XXXVII.—*Note on some Metamorphoses of Oxalic Acid.*

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WHEN oxalate of sodium is submitted to the action of sodium-amalgam in presence of water, some interesting effects ensue. If the action be not accelerated by elevation of temperature, and the amount of salt employed be large, a partial reduction only of the oxalic acid takes place, in accordance with the equation—

A more ready method of attaining the same result is found in the reaction of zinc, oxalate of zinc, and sulphuric acid. A large quantity of oxalate of zinc is placed, together with a few pieces of pure zinc, in a beaker, the mixture covered with water, and dilute sulphuric acid added very slowly, drop by drop. Milk of lime, in very slight excess, having been added, together with much water, and the mixture warmed, the whole was filtered, saturated with carbonic acid, again warmed, and filtered. The filtrate deposited, on cooling, some quantity of fine needle-shaped crystals of glyoxylate of calcium. This salt required about 160 parts of cold water for solution. Calcium and water determinations suggested for this salt the formula

while a series of careful qualitative experiments proved the identity of the acid of which it was the calcium-compound with Debus' glyoxylic acid. A larger yield of this product is obtained if, in the process just given, the use of lime be altogether omitted, the glyoxylic acid being extracted directly by means of ether from the concentrated and acidified solution of the mixed zinc-salts first formed. The syrupy ethereal solution is treated with carbonate of calcium, and the various calcium-salts thus made are separated by the method of Debus.

When lime-water was added to the solution of the glyoxylate, a white powder fell, agreeing in its amount of calcium with the formula

and suffering, when boiled for some time with water, the following change—

This transformation of oxalic acid into glycollic acid has however been previously accomplished. Under the name of *oxonic* acid, F. Schulze has described one of the products obtained by acting upon oxalic acid with zinc in presence of sulphuric acid. Schulze, indeed, in all probability, thus obtained glyoxylic acid; but his method of eliminating the new product of the reaction, by ebullition of the zinc-salts with excess of milk of lime, necessarily destroyed the glyoxylate first formed, producing oxalate and glycollate, as stated above. But if we adopt Schulze's plan, and instead of moderating in every way the reducing action in the experiment under review, we exalt its energy in every way, then glycollic acid is the chief product. The method of procedure in this case may be thus modified:—Into a retort containing a large quantity of zinc and dilute sulphuric acid, and heated by a lamp, small quantities of oxalic acid are introduced from time to time. When the desired quantity of acid has been added, a brisk evolution of hydrogen is maintained for some hours, and the liquid boiled with excess of zinc till the acids present are saturated. Excess of slaked lime having been added to the mixed salts, the whole is to be saturated with carbonic acid, boiled, and filtered. This filtrate, on concentration, deposits abundance of glycollate of calcium, in concentric tufts of fine crystals. Analysis and qualitative experiments confirmed the identity of the formula of this salt—

But in the mother liquor from which the glycollate had been deposited, another calcium-salt was contained. This salt was excessively soluble in water, thus differing from the oxalate, the glyoxylate, and the glycollate of calcium. When to its warm syrupy solution an exactly equivalent quantity of sulphuric acid was added, and the sulphate of calcium separated, star-shaped clusters of crystals filled the filtrate. Further examination proved these crystals to be an acid. As far as the small quantity of this substance at my disposal permitted, I have determined some of its properties and its probable composition.

The acid is soluble in water, and readily crystallizable. From

its boiling aqueous solution, it evaporates slowly, with a peculiar faint odour. It melts above 100°C . Its lime salt (the only one yet made) is very soluble in cold water, and confusedly crystalline. A combustion of this acid dried over sulphuric acid indicated the formula

while a calcium determination in the salt of that metal gave numbers nearly agreeing with the formula

If the preliminary examination of these substances has conducted me to a correct conclusion, and I am right in supposing the last-mentioned acid to have the formula assigned to it, we have a new isomer of acetic acid, differing remarkably from that body in several particulars. The series of reduction-products of oxalic acid will stand thus :

Oxalic acid	..	=	$\text{C}_2\text{H}_2\text{O}_4$, which - O gives
Glyoxylic acid	..	=	$\text{C}_2\text{H}_2\text{O}_3$, which + H_2 gives
Glycollic acid	..	=	$\text{C}_2\text{H}_4\text{O}_3$, which - O gives
New acid	..		$\text{C}_2\text{H}_4\text{O}_2$.

By addition of H_2 to the last term, glycol, $\text{C}_2\text{H}_6\text{O}_2$, might perhaps be formed.

The existence of a body $\text{C}_2\text{H}_4\text{O}_2$ has, I find, been predicted by Prof. Kekulé. He gives the following table (*Lehrbuch der Organischen Chemie*, Bd. ii, s. 18)—

Monatomic series :—

$\text{C}_2\text{H}_6\text{O}$ Alcohol.	$\text{C}_2\text{H}_4\text{O}_2$ Acetic acid.	$\text{C}_2\text{H}_4\text{O}$ Aldehyde.

Biatomic series :—

$\text{C}_2\text{H}_6\text{O}_2$ Glycol.	$\text{C}_2\text{H}_4\text{O}_3$ Glycollic acid.	$\text{C}_2\text{H}_2\text{O}_4$ Oxalic acid.
$\text{C}_2\text{H}_4\text{O}_2$ (Unknown.)	$\text{C}_2\text{H}_2\text{O}_3$ Glyoxylic acid.	$\text{C}_2\text{H}_2\text{O}_2$ Glyoxal.

It is thus clearly shown how a monatomic alcohol, losing H_2 , yields one aldehyde, and this, gaining O, yields one acid; while, on the other hand, a triatomic alcohol, by losing H_2 or 2H_2 yields two aldehydes, and each of these, by gaining O, yields another acid.

The new acid may thus be the missing first aldehyde of glycol, of which glyoxylic acid may be regarded as the second.

It will not be unreasonable to expect corresponding results from the action of nascent hydrogen on the homologues and analogues of oxalic acid, and the acid and neutral ethers* of these acids.

I have commenced a few experiments in this direction also.

Succinic acid, after the prolonged and energetic action of nascent hydrogen, as above described in the case of oxalic acid, suffers a similar change. I have not endeavoured to moderate the action so as to form the intermediate or butyloxylic acid, but have pushed it to the extreme, so that butylactic acid might be obtained.

The operation was performed in a retort; towards its conclusion a powerful odour, resembling that of butyric acid, was noticed in the aqueous distillate. The mixture of zinc-salts in the retort was evaporated, sulphuric acid added in excess, and the liquid shaken up with ether. From this ethereal solution (besides some unchanged succinic acid) a deliquescent acid was obtained, the properties and salts of which agreed completely with those of the butylactic acid of Wurtz. I have likewise submitted suberic and phthalic acids to the above-described treatment, and the reactions promise interesting results. But the products of these reactions, obtained only within the last few hours, await further purification and analysis; and it would be altogether premature to express any opinion as to their composition.