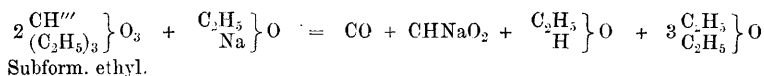


XXIII.—*On the Tetrabasic or Orthocarbonate of Ethyl.*

By HENRY BASSETT, F.C.S.

IN the early part of last year, I published in the Chemical News,\* a short note of some experiments on the subformate of ethyl, described by Williamson and Kay,† in which I gave a modified process by which it may be prepared in large quantity, namely, by adding sodium to a mixture of chloroform and absolute alcohol. Since then I have observed that, by adding an alcoholic solution of ethylate of sodium to chloroform, an evolution of very large quantities of gas takes place, consisting almost entirely of carbonic oxide, and the quantity of subformate of ethyl produced is very much smaller. This appears to be caused by the decomposition of some of the subformate by the ethylate of sodium, whereas, by adding the sodium to the mixture of alcohol and chloroform, there is always an excess of the latter, whereby this decomposition and consequent loss is prevented.

The secondary reaction may be represented as follows :



and in reference to this equation, I may observe that it explains the formation of ether and alcohol, which was noticed by Williamson when using dry ethylate of sodium. The formate is readily detected by the usual tests in the watery solution of the residue left after distilling off the alcohol.

After absorption of the carbonic oxide by subchloride of copper, a small quantity of inflammable gas remains, and this is probably ethylene, as Hermann, who has analysed the gas produced by the action of alcoholic potash on bromoform, states‡ it to consist of carbonic oxide, with a trace of ethylene, which he considers to be formed catalytically.

During these experiments, the idea naturally suggested itself of examining the action of ethylate of sodium on some other chlorides, more or less allied to chloroform, but unfortunately, the

\* Vol. vii, p. 158.

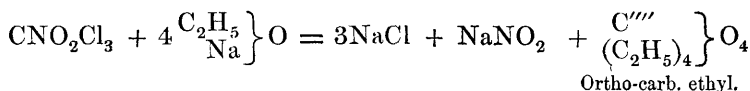
† Proceed. Roy. Soc. June, 1854.

‡ Ann. Ch. Pharm., xcv. 211.

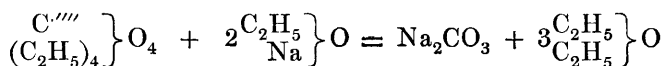
chlorinated derivatives of chloride of ethyl, and the various chlorides of carbon, are either not attacked at all, or very slightly so, by ethylate of sodium, at all events below the temperature at which the ethylate alone would undergo decomposition. By the employment, however, of chloropicrin, which is attacked with great facility, I have succeeded in obtaining a compound, the composition, properties, and decompositions of which show that it must be regarded as a tetrabasic carbonate of ethyl.

The details of the process are as follows :

40 grms. chloropicrin are mixed with 10 oz. absolute alcohol in a flask adapted to an upright condenser. The flask is supported on a water-bath, and the temperature raised to the boiling point of the alcohol. 24 grms. sodium are then gradually added in portions of about half a gramme, the temperature being kept up during the whole time, as the reaction is not so easily effected as with chloroform. The alcohol is then distilled off in the water-bath, and the residue dissolved in water, when an oil floats on the top. The reaction is represented below :



Besides chloride and nitrite, the watery solution contains some carbonate of sodium, arising doubtless from a secondary decomposition of some of the oily product :



The smell of ether is distinctly perceptible in the first portions of the alcoholic distillate.

The hydrogen evolved during the process is alkaline, from the presence of ammonia derived from reduction of the chloropicrin. By passing it into dilute hydrochloric acid, a solution was obtained, which, on addition of bichloride of platinum, gave a salt, the analysis of which gave the following result :

·5195 grm. gave ·229 grm. platinum, corresponding to 44·08 p. c.

The ammonio-chloride of platinum contains . . . 44·17 p. c.

The oil separated from the watery solution is washed, dried with chloride of calcium, and purified by fractional distillation. By this means the pure substance is obtained as a colourless oil,

of sp. gr. ·925, boiling at 158°—159°, having a peculiar aromatic smell, and giving the following results on analysis:

1. ·2835 grm. gave ·584 grm. carbonic acid and ·2665 grm. water.
2. ·2853 grm. gave ·586 grm. carbonic acid and ·269 grm. water.

These numbers agree closely with theory, as will be seen by comparison of the percentage amounts.

	I.	II.	$\left. \begin{array}{c} \text{C}'''' \\ (\text{C}_2\text{H}_5)_4 \end{array} \right\} \text{O}_4$
Carbon .....	56·18	56·02	56·25
Hydrogen.....	10·44	10·48	10·41

The substance, being rather difficult of combustion, required the employment of tubes rather longer than usual: granular oxide of copper was used, and oxygen passed through at the end of the process.

A determination of the vapour-density gave the following result:—

Difference in weights of flask ....	·519 grm.
Temperature of air..... ..	10°·5
Temperature of vapour.....	204°
Residual air..... ..	3·25 c.c.
Capacity of flask .. ..	141·5 c.c.

The vapour-density calculated from these data is 6·80

That required by the formula  $\left. \begin{array}{c} \text{C}'''' \\ (\text{C}_2\text{H}_5)_4 \end{array} \right\} \text{O}_4$  is 6·65

A small piece of sodium was ignited in the vapour, and the result carefully tested for nitrogen and chlorine; but not a trace of either was found.

On boiling a small quantity of the substance with alcoholic potash, a considerable quantity of carbonate was deposited.

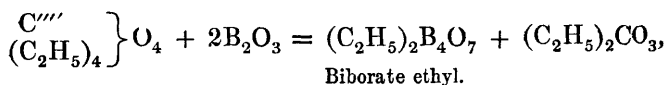
10 grammes of the oil were digested at 100° for about six hours with 8 grammes boric anhydride, and the resulting solution distilled to dryness. The distillate was washed with dilute potash, and afterwards with water, to separate traces of boric ether carried over, dried with chloride of calcium, and then purified by distillation. Nearly the whole came over between 124°—126°, the boiling point of ordinary carbonic ether being 125°.

The identity of the two substances is confirmed by the following analysis:—

·3215 grm. gave ·596 grm. carbonic acid and ·247 grm. water, leading to the percentage amounts—

	Experiment.	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CO <sub>3</sub> .
Carbon . . . . .	50·56	50·85
Hydrogen . . . . .	8·54	8·47

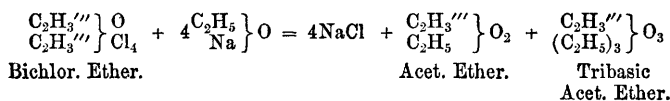
The reaction may be represented as follows :—



which is similar to what takes place with the subformate of ethyl, ordinary formic ether being in that case produced.

From the foregoing results there can, I think, be no doubt that the substance in question is really a tetrabasic carbonate of ethyl; and the discovery of analogous ethers may be not unreasonably expected.

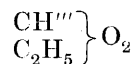
The next homologue to Williamson's tribasic formate of ethyl, the tribasic acetate, would in all probability be formed by the action of ethylate of sodium on Malaguti's bichlorinated ether, in the following manner :—



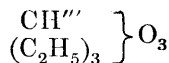
In connexion with this may be mentioned the well-known fact, that the density of glacial acetic acid is increased up to a certain point by the addition of water; and this apparent anomaly would seem to show a tendency to form a hydrate of analogous constitution, as the acid at its greatest density has the composition C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>.H<sub>2</sub>O, which might then be written  $\left. \begin{matrix} \text{C}_2\text{H}_3''' \\ \text{H}_3 \end{matrix} \right\} \text{O}_3$ . Valerianic acid is said to be invariably obtained in the form of a hydrate of analogous composition, when a solution of a valerianate is decomposed by an acid.

The ordinary and the tribasic formic ethers stand in a very interesting relation to the glycerides and the glycidic ethers described by Reboul :\*

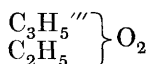
\* Ann. Chim.Phys. [3], lx, 1.



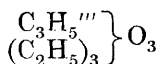
Formic ether.



Ortho-formic ether.



Glycidic ether.



Tri-ethylin.

The existence of two distinct series of isomeric bodies thus becomes probable, one derived from the triatomic alcohols, and the other from the fatty acids; and it would be interesting to ascertain whether the action of boric anhydride would produce the glycidic ethers directly from the glycerides.

In conclusion, I may make a few remarks suggested by the composition of the best defined basic salts of some of the acids derived from alcohols. These may be divided into two classes, namely, those whose normal basicity is less than their atomicity, and those in which it is the same. The most basic salts formed by the first class of acids appear to contain a number of atoms of metal equal to the number of atoms of water from which the original alcohol is derived. As examples may be mentioned, the bibasic lactates, the basic malates of copper and zinc, which contain three atoms of metal, some basic tartrates and citrates of copper containing four atoms, and a basic saccharate of lead containing six atoms of metal.

In the most basic salts of the second class, the number of atoms of metal exceeds the number of atoms of water from which the original alcohol is derived, and coincides with the atomic value of the alcohol-radicle, as altered by the removal of hydrogen. As examples may be given, the best-defined basic lead and copper salts of the fatty acids, which are similar in composition to the tribasic or ortho-formate of ethyl, the metallic orthocarbonates, also corresponding to the tetrabasic or orthocarbonate of ethyl, and several basic oxalates and succinates containing six atoms of metal, ethers corresponding to which yet remain to be discovered.