[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

THE COMPOSITION OF A CONSTANT-BOILING SOLUTION OF HYDROGEN BROMIDE IN WATER

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It has been shown by Hulett and Bonner,[1] and Foulk and Hollingsworth[2] that the composition of a solution of hydrochloric acid and water which boils at a constant temperature is sufficiently definite to permit this material to be used directly in the preparation of a standard solution for volumetric analysis. The present investigation was undertaken to determine the composition of a distillate of hydrobromic acid solution which boiled under a pressure of 760 mm. The composition of such a solution has been reported by various workers. Such a wide variation in results is noted that it seemed advisable to re-determine the weight of hydrogen bromide in the distillate of a constant-boiling mixture of hydrogen bromide and water.

Bineau[3] found that the residue after distilling a solution of hydrogen bromide under a pressure of 758 mm., contained 46.1–47.4% of hydrogen bromide, and that a compound of the formula $HBr.H_2O$ was formed. Roscoe[4] boiled his acid under a pressure of 762 mm. and found that the residue contained 47.86% of hydrogen bromide. The solution was analyzed volumetrically with silver nitrate. Léger[5] and Feit and Kubierschky[6] found 48%. Calm[7] states that the vapor of a boiling solution of hydrogen bromide contained the hydrate, $HBr.5H_2O$, corresponding to 47.43% of hydrogen bromide. Carrière and Cerveau[8] freed a concd. solution of hydrogen bromide from the small quantities of hydrogen chloride which it contained by fractional distillation. The purified acid was divided into two parts; the first was distilled over calcium bromide, the second served for the condensation of the vapors of hydrogen bromide which evolved from the first. It was this second portion, thus obtained at a convenient degree of concentration, that furnished the samples for the determinations. The mixture boiled under a pressure of 760 mm. and contained 47.5% of hydrogen bromide.

Experimental Work

Preparation of Materials

Water.—Conductivity water was used throughout this investigation.

Hydrogen.—A Kipp generator was used for making the hydrogen by the action of dil. sulfuric acid on zinc. The gas was then passed through concd. sulfuric acid and finally over potassium hydroxide.

Bromine.—A very pure sample of potassium bromide was recrystallized thrice from conductivity water. A solution of this salt was treated with potassium dichromate

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[1] Hulett and Bonner, THIS JOURNAL, **31,** 390 (1909).

[2] Foulk and Hollingsworth, *ibid.*, **45,** 1220 (1923).

[3] Bineau, *Ann. chim. phys.*, [3] **7,** 257 (1843); See *Ann.*, **116,** 214.

[4] Roscoe, *Ann.*, **116,** 214 (1860); *J. Chem. Soc.*, **13,** 146 (1860).

[5] Léger, *Compt. rend.*, **115,** 946 (1892).

[6] Feit and Kubierschky, *J. Pharm.*, [5] **24,** 159.

[7] Calm, *Ber.*, **12,** 613 (1879).

[8] Carrière and Cerveau, *Compt. rend.*, **177,** 46 (1923).

and an excess of sulfuric acid. The bromine was obtained by distilling the mixture in a Pyrex distilling flask, which was fitted with a ground-glass stopper and sealed to a Pyrex condensing tube. The bromine was collected in a Pyrex flask with a specially constricted neck to fit the lower end of the condenser. The bromine was redistilled thrice and large end-fractions were rejected.

Hydrogen Bromide.—The hydrogen bromide was prepared by passing a mixture of hydrogen and bromine over heated, platinized asbestos. The apparatus consisted of the following Pyrex apparatus connected in series: flasks for purifying and drying the hydrogen, a trap, a flask for bromine, a tube for the platinized asbestos, a trap and two flasks containing conductivity water for absorbing hydrogen bromide. The hydrobromic acid absorption flasks were kept cool by surrounding them with ice water during the run. These various parts were connected by glass seals and formed a continuous train of glass. Each hydrobromic acid flask was fitted with a siphon through the wall. The siphon had a glass stopcock and was used for both emptying and filling the flasks. At no time did the solution come in contact with anything other than glass, except the atmosphere for a short period of time.

Silver Nitrate.—The silver nitrate, a commercial C. P. sample, was recrystallized in platinum thrice from conductivity water.

Barometer.—The barometer was the standard Weather Bureau type.

The Distillation of the Constant-boiling Mixture Apparatus.—The distillation of hydrobromic acid solution was carried out in an apparatus similar to that used by Foulk and Hollingsworth. The neck of the 500cc. Pyrex distilling flask was lengthened and fitted with a ground-glass stopper. At certain points along the neck of the flask several small constrictions were made in such a manner that a thermometer could be entirely suspended within the neck of the flask. The side arm of the flask was sealed to a long Pyrex tube which led through a condenser shell to the receiving jar where the distillate was collected in small bottles. That part of the flask exposed to light, and the condenser were covered with a coat of black paint, except for a small window in the flask. The vessel containing the receivers for the various fractions was connected to the condenser and a pressure regulator similar to that used by Foulk and Hollingsworth.

Procedure

Five small bottles for receiving the distillate were placed in position in the large jar which was then carefully sealed. About 400 cc. of solution of hydrogen bromide was poured into the distilling flask, which was then heated. The barometer was read and the pressure regulator adjusted to give a pressure of 760 mm. on the hydrogen bromide solution.

After the distillation was well started this pressure did not vary more than 0.5 mm. of mercury. After one-half or two-thirds of the solution had passed over, two or three samples of 2 cc. each were collected. The excess of pressure and the flame were then removed and the samples transferred to weighing bottles and analyzed.

About 60 cc. of the mixture was used in the final distillation and distilled at the rate of about 1 cc. per minute.

Method of Analysis

The hydrogen bromide content of the distillate was determined by precipitation with silver nitrate. The samples were carefully washed from the weighing bottles into tall form 1-liter beakers with conductivity water. A very slight excess of dil. silver nitrate solution was cautiously added in the red light of a photographic dark room. The covered beakers were allowed to remain in a dark place for at least 24 hours before filtration. The precipitate of silver bromide was carefully washed into a platinum Gooch crucible, which had been washed with very dilute silver nitrate solution and finally with conductivity water. The precipitate was thoroughly washed with conductivity water, and dried to constant weight. The final heatings were made just below the fusion point of the salt. Corrections were made for the amount of silver bromide in the wash water. This amounted to 0.02 mg. per liter of solution. The operations of the precipitation of silver bromide were carried out only in the red light of the dark room. All weighings were reduced to a vacuum and made with weights that had been carefully calibrated.

Table I

Results of Analyses

Distn.	AIIa	IIB	BIIa	Ib	IIa	IIb
% HBr in distillate	47.772	47.799	(47.742)	47.803	47.805	47.797

Capital letters indicate separate distillations; Roman numerals, the different fractions; small letters, the individual samples. Sample BIIa is eliminated, due to a loss of part of the precipitate. The average, then, of the five results is 47.795% of hydrogen bromide in the solution. The maximum variation of the five accepted results is 0.033%.

Discussion

Preliminary work on the composition of the distillate showed that the ratio of hydrogen bromide to water varied somewhat with the rate of distillation. The amount of this variation was not studied quantitatively, but very careful attention was given to the matter of maintaining a constant rate, which was 1 cc. per minute. A large part of the bulb and the neck of the distilling flask was covered with a heavy coat of a mixture of asbestos and water glass to facilitate the control of the rate of boiling. That part of the flask not covered with asbestos was painted black, except for a small window and the lower portion where heat was applied.

No attempt was made to obtain the absolute value of the boiling point, which seemed to be very near 125°. An Anschütz thermometer was used in each distillation as an aid in determining the rate of approach to a constant boiling point. Not the slightest variation in the boiling point of the solution was noted with the mercury thermometer when read with a magnifying glass, after the pressure regulator was adjusted and showed an equilibrium condition. It was possible to keep the variation of the pressure constant within the maximum limits of 0.5 mm. of mercury.

A number of distillations of pure water were made in this apparatus in order to test the constancy of the boiling point and the efficiency of this method of regulating and maintaining a constant pressure. Equilibrium conditions with water were readily maintained.

The pressure was more readily controlled when the mixture was distilled at slower rates.

Summary

It was found that an aqueous solution of hydrogen bromide when boiled under a pressure of 760 mm. of mercury forms a distillate that contains an average value of 47.795% of hydrogen bromide, and boils at about 125°. The hydrogen bromide in the distillate obtained under a pressure of 760 mm. of mercury does not correspond to the formula $HBr.5H_2O$, containing 47.381% as reported by Calm.

The constant-boiling mixture is 5.9061 *N* (by weight); 1000 g. of water contains 915.27 g. of hydrogen bromide.

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THE BASIS FOR THE PHYSIOLOGICAL ACTIVITY OF CERTAIN -ONIUM COMPOUNDS.[1] THE MOBILITIES OF THE -ONIUM IONS. I. SULFONIUM IONS

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This is one of a series of papers to be presented on the physical-chemical properties of the -onium compounds. In the present article a description is given of the method and apparatus used, together with the results for the mobilities of the trimethyl- and triethylsulfonium ions.

From data already obtained and those to be described in forthcoming papers, it seems certain that the varied stimulating and paralytic effects on the propagation of the nerve impulse given by a series of -onium compounds is not due to properties that are ordinarily considered chemical. We have, therefore, begun in this Laboratory an extended investigation of the physical properties of a selected number of such compounds. Immediate plans include, in addition to a continuation of the mobility determination, a study of the effect of the ions on the potential of lipoid-water

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[1] This problem is being carried on in coöperation with Doctor Reid Hunt of the Harvard Medical School. The physiological data are the basis of a series of papers published elsewhere by him.

[1a] National Research Fellow in Chemistry.