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VII.—*On Compounds obtained by the Action of Anhydrous Sulphuric Acid on the Chlorides of Hydrogen and Ethyl.*

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It has been stated by Gerhardt* that the reaction which takes place between pentachloride of phosphorus and monobasic acids, is not the same as the reaction between the same body and bibasic acids. In the first case, two chlorides are formed, viz., chloride of hydrogen and chloride of the radical of the acid: thus, with acetic acid, the reaction is:

But, according to Gerhardt, the reaction between pentachloride of phosphorus and a bibasic acid consists of two stages. "When, for example, one atom of hydrated succinic acid is treated with one atom of the perchloride, the products are anhydrous succinic acid, hydrochloric acid, and oxychloride of phosphorus; but when anhydrous succinic acid is treated with an additional atom of perchloride, chloride of succinyl and oxychloride of phosphorus are obtained.

* Compt. Rend. XXXVI, 1052.

† The atomic weights used in this paper are those proposed by Gerhardt, viz.—
C = 12, S = 32; O = 16;

Similarly, Gerhardt describes the action of pentachloride of phosphorus on hydrated sulphuric acid, or on a sulphate, as consisting, *first*, in the formation of anhydrous sulphuric acid (together with hydrochloric acid and oxychloride of phosphorus.) *Secondly*, in the transformation of this anhydrous sulphuric acid, by another atom of pentachloride, into chlorosulphuric acid.

This supposed difference in the behaviour of monobasic and bibasic acids with perchloride of phosphorus, is connected by Gerhardt with the fact, that the atom of a monobasic acid does not contain the quantity of hydrogen requisite for the formation of water, while the atom of a bibasic acid contains the elements of its anhydride with the elements of one atom of water; and he supposes that it is on this atom of water only that the chloride of phosphorus first acts.

This account of the action of pentachloride of phosphorus on the bibasic acids has been shown by Dr. Williamson* to be inaccurate in the case of sulphuric acid. With this acid, the reaction does indeed take place by two stages, but the second is an exact repetition of the first, and each is exactly the same as the one stage of the reaction between chloride of phosphorus and a monobasic acid. For the sake of comparison, the reactions may be written side by side.

In each case, the change which the hydrated acid undergoes, may be stated, empirically, to be the replacement of an atom of binoxide of hydrogen by an atom of chlorine. And it is evident from the above equations, that this replacement can take place twice in a bibasic acid, but only once in a monobasic acid. The result of the replacement of one atom of binoxide of hydrogen in

* Proc. Roy. Soc. vii. 11.

hydrated sulphuric acid by chlorine, is the compound SO^3ClH , which is strictly intermediate between the hydrated acid and Regnault's chlorosulphuric acid (SO^2Cl^2). The capability of forming such a compound, intermediate between the hydrated acid and the chloride of the acid radical, seems to be a general character distinguishing bibasic from monobasic acids.

It is evident that between a hydrated tribasic acid (PO^4H^3) and its chloride, (POCl^3) *two* intermediate compounds may exist ($\text{PO}^3\text{H}^2\text{Cl}$ and PO^2HCl^2). As examples of bodies similarly constituted to Dr. Williamson's chlorohydrated sulphuric acid, (SO^3HCl), there may be mentioned Chiozza's chlorobenzoic acid ($\text{C}^7\text{H}^5\text{ClO}^2$)* and the substance which Dumas obtained by the reaction of chlorocarbonic acid on alcohol. This body is to chlorocarbonic acid and hydrated carbonic acid, what chlorohydrated sulphuric acid is to chlorosulphuric acid and hydrated sulphuric acid, but contains an atom of ethyl in place of an atom of hydrogen. Its formation is represented by :

Chlorohydrated sulphuric acid is formed, not only by the action of perchloride of phosphorus on hydrated sulphuric acid but by the action of chloride of sulphur and chlorine on sulphuric acid, by the action of chlorine on sulphurous acid in presence of moisture, in contact with platinum black at a red heat, and by the combination of hydrochloric acid with anhydrous sulphuric acid.

The present paper contains an analysis of chlorohydrated sulphuric acid obtained by the last process, and also an account of compounds similarly obtained from the chlorides of ethyl and methyl and anhydrous sulphuric acid.

Chlorohydrated Sulphuric Acid, SO^3ClH .—This substance was prepared by saturating anhydrous sulphuric acid with hydrochloric acid which had been dried by anhydrous phosphoric acid. The compound so formed agreed in all its properties with the chloro-

* This substance has been found by Mr. Lockwood, of this laboratory, to give salicylate of potash, and not chlorobenzoate of potash, when boiled with alcoholic potash. It is, therefore, chlorohydrated salicylic acid :

hydrated acid described by Dr. Williamson* as obtained from pentachloride of phosphorus and hydrated sulphuric acid.

The composition of chlorohydrated sulphuric acid was determined by decomposing a portion of it with water, and estimating the sulphuric and hydrochloric acids formed. This was done by neutralising the aqueous solution with baryta-water, and, after filtration from the sulphate of baryta, precipitating the hydrochloric acid as chloride of silver. Two experiments of this kind gave ·7487 grm. sulphate of baryta to ·4353 grm. chloride of silver, and ·6887 grm. Ba^2SO^4 to ·4189 Ag Cl. These results correspond with the percentages :

	I.	II.	Cal. (SO^3HCl .)
SO^3 . . .	69·87 .	68·93 .	68·67
HCl . . .	30·13 .	31·08 .	31·33

The process by which I obtained chlorohydrated sulphuric acid is similar to that by which Rose† obtained compounds of anhydrous sulphuric acid with the chlorides of ammonium, potassium, and sodium. Chlorohydrated sulphuric acid is, in fact, the acid of which Rose's compounds are the ammonium, potassium, and sodium salts; and is probably identical with the compound which Rose obtained‡ by the action of anhydrous sulphuric acid (or better, of Nordhausen acid) on chloride of sulphur.

Chlorosulphate of Ethyl $\text{SO}^3\text{C}^2\text{H}^5\text{Cl}$.—This substance was obtained by the direct combination of chloride of ethyl with anhydrous sulphuric acid. Its composition was determined by finding the weight of the product obtained by combining a known weight of SO^3 with chloride of ethyl.

The experiment was conducted in the following manner. A

* In the notice of chlorohydrated sulphuric acid published by Professor Williamson, that substance is described as distilling without alteration at 145°C .; but I am informed by him that he afterwards found that by long boiling it is partially decomposed; so that if a portion of chlorohydrated acid which has been distilled upwards for some time is distilled with a thermometer, chlorosulphuric acid distils first, then unaltered chlorohydrated, and, lastly, hydrated sulphuric acid. If the middle part of the distillate is again submitted to the same treatment, a fresh portion of chlorosulphuric and hydrated sulphuric acids may be obtained. By repeating this process, a given quantity of chlorohydrated sulphuric acid may be resolved almost completely into chlorosulphuric and hydrated sulphuric acids. The decomposition which takes place is :

† Pogg. Ann. XXXVIII. 117.

‡ Pogg. Ann. XLIV. 291, and XLVI. 177.

bottle containing anhydrous sulphuric acid was provided with a perforated stopper, to which was fused a horizontal glass tube about 2 feet in length, and $\frac{3}{8}$ in. in diameter. This tube was drawn out before the blow-pipe at intervals along its whole length so as to form a series of narrow bulbs from 2 to 3 inches long, connected by pieces of almost capillary tubing. This series of bulbs being connected with the bottle of anhydrous acid by the perforated stopper, the bottle was warmed, and the acid condensed in the further bulb by cooling it in a mixture of ice and salt. The freezing mixture was moved from one bulb to the next, going towards the acid bottle as each one became full of the acid. When all were filled, the two ends of the tube were fused, and the bulbs separated from one another.

One of these bulbs of acid was weighed, and sealed up in a glass tube with chloride of ethyl. The bulb was broken by shaking the tube, and when the acid was dissolved, the excess of chloride of ethyl was distilled off at about 15°C . When the product ceased to lose weight, the weight of the tube in which it was contained was ascertained, and also that of the bulb which had held the sulphuric acid. In this way the following results were obtained :

I.	weight of compound	7.5866
II.		7.4757
III.		7.3776
Anhydrous acid used		4.1424 grammes.

	Found			Calc.
	I.	II.	III.	
SO_3	54.601,	55.41,	56.14	55.36
$\text{C}_2\text{H}_5\text{Cl}$	45.399,	44.59,	43.86	44.63

From these weighings it would appear that, at the first, a little chloride of ethyl remained with the sulphuric acid compound, and, in the last, some of the chloro-ethylated sulphuric acid had distilled over.

The pure compound is a colourless oily liquid, heavier than water, at the bottom of which it will lie for weeks without thoroughly decomposing. Sulphuric and hydrochloric acids may, however, be detected immediately after its immersion, and, on neutralising the liquid with baryta, a soluble salt is formed, which I believe to be sulphovinate of baryta.

The compound has a peculiar, sharp, pungent smell. When dry ammonia is passed into it, part of it is precipitated as a white solid body, and, if water is now added, it emits a nutty odour; the solution forms a soluble barium-salt.

A similar compound is formed with chloride of methyl, but could not be satisfactorily examined, on account of the difficulty of condensing the chloride.

I have since formed a body smelling exactly like the ethyl-compound by adding absolute alcohol to chloro-sulphuric acid. The action is probably as follows :

I have also tried the action of chloride of ethyl, $\text{C}_2\text{H}_5\text{OCl}$, on anhydrous sulphuric acid. It dissolves the acid very rapidly, with evolution of heat, and forms a colourless compound, which afterwards turns yellow and then red, even while sealed up. It is rapidly decomposed on opening the tube; and from this cause I was precluded from determining its composition.

When dropped into water, it sinks to the bottom and gradually dissolves, forming an acid liquid. This liquid forms with baryta a soluble salt, which yields a gelatinous precipitate on the addition of an alkali.