XXXIII.—*Note on the Preparation of Ethyl Chloride and its Homo-logues.*

By CHARLES E. GROVES.

CHEMICAL manuals describe several processes for the preparation of ethyl chloride from alcohol, the two most important of which are :—

1. To saturate alcohol with dry hydrochloric acid, and after allow-ing the mixture to stand for some time, distil in a water-bath.

2. To distil a mixture of alcohol, sulphuric acid, and common salt.

Any one who has endeavoured to prepare large quantities of ethyl chloride by these methods must know how unsatisfactory they both are. The first, although it yields pure ethyl chloride, is open to the objection that only a comparatively small proportion, not more than about 15 per cent. of the alcohol, is converted into the ether, whilst at the same time torrents of hydrochloric acid are given off. The second process, besides these disadvantages, has the additional one that the chloride is very apt to be contaminated with ethyl oxide, as was first observed by Boullay.

Ethyl Chloride.

When a solution of hydrochloric acid in alcohol, which has been recently prepared, is gently heated, the first effect is to expel a portion of the gas dissolved, the temperature not yet being sufficiently elevated to cause the formation of any considerable quantity of ethyl chloride, and then, as the temperature rises, a portion of the hydrochloric acid reacts with the alcohol, producing ethyl chloride, which comes off with the hydrochloric acid, so that after a time nothing is left in the retort but slightly diluted alcohol containing some hydrochloric acid and ethyl chloride in solution. Now it seemed probable that if gaseous hydro-chloric acid were passed into boiling alcohol, it would react at that temperature with the ethyl hydrate and produce ethyl chloride ; thus, the use of so large an excess of hydrochloric acid would be avoided, and a much larger proportion of the alcohol would be converted into the haloïd ether.

The apparatus employed in this and the subsequent experiments consisted of a flask with a bent tube passing through the cork nearly to the bottom, to convey the hydrochloric acid into the boiling liquid, and an inverted condenser in which the alcohol vapour was condensed and flowed back again into the flask. The upper end of the condenser was usually connected with a wash-bottle partly filled with water to remove hydrochloric acid. On making the experiment just suggested, in this apparatus, it was found that a large portion of the alcohol was converted into the ether, but at the same time the latter was always accompanied by some gaseous hydrochloric acid. Although this was a great improvement on the ordinary process, it was far from being perfect, for when the alcohol had become somewhat dilute, the hydrochloric acid almost ceased to act on it. Experiments were consequently made in the same apparatus by passing hydrochloric acid into boiling mixtures of sulphuric acid and alcohol. When these were in such proportions that their point of ebullition was between 140° and 150°, in fact, such as would yield ether when heated alone, it was found that although ethyl chloride was produced, it was accompanied by a comparatively large quantity of the oxide, the two reactions—

$$SO_3C_2H_5.OH + C_2H_5.OH = C_2H_5.O.C_2H_5 + SO_4H_2$$
$$SO_3C_2H_5.OH + HCl \quad = C_2H_5Cl \quad + SO_4H_2$$
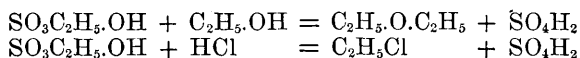
taking place simultaneously. When the amount of sulphuric acid was reduced until ethyl oxide ceased to be produced, the action was not perceptibly different from that which occurred when pure alcohol was used.

As sulphuric acid had proved to be ineffectual in facilitating the conversion of the last portions of the alcohol into the haloïd ether, it was determined to try some other compounds which had a strong attraction for water. Calcium chloride naturally suggested itself as the most convenient, and accordingly dry hydrochloric acid was passed into a boiling mixture of alcohol and the calcium salt, but the result was almost identical with that obtained with pure alcohol, ethyl chloride being formed in quantity, but accompanied by much hydrochloric acid. On repeating the experiment, however, but substituting zinc chloride for the calcium chloride, a very unexpected result was obtained.

Fused zinc chloride was dissolved in about one and a-half to twice its weight of alcohol of 95 per cent.; considerable heat was evolved and the solution contained, suspended in it, a white compound insoluble in the alcohol and probably a zinc oxychloride. This mixture was introduced into the apparatus previously described, and a current of gaseous hydrochloric acid passed into the boiling liquid: the first effect produced was to dissolve the suspended oxychloride, and even for some

time after this had taken place, the gas still continued to be completely absorbed. Presently, however, a few bubbles of gas began to pass through the wash-bottle connected with the other end of the condenser, and in the course of a few seconds the current of ethyl chloride vapour passing out through the water in the wash-bottle was as rapid as that of the hydrochloric acid passing in at the other side of the decomposition flask. In fact, the hydrochloric acid, even when a very rapid stream was passing, was so completely converted into ethyl chloride that, on holding a rod dipped in ammonia in the current of vapour issuing from the apparatus, no appreciable cloud could be observed. This continued until almost the whole of the ethyl hydrate was converted into the chloride; ultimately hydrochloric acid began to pass through the apparatus, and in a few minutes the formation of ethyl chloride ceased, the gas which issued being completely absorbed by the water in the wash-bottle. On disconnecting the apparatus and examining the solution of zinc chloride remaining in the flask, it was found to be quite free from alcohol, the whole of it having been converted into ethyl chloride, with the exception of the small portion which was carried away mechanically by the vapour of the latter. This reaction is so precise that it is quite comparable with those which take place with inorganic compounds, and offers an excellent method for the preparation of large quantities of the chloride, a kilogram of which can readily be prepared in a few hours. It forms a very good lecture experiment.

I am unable to offer any satisfactory explanation of the peculiar action of zinc chloride. It is not merely a dehydrating action, since a concentrated aqueous solution of the chloride is almost as effectual as the anhydrous compound; moreover, neither calcium chloride nor sulphuric acid produce this effect. The supposition that the compound of zinc chloride with alcohol, $(C_2H_6O)_2ZnCl_2$, is decomposed into ethyl chloride, zinc oxide, and water—

$$(C_2H_6O)_2ZnCl_2 = 2C_2H_5Cl + H_2O + ZnO,$$

seems to be precluded by the fact that the alcoholic solution of zinc chloride employed gave no ethyl chloride when boiled; besides, although water decomposes the alcoholate, yet an aqueous solution of zinc chloride will act. Although it was rendered improbable by the results obtained with calcium chloride that the combination of a metallic chloride with the alcohol modified the action of the hydrochloric acid on the latter in any specific manner, yet it seemed desirable to ascertain, if possible, whether this was the case. Anhydrous ferric chloride, Fe_2Cl_6, was dissolved in alcohol of 95 per cent., during which a considerable development of heat took place, and on placing the solution in the apparatus previously described and boiling it, no ethyl chloride was

evolved, but the ferric chloride was evidently decomposed, a brown, insoluble compound, probably an oxychloride being formed.   On passing in gaseous hydrochloric acid, this gradually dissolved, giving a clear yellow solution, and ethyl chloride began to be produced ; it was, however, accompanied by hydrochloric acid, and the result did not appreciably differ from that in which pure alcohol was employed.   On introducing some zinc chloride into this alcoholic solution of ferric chloride, the evolution of hydrochloric acid ceased, and pure ethyl chloride was evolved, as in the former experiment.

A very convenient method of collecting the ether is to pass the vapour into spirit which should be kept cool by surrounding it with cold water; at 16° alcohol will readily take up half its weight,* and this solution may be kept in an ordinary bottle and the chloride expelled when required, by gently heating the mixture.   After being washed with concentrated sulphuric acid, it is quite pure, the minute proportion of the higher homologues produced along with it from the fusel oil always present in the alcohol being retained by the spirit.

It is frequently stated in text books that the vapour of ethyl chloride is absorbed by concentrated sulphuric acid, which I believe is done on the authority of Kuhlmann (*Ann. Chem. Pharm.*, xxxiii, 108), who, after speaking of the readiness with which it combines with sulphuric anhydride, says, "Aqueous sulphuric acid likewise absorbs hydrochloric ether."   This statement is very apt to mislead, as sulphuric acid only dissolves 1·3 per cent. of its weight, or four times its volume, at 13° C., only 1° above its boiling point,—which, according to Linnemann (*Ann. Chem. Pharm.*, clx, 214), is 12·18°,—1·03 per cent., or three volumes at 20°, and 0·7 per cent. at 50°.   This amount is so small that the best method of obtaining the ether dry and free from alcohol is to wash it by passing the vapour through concentrated sulphuric acid, as previously stated.

Action of Hydrochloric Acid on Alcohol.

Reynoso (*Ann. Chim. Phys.* [3], xlviii, 385) found that a mixture of alcohol and aqueous hydrochloric acid heated in a sealed tube to 100° yields ethyl chloride, but at the same time ethyl oxide is produced, although the quantity is very small.   At 240° the amount of the latter is much greater, especially if there be but little hydrochloric acid present, the ether being produced by the action of the ethyl chloride on the alcohol, thus :—

$$C_2H_5Cl + C_2H_5.OH = C_2H_5.O.C_2H_5 + HCl.$$
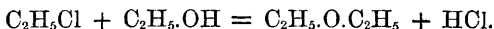
* I found that alcohol of 95 per cent., when saturated at 21°, dissolved 48·3 per cent. of its weight of ethyl chloride.

Moreover, Boullay has shown that a solution of gaseous hydrochloric acid in alcohol undergoes slow decomposition at the ordinary temperature, with formation of the haloïd ether, which may be separated by the addition of water. On combining these two experiments, and heating a saturated solution of hydrochloric acid in alcohol to 100° in a closed tube for a few hours, the action was found to be much more rapid, a layer of the ether soon making its appearance on the surface of the alcohol.*

A series of quantitative experiments were made by heating alcohol with hydrochloric acid in sealed tubes to 100°, both with and without the addition of dehydrating agents. The numbers given represent the mean of closely agreeing results, calculated for 100 parts of absolute alcohol.

a. 105 parts of alcohol containing 100 parts absolute alcohol, C_2H_6O, mixed with 296 parts of a solution of hydrochloric acid containing 90 of dry hydrochloric acid, gave 52 parts of ethyl chloride after five hours' heating, and 16 more after being heated for four hours longer : total 68 parts, the theoretical being 140. In this way (Reynoso's) only 48·5 per cent. of the alcohol was converted, although a considerable excess of hydrochloric acid was present.

b. 105 parts of alcohol, containing 100 of C_2H_6O, were mixed with 286 parts of a solution of hydrochloric acid containing 86 of the dry acid, and with 180 parts of calcium chloride. After being heated three hours, 101 parts of ethyl chloride were produced, in the next four hours 28 parts, and in the next four hours 3 parts : total 132 parts, corresponding with the conversion of 94·3 per cent. of the alcohol.

c. A similar experiment, in which the proportions of calcium chloride and dry hydrochloric acid were 280 and 84 respectively, showed that here 96·1 per cent. of the alcohol was converted. In both these experiments there was excess of hydrochloric acid.

d. An equal quantity of the alcohol saturated with 75 parts dry hydrochloric acid, and heated for six hours, gave 95 parts of the ether, and in the next six hours 10 parts more, the total being 105 parts ethyl chloride, equivalent to the conversion of 93 per cent. of the hydrochloric acid.

e. An experiment made in a similar way, but with the addition of 80 parts of calcium chloride, equivalent to about one molecular weight of the calcium salt to three of alcohol, showed that 99 per cent. of the hydrochloric acid had been transformed into the haloïd ether. After the contents of the tube have been heated some hours, three layers of liquid make their appearance, the upper one being ethyl chloride, the

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* Nearly all the ethyl chloride employed in studying "The Action of Chloride of Ethyl upon Ammonia" (*Journ. Chem. Soc.*, xiii, 331), was prepared by this method and by passing hydrochloric acid through boiling alcohol.

lower fused crystals of the hydrated calcium chloride, and the intermediate one a solution of ethyl chloride and calcium chloride in alcohol. In this and the previous experiment, d, the alcohol was slightly in excess.

f. A mixture of 100 of alcohol, C_2H_6O, to 128 of sulphuric acid absorbed only 14 parts of dry hydrochloric acid gas, of which about 75 per cent. were converted into the haloïd ether when heated. A mixture in the proportion of 280 of sulphuric acid to 100 of alcohol absorbed only 4 parts of hydrochloric acid, from which it would seem that the latter is but slightly soluble in mixtures of alcohol with a large proportion of sulphuric acid.

In all these experiments, after the first heating, the tubes were opened to allow the ethyl chloride to escape, again closed, and the residual mixture submitted to the same treatment.

Preparation of Methyl Chloride.

When a current of hydrochloric acid was passed into a boiling solution of zinc chloride in twice its weight of wood spirit in the apparatus employed for the preparation of ethyl chloride, similar phenomena were observed; the hydrochloric acid was completely absorbed, and methyl chloride was given off. The methyl alcohol was thus completely converted into the chloride, whilst the impurities which accompany it in the crude wood spirit were converted into a black tarry mass. The method of Dumas and Peligot (*Ann. Chim. Phys.* [2], lviii, 25) usually given of heating a mixture of 2 parts of sodium chloride, 1 of wood spirit, and 3 of sulphuric acid, yields methyl chloride in an impure state, contaminated as it is with methyl oxide and sulphurous anhydride.

If the methyl chloride could be readily reconverted into the alcohol, it would probably afford the best method of obtaining the latter in the pure state.

Amylic alcohol may be converted into the chloride by the same process; but as the latter has a comparatively high boiling point, the inverted condenser should be replaced by a long tube, and the amyl chloride which distils over collected in a receiver, and after being washed with water to remove adhering hydrochloric acid, dried and rectified

Glycerin, when treated with zinc and hydrochloric acid, yields a viscous substance, soluble in water. Phenol and cresol are not acted on.