromine in the silver bromide were .1507 and .2196 grams.

Action of Bromic Acid on Cadmium. Cadmium slowly dissolves in normal bromic acid, no hydrogen being set free. The bromine set free corresponded very nearly to the theoretical supposing that two atoms of bromine correspond to one of cadmium.

1. .4507 gram cadmium gave .1240 gram bromine. Calculated .1280.
2. .2935 grams cadmium gave .0840 grams bromine. Calculated .0835.

Action of Bromic Acid on Copper. The copper used was in the form of fine wire of the electrolytic metal. It dissolves readily, and its solution takes place readily in the approximately normal acid.

1. .3706 grams copper gave .1976 grams bromine. Calculated .1864.
2. .3766 grams copper gave .2020 grams bromine. Calculated .1894.

Action of Bromic Acid on Tin. Tin is slowly dissolved by bromic acid. There remains a very small amount in the form of undissolved oxide. The results indicate that the metal goes into the stannic condition.

1. .3365 grams of tin gave .1796 grams bromine.
2. .3307 grams tin gave .1768 grams bromine.

The calculated amounts of bromine supposing the tin completely oxidized to the stannic condition are .1809 and .1778 grams.

Some study was made of the action of bromic acid on silver and bismuth. Both are oxidized quite slowly in the cold. Of course the silver is soon coated with insoluble silver bromide and bromate. So far as investigated the action of bromic acid on silver is quite analogous to that of chloric acid; that is, the ratio of the silver as AgBr is to that as AgBrO_3 as 1 to 5. Of course no bromine is given off in the cases of the other metals, the bromic acid being fixed as silver bromide as fast as formed.

The action of bromic acid on metals is about as might have been anticipated from the knowledge of the action of chloric acid. Bromic acid is a less stable acid and more readily acts as an oxidizing agent. The cases are fewer in which it acts upon metals with the liberation of hydrogen, and the amounts of hydrogen are smaller in proportion to the metal attacked. Its ready reduction by hydrobromic acid, causes the latter to be oxidized as fast as formed with the liberation of practically the full equivalent of bromine demanded by the equation already given.