

CLXXIX.—*A Process for the Dehydration of Alcohol.*

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SINCE the water present in alcohol is very completely consumed in the estimation process described in the preceding paper, it seemed possible that the reaction might be utilised as a method of dehydrating alcohol. Dry ethyl alcohol is a very hygroscopic substance from which it is difficult to remove the last traces of water. The ideal process would be to employ a rapid, irreversible, and preferably homogeneous reaction in which the water is consumed; also the

dehydrating agent and the products of the reaction should be non-volatile so that the alcohol may be distilled off uncontaminated. This ideal is not attained completely by any of the methods in use at present for the preparation of anhydrous alcohol.

The reaction between sodium or potassium ethoxide, an ester, and water in alcohol approaches very close to the ideal suggested, in respect of rapidity, irreversibility and homogeneity. The reactants and products are all non-volatile with the exception of the ester. This difficulty, however, can be surmounted by the use of an ester of high boiling point such as ethyl succinate, from which the alcohol can be separated by fractional distillation. The process evolved is as follows: The alcohol to be dehydrated is contained in a flask, fitted with a fractionating column, attached to a condenser which can be used either for refluxing or for distillation, without disconnexion. The requisite amount of sodium is dissolved in the alcohol, and the corresponding quantity of ethyl succinate added. The mixture is refluxed for about 2 hours and then distilled, the condenser being closed by a calcium chloride tube to prevent the entrance of moisture.

25 Grams of ethyl succinate and 7 g. of sodium suffice to remove 0.5% of water from a litre of alcohol, and scarcely any loss of alcohol occurs. It is well to use approximately the above quantities even when the water present is much less than 0.5%, so that a considerable excess of the "dehydrating agents" remain, and the water is rapidly consumed. The residue can be used to dry a further smaller quantity of alcohol. An attempt has been made to estimate the amount of water in samples of this "super-dry" alcohol by the method described in the previous paper. The results, however, are indicative rather of the slight imperfections in the estimation process than of the true amount of water in this alcohol, which is too small to be estimated accurately by any known method. The mean of three such estimations was 0.01%. It is highly probable, especially in view of the enhanced hygroscopic nature of extremely dry alcohol, that the greater part of this water found its way into the alcohol during the estimation.

There remain two criticisms which may be levelled at this process for the preparation of anhydrous alcohol: (1) a certain amount of the ester may distil over with the alcohol; (2) the ethoxide and the ester may react directly to form ethyl ether, which also would contaminate the product. These will be dealt with in turn.

It was considered unlikely that ethyl succinate would be carried over with the alcohol, owing to its high boiling point (216.5°), and a very short fractionating column was used. The alcohol, when tested, however, was found to contain 0.04 g. of ester per litre.

This impurity could probably be removed by the use of a more efficient fractionating column.

The second possibility was suggested by Cashmore, McCombie, and Scarborough (J., 1921, **119**, 970) to explain the fact that esters react with potassium ethoxide in "dry" alcohol. They state "the quantity (of ether) formed would be too small to detect." The present work renders it certain that the main reaction in their case was due to the water present in the "dry" alcohol used, since even at 70° no measurable reaction occurs after the water has disappeared. If ether were formed, of course, the titres would decrease.

This point was subjected to a more rigorous test by carrying out the reaction in concentrated solutions at 100° in sealed tubes. The titres remained constant within the limits of experimental error over a period of 11 hours. It can be safely asserted that the suggested reaction does not take place to a measurable extent, if at all, even under the above conditions, and that no ether will be formed in the dehydration of alcohol by the method described above.

From all points of view, this process is exceedingly efficient for the thorough dehydration of alcohol.

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