

# PREPARATION *of* CONSTANT-BOILING HYDROBROMIC ACID

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ALTHOUGH constant-boiling hydrobromic acid is very useful both as a reagent and as a starting material for the preparation of the fuming acid it is rarely found in any quantity in chemical laboratories, partly because of its expense. The usual methods of preparation—absorbing the required amount of hydrogen bromide generated by dropping bromine on red phosphorus<sup>1</sup> or into boiling tetralin,<sup>2</sup> passing a mixture of gaseous bromine and hydrogen over a catalyst,<sup>3</sup> or by the interaction of sulfur dioxide and bromine in the presence of water while giving a satisfactory product require more or less elaborate apparatus, and considerable attention. Many texts of inorganic chemistry state that pure hydrobromic acid cannot be prepared by the action of sulfuric acid on a bromide because of the oxidation of the hydrobromic acid to bromine and the formation of sulfur dioxide. However, Pickles<sup>4</sup> reported the preparation of the acid by distilling a mixture of two moles of potassium bromide dissolved in enough water to give

400 ml. of solution and one mole of conc. sulfuric acid to which had been added 0.014 mole of stannous chloride to prevent the oxidation of the hydrobromic acid. He reported a 95 per cent. yield of acid nearly free of chloride ion.

Druce<sup>5</sup> stated that Pickles' procedure was unsatisfactory because of the severe bumping due to the solid potassium sulfate which formed as the distillation progressed. He suggested the use of 1.54 moles of sulfuric acid for each mole of potassium bromide. After the solution has stood overnight and the potassium acid sulfate has been filtered off, no solid appears during the distillation of the constant-boiling acid. Our attempts to duplicate the work of Druce were uniformly unsuccessful. In all runs the distillate contained hydrogen sulfide, or free sulfur. In several instances, stannic sulfide collected in the condenser. A run was then made with the omission of the stannous chloride. The yield of constant-boiling hydrobromic acid was satisfactory (85 per cent.). The distillate contained no free bromine, as shown by extraction with carbon tetrachloride, but did contain from 0.01 to 0.015 per cent. of sulfate ions. This quantity of sulfate ion is not excessive and the percentage is practically that present in an analytical grade of hydrobromic acid supplied by a well-known producer. However, redistillation yielded a product in which no precipitation of barium sulfate took place after barium chloride had been added to 70 ml. of acid diluted to 100 ml., even after several days' standing. The simplicity of the procedure, together with the little attention re-

<sup>1</sup> BILTZ, BLANCHARD, AND HALL, "Laboratory methods of inorganic chemistry," John Wiley & Sons, Inc., New York, 1928, p. 71. BORNEMANN, "Anorganische Preparative," Verlag von L. Voss, Leipzig, 1926, p. 46. VANIANO, "Handbuch der preparativen Chemie," Verlag von F. Enke, Stuttgart, 1913, p. 51.

<sup>2</sup> MULLER, *Monatsh.*, **49**, 29 (1928).

<sup>3</sup> BILTZ, BLANCHARD, AND HALL, "Laboratory methods of inorganic chemistry," John Wiley & Sons, Inc., New York City, 1928, p. 71. RICHARDS AND HONIGSCHMIDT, *J. Am. Chem. Soc.*, **32**, 1577 (1910). RUHOFF, BURNETT, AND REID, "Organic syntheses," John Wiley & Sons, Inc., Vol. XV, 1935, p. 35. KAMM AND MARVEL, "Organic syntheses," Collective Vol. 1. John Wiley & Sons, Inc., New York, 1932, p. 23.

<sup>4</sup> PICKLES, *Chem. News*, **19**, 89 (1919).

<sup>5</sup> DRUCE, *ibid.*, **126**, 1 (1923).

quired and the purity of the product, should commend this method of preparation.

*Method.*—Add 120 g. of powdered potassium bromide to 200 ml. of water. Place the container in cold water, and slowly add 90 ml. of conc. sulfuric acid (1.7 moles). The temperature should not go appreciably above 75°; otherwise a small amount of free bromine may be formed. However, the formation of a small amount of bromine is not particularly serious, since it will come over with the distillate boiling between 100–115°. Cool the solution to room temperature and remove the potassium acid sulfate by filtering through a hardened filter paper in a Buchner funnel. Place the filtrate in a 500-ml. distilling flask connected to a water condenser fitted with an adapter, and heat over a wire gauze. If the presence of 0.01–0.015 per cent. of sulfate ion is not objectionable reserve the distillate which starts to come over 1° below the temperature of the constant boiling mixture. The distillation should be stopped when the temperature drops. The specific gravity of the solution will vary because of the variation of composition with the barometric pressure. A yield of approximately 85 per cent. will be obtained. The yield may be increased by redistilling the low boiling portions.

If constant boiling hydrobromic acid free from sulfate ion is wanted, collect the distillate over a range starting 5° below the temperature at which the constant-boiling acid distills. Redistill this acid and reserve only the distillate coming over at the constant-boiling temperature to obtain acid of the highest specific gravity. The addition of barium hydroxide before the second distillation did not give a purer product. The yield is approximately 85 per cent. of that calculated.

The yield of product was considerably lowered by reducing the ratio of potassium bromide to sulfuric acid.

The boiling point of a constant boiling mixture is 122.5° at 740 mm. and 126° at 760 mm. The specific gravity of 35 per cent. hydrobromic acid is 1.315, of 40 per cent. is 1.377, of 45 per cent. is 1.445 and of 50 per cent. is 1.517.

#### SUMMARY

A simple method of preparing constant boiling hydrobromic acid has been described which involves the use of chemicals and apparatus ordinarily found in a chemical laboratory.