X.—*Researches on the Constitution of Organic Acids.*

By M. CHARLES GERHARDT.

COMMUNICATED BY DR. WILLIAMSON.

The experiments which I am about to lay before the Society, are intended as the commencement of a series of researches undertaken with a view to find a general expression for the molecular constitution of organic acids; or rather, to explain the properties of double decomposition belonging to this class of compounds. I endeavoured to connect organic acids, numerous and various as they are, by a general formula which would be for them what the formula of ammonia is for the organic alkalies; in a word, I sought among the compounds of mineral chemistry for a body which is reproduced by simple substitutions of one or other of its elements, as ammonia is reproduced from the organic alkalies by substitution of the groups methyl, ethyl, phenyl, &c., by one, two or three atoms of hydrogen. This term of comparison, this body, typical of acids, I believe I have found. For the understanding of my experiments, it is necessary to name this body at once. It is *water*, in the molecule of which I assume one atom of oxygen and *two* atoms of hydrogen,

two atoms which may be replaced by simple metals, or by complex groups like methyl, ethyl, &c.

The results obtained a short time ago on this subject by Dr. Williamson in England, and by M. Chancel in France, are well known. These chemists have indeed proved that alcohol, common ether, and their homologues, represent molecules of water in which the two atoms of hydrogen are partly or wholly replaced by complex groups; so that common alcohol represents water in which half the hydrogen is replaced by the group ethyl ($\text{C}_2 \text{H}_5 = \text{Et}$)

whilst common ether represents the same molecule of water in which the two atoms of hydrogen are so replaced:

According to this theory, now almost universally adopted, the

compound formed by replacing one atom of hydrogen in alcohol by potassium, is to be considered as water in which the two atoms of hydrogen are replaced, one by ethyl, the other by potassium :

It may be called potassic ethylate, that is, the potassium-salt of an acid which is nothing else than common alcohol, a weak acid evidently, for water decomposes its salt into alcohol and caustic potash. In like manner, common ether is the ethyl-salt of this ethylic acid. The starting point for my experiments was supplied by this analogy, together with the fact that ethylic acid gives rise to a chloride (hydrochloric ether, or chloride of ethyl) when acted upon by pentachloride of phosphorus; and that, according to M. Cahours' experiments, various organic acids, such as benzoic, nitrobenzoic, cuminic, anisic, and cinnamic, experience an exactly similar change by the influence of the same reagent.

As potassic ethylate, in reacting on ethylic chloride, forms potassic chloride and ethylic ethylate, that is common ether (the experiment is well known), I sought with the chloride of one of the above-mentioned acids, and the potassium- or sodium-salt of the same acid to obtain a body corresponding to common ether; in other words, I sought to obtain the anhydrous acid, as ether itself is nothing but alcohol minus water.

With sodic benzoate and benzoic chloride, the experiment succeeds perfectly well. The soda-salt should be dried and mixed with an equivalent weight of the chloride; the mixture is then heated to 130° C. in a sand-bath, at which temperature a limpid solution is formed, which decomposes with deposition of chloride of sodium when heated a few degrees higher. The action is then complete, not a trace of gas is evolved, and the fearful smell of the benzoic chloride entirely disappears. The product suspended in cold water, and washed with carbonate of soda, leaves a white substance without odour, and perfectly colourless, which analysis shows to be anhydrous benzoic acid :

that is to say, benzoic benzoate; for it is to benzoic acid what ether is to alcohol, and if benzoic acid is represented similarly to alcohol, as water in which one atom of hydrogen is replaced by the group benzoyl $\text{C}_7 \text{H}_5 \text{O} = \text{Bz}$:

then my new substance is water, in which the two atoms are similarly replaced :

The following are the properties of this anhydrous benzoic acid. It is obtained in the form of beautiful oblique prisms, which melt at $33^{\circ}\text{C}.$; they are volatile without decomposition, insoluble in water, soluble in alcohol and ether; these solutions are perfectly neutral. When dissolved in hot alcohol, the acid is deposited, on cooling, in the form of an oil, which remains a long time without solidifying; the same thing occurs when the substance is distilled; in which case it sometimes remains liquid for several hours. Cold water has no action upon it; but boiling water transforms it, little by little, into common benzoic acid. The same transformation is effected in a few moments by boiling ammonia. Alcohol itself transforms anhydrous benzoic acid in the course of time into benzoic ether; the group benzoyl is then replaced by the group ethyl.

Having succeeded so well with the chloride of benzoyl and benzoate of soda, I made similar experiments with other chlorides and other salts. I did not of course limit myself to cases of the action of chlorides upon salts of the same acid; but took the chloride of benzoyl, and successively, salicylate, cuminate, cinnamate and acetate of potash. Benzoic salicylate, cuminate and cinnamate were thus formed. These products are for the most part very fusible solid bodies, or oils heavier than water, without smell, and are rapidly decomposed by the alkalies in a similar manner to benzoic acid with alkalies. Several of them are not volatile without decomposition; thus the benzoic salicylate, when distilled in a moist state, decomposes into salicylic acid and a neutral body, fusible at $72^{\circ}\text{C}.$, which is the true benzoyl,* isomeric with the benzoyl of M. Laurent :

* There can be no doubt that this substance is identical with the compound discovered by Ettling among the products of distillation of benzoate of copper, which was subsequently analysed by Dr. Stenhouse, who gives the same formula, namely,

Stenhouse states that the fusing-point of this substance is 70° , and that it yields benzoate of potassa when heated with solid hydrate of potassa, hydrogen being evolved. The compound

obtained by Ettling among the products of distillation of salicylate of copper, and described by him by the name of *parasalicyl*, has the same composition as M. Gerhardt's benzoic benzoyl, but differs from it in its properties, fusing as it does at 127° , and being, as it appears, only slightly acted upon by potassa. Probably this substance stands to benzoic benzoyl in the same relation as salicylic acid to benzoic acid.—A. W. H.

that is to say, it is to hydrogen, H_2 , what hydrated benzoic acid and anhydrous benzoic acid are to water. Hydrate of potash in a state of fusion converts it into benzoate, with evolution of hydrogen.

I will limit myself for the moment to this summary announcement of my experiments, and propose following them out with all the care which the subject requires.

If a general conclusion may now be drawn from these results, I would say that they destroy the kind of privilege hitherto enjoyed by a small number of bodies known by the generic name of alcohols, of being susceptible of joining other organic bodies. Alcohols and hydrated acids are evidently bodies of the same kind. Philosophically, alcohols, acids, ethers, salts, and anhydrous acids, may be reduced to the same generic formula—to the formula of water, in which 1 or 2 atoms of hydrogen are replaced, either by simple metals or by hydrocarburetted groups (methyl, ethyl, phenyl, &c.), or else by oxygenated groups (benzoyl, cuminyl, acetyl, &c.)

I have now succeeded in preparing anhydrous acetic acid in a state of perfect purity, and giving by analysis numbers exactly agreeing with those calculated from its formula. The following is the method of preparing it: Acetate of potash is fused, so as to expel all water of crystallization, and is then mixed in a small retort with about half its weight of benzoic chloride. On the application of a gentle heat, the reaction speedily occurs—benzoic acetate being no doubt formed at first. But the reaction does not stop there. A limpid body distils over, with a very powerful smell, reminding of acetic acid and flowers of “acebessine.” On rectification, this liquid boils constantly at 137°C. ; it falls to the bottom in water, and does not mix with it at once, but only after continued agitation. Hot water dissolves it at once, with production of acetic acid. The following figures show the result of combustion:

	Analysis.	Calculation.
Carbon . .	46·87	47·05
Hydrogen . .	5·95	5·88

It is therefore $\text{C}_4 \text{H}_6 \text{O}_3$ or, rather $\begin{smallmatrix} \text{C}_2 & \text{H}_3 & \text{O} \\ \text{C}_2 & \text{H}_3 & \text{O} \end{smallmatrix} \cdot \text{O}^*$

This anhydrous acetic acid evolves great heat on mixture with dry

* A similar view regarding the constitution of acetic acid has been proposed by Professor Williamson.—Ch. Soc. Qu. J.—Eds.

aniline; the mixture solidifies entirely on cooling. If an excess of aniline is avoided, only one body is produced, crystallizing in beautiful nacreous plates. This body is shown by analysis to be acetaniline.

It is remarkable that no salt of aniline is formed at the same time. We must therefore consider the action as consisting of a double decomposition between the aniline and the anhydrous acid; thus

forms

We must, I think, consider amides and anilides as ammonia in which more or less hydrogen is replaced. I am now engaged in the investigation of this point.

Amidogen-acids would correspond to hydrated oxide of ammonium.