

XIV. "On some new derivatives of Chloroform." By A. W. WILLIAMSON, Ph.D., &c. Communicated by Dr. SHARPEY, Sec. R.S. Received June 15, 1854.

According to the results of recent researches in the constitution of salts and the methods thence introduced of explaining chemical reactions, it is equally correct to represent such a reaction as that of hydrochloric acid on hydrate of potash, as consisting in an exchange of hydrogen of the one for potassium of the other, or of chlorine in one for peroxide of hydrogen in the other. In Mr. Kay's researches as described in the following brief outline, this notion has obtained very striking illustration; for he has obtained a peculiar body in which the chlorine of chloroform is replaced by peroxide of ethyle by the action of chloroform on three atoms of ethylate of sodium, which product may be equally well conceived to be a body in which the hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform.

According to the older theories of the capacity of saturation of salts, this compound would contain a tribasic modification of formic acid, for it has the same relation to formic ether as a so-called tribasic phosphate has to a monobasic one.

To one equivalent of chloroform were added, by degrees, three equivalents of dry and powdered ethylate of soda, a violent action taking place with the evolution of much heat; the liquid was entirely distilled from the residue (chloride of sodium) by means of an oil-bath, and then subjected to a series of fractional distillations, which yielded a small distillate between 50° and 60° C., smelling strongly of vinous ether, a large distillate (about three-fourths of the whole) between 77° and 78° C., which was chiefly alcohol, and another small distillate (about one-sixth) between 145° and 145.3° C.

The distillates obtained by the above process, except that of alcohol, being small, the following modification was adopted.

Sodium was dissolved in absolute alcohol until the action became feeble, chloroform was then added, care being taken to keep the liquid alkaline; more sodium was then added, and the process repeated several times, until the chloride of sodium precipitated became very bulky. The liquid was then distilled off and chloroform

added to the residue, and also distilled off. To this first distillate sodium was again added, and treated with the last distillate instead of pure chloroform, the same precautions being used as before. This method gave similar distillates, and in about the same proportion as that first used; the highest distillate however boiled constantly at 146° instead of at 145.3° C.

This compound which boils at 145° to 146° C. is a colourless limpid liquid, only slightly soluble in water, having a strongly aromatic odour, readily inflammable and burning without much smoke; its specific gravity is .8964; it remained liquid at 0° F.

Several analyses made of this body agree in giving to it the formula $C_7H_{16}O_3$, which would also be the empirical formula of a tribasic formic-ether; the density of its vapour also corresponds very closely with the same formula.

Pentachloride of phosphorus added to a portion of the compound produced a heavy liquid having the odour of chloroform.

A small quantity of the body was dissolved in alcohol, distilled upwards for two or three hours with solid hydrate of potash and then distilled off; the residue was next dissolved in water and made exactly neutral by hydrochloric acid, filtered to remove the turbidity, and then a few drops of chloride of mercury added; after a little time and by the application of heat, a very slight precipitate of subchloride of mercury was formed; also the colour of sesquichloride of iron was a little darkened by another portion of the solution, thus showing that the action of potash on the compound had produced formic acid, but in very small quantity.

An equivalent of dry hydrochloric acid was passed into a portion of the compound; the gas was wholly absorbed, a considerable amount of heat being evolved and the liquid assuming a brownish colour; the liquid after the absorption of the gas still remained perfectly neutral. It was next distilled with the thermometer: it began to boil at 20° C. and rose gradually to 100° ; it was collected in three portions, the first (about one-sixth of the whole) passing over between 20° and 50° , the second (about one-third) between 50° and 68° , the third (one-half) between 68° and 100° . I was unable to carry these distillations further in consequence of the small quantity of the liquid available.

Two equivalents of dry hydrochloric acid were passed into a larger quantity of the compound; towards the close the gas was ab-

sorbed less freely, a portion passing through; after this treatment, the liquid fumed and was highly acid; it was distilled upwards for some time by which a portion of free hydrochloric acid was expelled, and then distilled fractionally; about one-third came over between 56° and 60° C., one-fourth between 60° and 70° , one-sixth between 70° and 80° , and the remainder (about one-fourth) between 80° and 88° . To the lowest distillate about an equal bulk of water was added; the substance floated on the surface and seemed to be little, if at all dissolved by the water; a sufficient quantity of carbonate of soda was next added to neutralize the free acid, and the liquid pipetted from the water, it was then distilled upwards for some time with dry chloride of calcium, and afterwards distilled off; this distillate was found to boil constantly at 55.5° C. An analysis made of this body agrees closely with the formula $C_6H_{14}O_5$.

The distillate which came over between 60° and 70° after being treated in the same way as the lower distillate, also yielded a liquid which boiled at 56° C.

As both methods hitherto used for the purpose of obtaining the body $C_7H_{16}O_3$ afforded only small quantities, the treatment of chloroform with an alcoholic solution of potash was tried; for this purpose 12 oz. of solid hydrate of potash and 20 oz. of quicklime were added to about three pints of absolute alcohol, and the alcohol distilled upwards for six or seven hours; 6 oz. of chloroform were then added gradually, the upward distillation being continued about two hours longer; the liquid was next distilled off to dryness by means of an oil-bath, and submitted to fractional distillation; by this method a much larger quantity of the compound was obtained than by the former processes; it was found to boil constantly at 146° C., and its analysis agreed almost exactly with the formula. In this process the lowest distillate had the same smell of vinous ether which was before observed in the other methods.

An attempt was made to produce the intermediate compounds $CHCl_3$, AeO , and $CHCl$, $2AeO$, by adding dry and powdered ethylate of soda very gradually to a large excess of chloroform; but the liquid after being separated from the precipitate, was found, on distilling fractionally, to resolve itself into chloroform, alcohol, and the body ($C_7H_{16}O_3$) already obtained, the presence of no other substance being observable.

With a view of obtaining a compound analogous to the body $C_7H_{16}O_3$, in which amyle should be introduced instead of ethyle, dry amylate of soda was prepared, to three equivalents of which one equivalent of chloroform was added, the liquid separated from the precipitate and then distilled fractionally; a large proportion of fusil-oil was obtained, together with a small proportion of a body which boiled at a high temperature,—from 260° to $290^\circ C.$, but chiefly from 260° to 270° ; the purification of this substance was not carried further, as at each distillation a considerable portion was decomposed even in an atmosphere of hydrogen, the small quantity of the liquid available precluding any more attempts at distillation.