A Modification of the Adams' Method of Preparing Alkyl Iodides.

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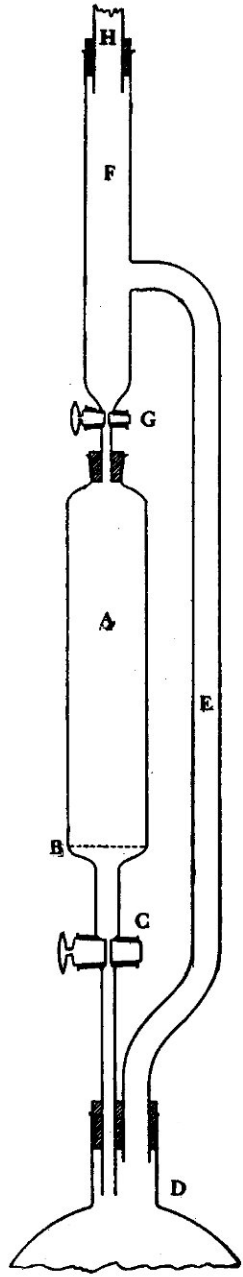
INTRODUCTION

The alkyl iodides are among the most important of organic reagents. Usually their cost ready prepared is high in comparison with the price of the raw materials. In most laboratories these reagents, especially methyl and ethyl iodides, are prepared as needed. Consequently any simplification in the procedure for their production is desirable. Adams and Voorhees have published a very satisfactory method in The Journal of the American Chemical Society, Vol. XLI. pp. 789-798, (May, 1919). This method is based on the reaction between an alcohol, phosphorus, and iodine. A mixture of red and yellow phosphorus, together with the alcohol corresponding to the iodide which is to be prepared, is boiled in a flask fitted with a special apparatus for dissolving iodine in the condensed vapors from the distillation and introducing the iodine gradually as as olution into the reaction flask. With this apparatus the preparation of alkyl iodides is smoothly and almost automatically accomplished.

The special apparatus, however, is rather too complicated to be made in the laboratory and somewhat expensive to have constructed by a professional glassblower. The purpose of this paper is to suggest a form which, it has been found, is simple enough for the average student to build, yet which works as efficiently. The accompanying cut illustrates the special apparatus in its simplified form. The iodine holder is a separatory funnel A, which is fitted to the reaction flask D by a rubber stopper. Through this stopper also extends a glass tube E, in which the vapors pass upward and the excess of the distillate flows down. This tube leads into a larger tube F, the lower end of which is constricted to join a stopcock which leads into the top of the separatory funnel. To the upper end of tube F is attached an efficient reflux condenser H.


H
F
G
A
E
B
C
D

DETAILED DESCRIPTION OF APPARATUS

The cylindrical separatory funnel A is 1200 c.c. in volume and holds 2 kg. of loose iodine crystals. A funnel of a different volume may be used if such a one is not available. A piece of perforated platinum foil B, or a mat of coarse glass wool is put in the bottom to prevent clogging of the stopcock by iodine crystals or solid impurities. The stopcock C should be as large as 5 mm. in bore as a further precaution.

For the production of up to 4 kg. of alkyl iodide, a 5 liter, round bottom, short ring neck, pyrex flask D is used. For larger quantities a flask up to 12 liters in capacity may be substituted. The reaction flask is heated by an oil bath.

The tube E should be 2.5 cm. in diameter. This has been found sufficiently large to allow the vapors to rise without interrupting the return of the distillate. It is the same diameter as that recommended by Adams and Voorhees for the lower part of their special apparatus.

The tube F should be 4 cm. in diameter to allow for preliminary condensation. A space is left below the point where tube E enters to act as a reservoir for the distillate.

The stopcock G should be 2 or 3 mm. in bore. It was found convenient to use for this purpose the stopcock from a small, broken, separatory funnel. Funnels in this condition are usually all too common about the laboratory. The tube from this stopcock is connected to the top of the iodine container by a rubber stopper. The bottom of the tube is flush with the bottom of the stopper so that the liquid will flow down the sides of the container instead of forming a channel through the middle of the iodine. Not as much difficulty from this source is encountered when a cylindrical rather than a globular separatory funnel is used.

A condenser H is attached through a rubber stopper. It should be 2.5 cm. in diameter and, when making methyl iodide, at least 210 cm. long. The condenser should be well cooled with a strong stream of water. In hot weather especially there will be some loss of methyl iodide through the condenser. If

to the top of the condenser is attached a tube leading under a slush of ice and water, this methyl iodide can be recovered. Of course the tube must have in it a trap—preferably a Bunsen valve—to prevent water from being drawn back into the apparatus.

THE PREPARATION OF METHYL IODIDE

Methyl iodide is the only one of the series prepared with this apparatus by the writer. The details of the method used are given here for the sake of completeness, though they are largely adapted from the directions given by Adams and Voorhees.

In the reaction flask put 1600 g. of absolute methyl alcohol, 200 g. of yellow phosphorus and 240 g. of red phosphorus. The absolute methyl alcohol can be conveniently prepared by adding magnesium turnings and a few crystals of mercuric chloride to the technical alcohol. After refluxing, distill using a good fractionating column. Any acetone present is reduced during the formation of magnesium alcoholate, and the alcoholate reacts with the water present. Fill the separatory funnel A with 2 kg. of iodine, being careful not to let crystals fall below the perforated platinum foil. Set up the rest of the apparatus and open both stopcocks C and G. Heat the oil bath to 100° C. At first alcohol distills, is condensed and flows back into the reaction flask through the iodine container. When the iodine solution begins to enter the flask, partly close stopcock G so that the reaction proceeds not too violently. After some methyl iodide is formed, it, being more volatile than the alcohol, acts as the solvent for the iodine. The temperature of the bath is then lowered to about 70-75° C. The flow through stopcock G at this point has to be further cut down because iodine is more soluble in methyl iodide than in methyl alcohol.

When all the iodine has been dissolved, close both stopcocks, with a rotary motion lower the separatory funnel and fill with a second charge of 2 kg. of iodine. Raise the separatory funnel to its former position. Open stopcock C wide, then stopcock G part way as before.

When all the iodine has reacted, allow the flask to cool. Then, instead of the special apparatus, attach a condenser arranged for downward distillation. The condenser previously used for refluxing is suitable for this purpose. The lower end is attached to an adapter dipping under a slush of ice and water. After the methyl iodide has all distilled over, wash once with water containing a little sodium hydroxide and separate. Care should be taken in disposing of the residues left in the flask after this distillation because they contain yellow phosphorus. Dry the crude product with anhydrous calcium chloride, separate and distill a second time. Unless special precautions are taken a loss of yield will result in this second distillation because of the high vapor pressure of methyl iodide. Very little material will escape if the following device is used. One end of a coil of glass tubing 2 mm. in diameter is attached to the end of the condenser. The coil is cooled in a freezing mixture. The other end of the coil is connected with a tube leading through a stopper into the collecting vessel also cooled in a freezing mixture. A Bunsen valve is inserted into the stopper of the collecting vessel to prevent the entrance of moisture from the air. One should obtain over 90 per cent of the theoretical yield based on the iodine used. In one run using all precaution against volatilization the yield was found to be 95 per cent.