VIII.—*On a new method of preparing Propionic Acid: viz. by the action of Carbonic acid upon an Ethyl compound.*

By J. A. WANKLYN, Esq.

IN the course of experiments made on the action of highly electro-positive metals upon zinc-ethyl, I obtained, some time ago, crystalline compounds containing the metal employed in union with ethyl. These bodies, of which a detailed account will shortly be published, react most energetically upon bodies containing an electro-negative constituent.

Such, indeed, is the electro-positive energy of the sodium compound, that dry carbonic acid itself is thereby decomposed, with evolution of heat, the resulting product, as will further on be proved, being propionate of soda.

I proceed to describe the experiments with carbonic acid and the new body containing ethyl and sodium.

Sodium-ethyl* was prepared by acting upon zinc-ethyl with sodium, whereby metallic zinc was precipitated and a crystalline compound containing sodium-ethyl and zinc-ethyl was produced. This body, which dissolved readily in excess of zinc-ethyl, was introduced into a bulb so constructed as to admit of the passage of a gas. On attempting to free the crystalline compound from adherent zinc-ethyl by the transmission of carbonic acid, great evolution of heat occurred, zinc-ethyl distilled off, and the contents of the bulb formed an amorphous white solid. This latter effervesced with water, forming a solution, which, when treated with sulphuric acid, evolved the odour of propionic acid. In proof that this heating and solidifying were due neither to free oxygen nor to moisture, I may mention that an experiment was made with the same apparatus, in which hydrogen was substituted for carbonic acid, and that no such effects occurred as had been noted in the former case.

Different samples of sodium-ethyl prepared from zinc-ethyl as aforesaid were exposed to the action of carbonic acid.

In one case, the subsequent treatment of the amorphous solid was as follows:—it was put into water, distilled with dilute

* Sodium-ethyl cannot be obtained by the action of sodium upon iodide of ethyl.

sulphuric acid, and the distillate subsequently redistilled alone, in order to separate anything which might have been mechanically carried over during the first distillation. The second distillate containing the dilute pure acid was warmed with carbonate of baryta, filtered and evaporated to dryness in the water-bath. The residue, which was crystalline and completely soluble in water, was afterwards dried in the air-bath at about 130°C ; until it no longer lost weight.

A baryta determination—made by moistening the salt with strong sulphuric acid, and afterwards igniting cautiously to expel the excess of sulphuric acid and the organic matter, gave this result—

·288 grm. of the substance yielded ·237 grm. of sulphate of baryta.

The substance, therefore, contained 48·38 per cent. of barium.

Propionate of baryta contains 48·41 per cent. of barium.

From another sample of sodium-ethyl, the amorphous mass given by the action of carbonic acid was treated thus:—First, with a little moist ether, whose purity had been well ascertained. The object of this deviation from the plan followed in the former case was to avoid a troublesome elevation of temperature which occurs when zinc-ethyl (adherent to the propionate of soda) is suddenly acted upon with water. After the addition of water and the expulsion of the ether which had been added, by heating in the water-bath, a distillation with dilute sulphuric acid was made as before.

The distillate, after supersaturation with carbonate of soda, was evaporated to dryness in the water-bath; and an endeavour was made to obtain concentrated propionic acid from this soda-salt by distillation with strong sulphuric acid. This operation was carefully conducted in the air-bath, the materials being contained in a small bulb retort. Neither carbonization nor evolution of sulphurous acid was observed, and the resulting distillate had the smell of propionic acid. From it a silver-salt was made by the use of pure oxide of silver. This salt, forming beautiful, but exceedingly light crystals, was crystallised by cooling its solution in hot water. The crystals were separated from the mother-liquid and dried in vacuo.

I. ·0466 grm. of the substance gave, on cautious ignition, ·0272 grm. of metallic silver.

II. A combustion was made by heating the substance placed in

PROPIONIC ACID.

105

a small platinum boat in a stream of dry air freed from carbonic acid. The products of combustion were led over red-hot oxide of copper, and, in fact, the arrangement was essentially the same as that which gives remarkably accurate results in the hands of Hofmann and others. So treated, .0632 grm. of the substance gave

.0447 grm. of carbonic acid.

.0154 grm. of water.

.0377 grm. of silver.

Here follow the collected results compared with the composition of propionate of silver.

Propionate of Silver.	Calculated		Found.	
			I.	II.
C ₆	36	19.89	—	19.29
H ₅	5	2.76	—	2.71
O ₄	32	17.68	—	18.35
Ag	108	59.67	58.4	59.65
	181	100.00		100.00

The reaction which takes place between carbonic acid and sodium-ethyl admits, therefore, of the following expression :—

And since there can be no doubt that homologous bodies would give analogous results with carbonic acid—that, for instance, *sodium-methyl* would give acetate of soda—we may write the following as a general formula expressing the reaction which has been realized.

Inspection of the formula will at once show that a synthesis exactly corresponding to the well-known and beautiful analysis of the series of volatile fatty acids $\text{C}_2\text{O}_2 \text{C}_n\text{H}_{n+1} \left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{O}_2$ made by Kolbe some years ago, has now been effected. In fact, such a reaction as that described here is what that distinguished chemist, in conjunction with Frankland, predicted in his memoir* of last year.

* Ann. Ch. Pharm. ci. 265.