

XX. *On some Compounds and Derivatives of Glyoxylic Acid.*By HENRY DEBUS, *Ph.D., F.R.S.*

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ORGANIC substances of simple composition, like marsh-gas, ethylene, alcohol, and acetic acid, are deserving of most careful study, not merely on account of their being representative members of numerous and important classes of bodies, but also because they form connecting links between the compounds of inorganic chemistry and the more complicated forms of organic nature.

Glyoxylic acid belongs to this class of bodies, because it bears the same relation to oxalic acid that sulphurous acid does to sulphuric acid, and because it stands to glycolic acid as common aldehyde, C_2H_4O , does to alcohol, C_2H_6O . These relations suggested the experiments which will be described in the following pages.

*Combinations of Glyoxylates and Sulphites.**a. Glyoxylic Acid and Bisulphite of Soda.*

If a concentrated solution of bisulphite of soda be mixed with one-fourth of its volume of nearly anhydrous glyoxylic acid, a white crystalline precipitate will separate from the mixture in the course of a day or two. This precipitate is to be collected on a filter, washed with cold water, and recrystallized from its solution in the smallest possible quantity of hot water.

The substance thus prepared presents itself in small colourless crystals, which dissolve easily in water, and evolve sulphurous acid with sulphuric acid. The aqueous solution is not altered by the addition of potash or ammonia, but yields a copious white precipitate with acetate of lead. The solid substance, heated on a piece of platinum foil, burns without any unusual appearance. Analysis furnished the following results:—

I. 0.361 grm., heated with concentrated sulphuric acid, gave 0.254 grm. of sulphate of soda. Another quantity of sulphuric acid, of the same quality as that used in this experiment, was evaporated in a platinum crucible; the weight of the latter was found to be unchanged.

II. 0.4365 grm., dissolved in hydrochloric acid and evaporated, left, after ignition, 0.2515 grm. of chloride of sodium. This residue furnished, after treatment with sulphuric acid, 0.306 grm. of sulphate of soda.

0.573 grm., oxidized with a mixture of chlorate of potash and hydrochloric acid, and the sulphuric acid precipitated with chloride of barium, gave 0.69 grm. of sulphate of baryta.

MDCCCLXIII.

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0.565 grm. of another preparation, burnt with chromate of lead, gave 0.248 grm. of carbonic acid and 0.051 grm. of water.

The substance therefore contains in 100 parts—

	I.	II.
Carbon	—	11.97
Hydrogen	—	1.00
Sodium	22.8	22.67
Oxygen	—	—
Sulphur	—	16.55

The formula $C_2 H Na O_3 + S H Na O_3$ requires—

Carbon	2	24	12
Hydrogen	2	2	1
Sodium	2	46	23
Oxygen	6	96	48
Sulphur	1	32	16
		<u>200</u>	<u>100</u>

The substance is consequently a compound of glyoxylate of soda with bisulphite of soda, and the above numbers confirm the formula $C_2 H_2 O_3$.

b. Glyoxylate of Lime with Bisulphite of Lime.

Glyoxylate of lime rapidly dissolves in a saturated solution of sulphurous acid. If this solution be concentrated on the water-bath and afterwards allowed to stand in the exsiccator, a fine crop of colourless crystals separates. These crystals have to be purified by recrystallization from water, and dried over sulphuric acid *in vacuo*.

This substance, like the soda compound, easily dissolves in water, and its concentrated solution comports itself with reagents as follows:—Sulphuric acid produces a white precipitate of sulphate of lime and liberates sulphurous acid; lime-water, chloride of barium, and ammonia respectively cause the formation of a white precipitate, whilst carbonate of lime has no decomposing influence. The form of the crystals could not be determined.

Analysis gave the following results:—

0.351 grm. furnished 0.145 grm. carbonate of lime.

0.56 grm. of another preparation, oxidized with a mixture of chlorate of potash and hydrochloric acid, and the sulphuric acid precipitated by chloride of barium, gave 0.555 grm. of sulphate of baryta.

The substance therefore contains in 100 parts—

Calcium	16.52
Sulphur	13.62

These numbers correspond to a double salt of bisulphite and glyoxylate of lime.

The formula $2(\text{C}_2 \text{H Ca O}_3 + \text{S H Ca O}_3) + 5\text{H}_2 \text{O}$ requires—

Calcium	16·73
Sulphur	13·38

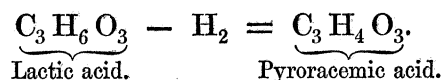
Considering the mode of preparation, the mother-liquor of the salt ought to contain glyoxylic acid. In order to ascertain its presence by experiment, the mother-liquor was evaporated to dryness on the water-bath and the residue exhausted with alcohol. The latter had dissolved an acid which yielded, when treated with carbonate of lime, a salt that contained no sulphur and would not crystallize, but which in other respects comported itself like glyoxylate of lime.

If a compound be the derivative of a substance of an easily changeable nature, its composition, as represented by its rational formula, should always be checked by special experiments. It therefore appeared desirable to regenerate the glyoxylate of lime assumed to form a constituent part of the salt in question. For this purpose an aqueous solution of the latter was mixed with sufficient oxalic acid to precipitate all the lime; the clear filtrate, in order to expel the sulphurous acid, was evaporated on the water-bath till it assumed the consistency of a thin syrup; this residue, which proved to be glyoxylic acid, was dissolved in water and converted, by treatment with chalk, into a crystalline salt that both in form and other properties agreed with glyoxylate of lime.

Glyoxylic acid is a strong acid; it dissolves zinc and expels carbonic acid from carbonates. The experiments described hereafter show that it shares some distinguishing properties with the aldehydes. It may therefore be assumed that, if the acid properties of glyoxylic acid were less marked, it would combine with the bisulphites like hydride of salicyl.

Compound of Glyoxylate and Lactate of Lime.

Like as glyoxylic acid is formed from ethylic alcohol, so will the homologous acid $\text{C}_3 \text{H}_4 \text{O}_3$ probably be formed from the alcohol $\text{C}_3 \text{H}_8 \text{O}$. But since propylic alcohol is only procurable with great difficulty, I attempted the preparation of $\text{C}_3 \text{H}_4 \text{O}_3$ from lactic acid.



Two experiments made with nitric acid of 1·2 sp. gr. and lactic acid did not give the desired result. At a low temperature no action appeared to take place, and at a higher temperature, or with more concentrated nitric acid, only the formation of oxalic acid could be expected.

It is well known that platinum when alloyed with silver is dissolved by nitric acid. It therefore appeared not unlikely that lactic acid, when mixed with alcohol, would be oxidized at a moderate temperature by nitric acid. The experiment was made with a mixture of equal weights of lactic acid and alcohol and a suitable quantity of nitric acid, on the plan which I employed for the preparation of glyoxylic acid. An acid was thus obtained which, when treated with lime, furnished neither glyoxylate nor lactate of

lime. The salt obtained was white and crystalline, required more boiling water for its solution than either C_2HCaO_3 or $C_3H_5CaO_3$, and, when the hot solution cooled, separated therefrom in white crystalline crusts.

Analysis gave the following results:—

0.241 grm. furnished 0.11 grm. of carbonate of lime.

0.425 grm., burnt with chromate of lead, gave 0.423 grm. of carbonic acid and 0.144 grm. of water.

The substance therefore contains in 100 parts—

Carbon	27.14
Hydrogen	3.76
Calcium	18.25
Oxygen	—

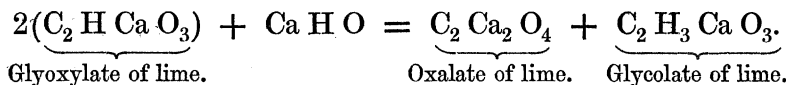
The formula $C_5H_8Ca_2O_7$ requires—

Carbon	5	60	27.27
Hydrogen	8	8	3.63
Calcium	2	40	18.18
Oxygen	7	112	50.92
		220	100.00

According to its formula this substance might be composed as follows:—

Glyoxylate of lime	C_2HCaO_3
Lactate of lime	$C_3H_5CaO_3$
Water	H_2O
	$C_5H_8Ca_2O_7$

The following experiments confirm this composition:—The solution of the compound $C_5H_8Ca_2O_7$ yields with lime-water a white precipitate, which immediately after its formation is found to be soluble in acetic acid; this precipitate, however, after the lapse of some time, or by exposure to a temperature of 212° , becomes insoluble in this acid. The same property distinguishes the soluble glyoxylates.



If the formula $C_2HCaO_3 + C_3H_5CaO_3 + H_2O$ be the correct expression of the composition of the salt in question, then a quantity represented by the above formula ought to be decomposed by boiling lime-water into one atom of lactate, half an atom of glycolate, and half an atom of oxalate of lime; the quantity of the latter may be easily determined.

0.76 grm. of the substance was dissolved in water and boiled with an excess of clear lime-water until the decomposition was complete; in order to prevent carbonate of lime from mixing with the precipitate, a slight excess of acetic acid was added; the precipitated oxalate of lime was collected on a filter and converted in the usual manner into

carbonate of lime; the weight of the latter was found to be 0.168 grm., which corresponds to 28.3 per cent. of oxalate of lime. The formula $C_5 H_8 Ca_2 O_7$ requires 29.0 per cent. of oxalate. In order to confirm the conclusion to be drawn from this experiment, the substance $C_5 H_8 Ca_2 O_7$ was prepared from lactate and glyoxylate of lime. For this purpose equivalent quantities of $C_3 H_5 Ca O_3$ and $C_2 H Ca O_3$ were respectively dissolved in the least possible quantity of boiling water, and the solutions were then mixed. From the cooling liquid a large quantity of crystals separated, which were identical in properties with the body $C_5 H_8 Ca_2 O_7$. Two determinations of the solubility in water of I., the substance prepared as just described, and of II., the body obtained by the oxidation of a mixture of lactic acid and alcohol by means of nitric acid, placed the identity of the two substances beyond a doubt.

I. 5.003 grms. of the solution, saturated at $18^\circ C.$, left after evaporation at $100^\circ C.$ 0.0265 grm. of residue.

II. 3.151 grms. of the solution, treated in the same manner as I., left 0.017 grm. of residue. Therefore at $18^\circ C.$

One part of I. dissolves in 187 parts of water.

One part of II. dissolves in 184 parts of water.

The formula $C_5 H_8 Ca_2 O_7 = (C_2 H Ca O_3 + C_3 H_5 Ca O_3 + H_2 O)$ may therefore be considered the true expression of the composition of the compound. The last member of this formula may be eliminated by heat; it appears, however, that the remainder, $C_2 H Ca O_3 + C_3 H_5 Ca O_3$, suffers some change by this process.

The tendency to form this double salt is perhaps the reason why the oxidating influence of the nitric acid only affects the alcohol and does not extend to the lactic acid.

Ammoniacal Compounds of some Glyoxylates.

a. Glyoxylate of Lime and Ammonia.

Pure and well-crystallized glyoxylate of ammonia was dissolved in the least possible quantity of hot water, and the solution thus obtained was divided into two equal parts. One part, on being mixed with chloride of calcium, assumed the appearance of a transparent jelly, which resembled silicic acid when precipitated by hydrochloric acid from a concentrated solution of silicate of potash; the vessel, in fact, could be inverted without any portion of its contents being lost; after the lapse of a few hours white opaque points were observed in the jelly, which gradually increased in number and magnitude, until at last the whole of the jelly-like substance was converted into a fine crop of prismatic crystals; these were found to agree in form and other properties with glyoxylate of lime.

To the other part of the solution of glyoxylate of ammonia a mixture of chloride of calcium and acetate of ammonia was added. In this instance no immediate change took place, but in the course of twenty-four hours a white precipitate, a compound of glyoxylate of lime and ammonia, made its appearance; the precipitate was collected on a filter, washed with cold water, and dried over sulphuric acid.

A similar result was obtained by precipitating a solution of glyoxylate of ammonia with acetate of lime, just sufficient ammonia being at the same time added to keep the liquid neutral; the compound thus prepared is colourless or slightly yellow, dissolves sparingly in water, but is easily soluble in dilute acetic acid; it becomes highly electrical when rubbed in a mortar, and burns like tinder on a piece of heated platinum foil, leaving carbonate of lime. The aqueous solution possesses an alkaline reaction, and shows no change on the addition of lime-water.

The following experimental results determined its composition:—

0.139 grm. furnished 0.061 grm. of carbonate of lime.

0.236 grm., burnt with soda-lime, gave 0.293 grm. of ammonio-chloride of platinum.

0.26 grm., burnt with chromate of lead, gave 0.206 grm. of carbonic acid and 0.088 grm. of water.

The substance therefore contains in 100 parts—

Carbon	21.6
Hydrogen	3.76
Calcium	17.7
Nitrogen	7.8
Oxygen	—

According to the formula $3(\text{C}_2\text{H Ca O}_3)$, 2N H_3 , H_2O , we obtain

Carbon	6	72	21.75
Hydrogen	11	11	3.32
Calcium	3	60	18.12
Nitrogen	2	28	8.45
Oxygen	10	160	—
		331	

The calculated numbers do not agree very well with those found by experiment; the differences, however, are not greater than those which might be expected from the circumstance of the analysed substance having been obtained in the form of a precipitate.

If, therefore, glyoxylate of ammonia be decomposed by acetate of lime, acetate of ammonia and glyoxylate of lime are formed; the latter, however, withdraws a part of the ammonia from the acetate of ammonia, and thus produces the compound which has just been mentioned. Some grammes of this substance were mixed with oxalic acid solution sufficient to convert two-thirds of its lime into oxalate. If the composition ascribed to the compound be correct, the filtrate from the oxalate of lime ought to contain glyoxylates of lime and ammonia; the filtered liquid was evaporated over sulphuric acid *in vacuo*, when a crust, consisting of small prisms arranged round a common centre, remained. This substance was repeatedly recrystallized from water; and in each process the crystals which form first, were separated from those which made

their appearance after a half or three-quarters of the solution had been evaporated. In this manner two kinds of crystals were obtained: those which separated first, were found to be identical with glyoxylate of lime; and those which formed last, possessed the properties of glyoxylate of ammonia. This experiment, therefore, confirms the formula $3(\text{C}_2\text{H Ca O}_3)$, $2\text{N H}_3 + \text{H}_2\text{O}$, which was deduced from analytical results.

A compound of a similar nature may be directly obtained from glyoxylate of lime and ammonia. For this purpose a hot and concentrated solution of $\text{C}_2\text{H Ca O}_3 + \text{H}_2\text{O}$ is to be mixed with a few drops of ammonia, and filtered; ammonia is then to be added to the filtrate so long as a precipitate forms; the latter is to be collected and washed with cold water. The compound, thus prepared, possesses the same properties as the one obtained from glyoxylate of ammonia and acetate of lime.

The analytical results were as follow:—

0.161 grm. gave 0.079 grm. of carbonate of lime.

0.227 grm., burnt with soda-lime, gave 0.316 grm. of ammonio-chloride of platinum.

0.488 grm., burnt with chromate of lead, furnished 0.402 grm. of carbonic acid and 0.126 grm. of water.

Therefore 100 parts of the substance contain—

Carbon	22.47
Hydrogen	2.86
Calcium	19.62
Nitrogen	8.74
Oxygen	—

and the formula $3(\text{C}_2\text{H Ca O}_3)$, 2N H_3 requires—

Carbon	6	72	23.00
Hydrogen	9	9	2.87
Calcium	3	60	19.16
Nitrogen	2	28	8.94
Oxygen	9	144	—

This compound, therefore, differs from the preceding one by containing one atom of water less.

If a quantity of this substance be treated with oxalic acid solution, sufficient to convert its lime into oxalate, the supernatant liquid comports itself like a solution of glyoxylic acid and glyoxylate of ammonia.

b. Glyoxylate of Silver and Ammonia.

A concentrated solution of glyoxylate of ammonia yields with nitrate of silver a crystalline precipitate of glyoxylate of silver. But if the solution of glyoxylate of ammonia contain other ammoniacal compounds, such as nitrate of ammonia, the precipitate is found to contain ammonia besides the other components already mentioned.

A specimen prepared under the last-mentioned circumstances and afterwards dried *in vacuo*, was found to contain in 100 parts—

Nitrogen	5·8
Silver	59·01

These numbers were calculated from the following determinations:—

0·442 grm., burnt with soda-lime, gave 0·408 grm. of ammonio-chloride of platinum.

0·238 grm., after treatment with hydrochloric acid, furnished 0·172 grm. of chloride of silver and 0·011 grm. of metallic silver.

The formula $4(\text{C}_2\text{H Ag O}_3)$, $3\text{N H}_3 - 3\text{H}_2\text{O}$ requires—

Nitrogen	5·82
Silver	59·9

The absence of nitric acid in this salt was proved by a special experiment with proto-sulphate of iron and sulphuric acid. The silver could not be determined by simple ignition, because heat decomposes the compound with explosive violence.

c. Glyoxylate of Lead and Ammonia.

Acetate of lead produced, in a liquid containing glyoxylate and acetate of ammonia, a heavy white precipitate.

0·409 grm. of this precipitate, dried over sulphuric acid, furnished 0·243 grm. of metallic lead.

0·589 grm., burnt with soda-lime, gave 0·209 grm. of ammonio-chloride of platinum.

The compound contains, therefore, in 100 parts—

Nitrogen	2·22
Lead	59·4

The formula $7(\text{C}_2\text{H Pb O}_3)$, $2\text{N H}_3 - 2\text{H}_2\text{O}$ requires—

Nitrogen	2·27
Lead	58·7

This substance, on being pounded in a mortar, became highly electrical.

A solution of crystallized glyoxylate of ammonia in ammonia, when raised to temperatures below 212° , turns brown, and forms derivatives of an acid character; neither these substances, however, nor their salts could be obtained in crystals.

The compounds of ammonia with the glyoxylates are easily decomposed by heat, and by nitric acid and other reagents; the products of decomposition could not be examined, because their physical properties precluded their preparation in a pure state. An experiment, which showed the attraction between glyoxylates and ammonia, may be mentioned here. If a quantity of $3(\text{C}_2\text{H Ca O}_3)$, 2N H_3 be boiled with caustic potash, a part of the ammonia is very slowly expelled; if the liquid be evaporated to dryness, and the residue be raised to a higher temperature, it assumes a beautiful purple colour,

and at the same time emits streams of ammonia. This red substance is very changeable, and is formed, even under the most favourable circumstances, in but very small quantities.

Action of Hydriodic Acid on Glyoxylates.

Hydriodic acid and glyoxylate of lime were heated together for several days in sealed glass tubes, the temperature varying from 100° C. to 110° C. In order to decompose a part or the whole of the hydriodic acid, the contents of the tubes were exposed for some time to the influence of the atmosphere, and finally saturated with carbonate of lime. The whole was then boiled and filtered, and the filtrate mixed with alcohol. A precipitate was formed which proved to be a quantity of glyoxylate of lime, little inferior to that which was originally taken for the experiment.

Action of Sulphuretted Hydrogen on Glyoxylates.

Through a concentrated solution of glyoxylic acid a current of sulphuretted hydrogen was passed until the liquid appeared to be completely saturated; no perceptible action took place, and even after twenty-four hours' contact the liquid seemed to be unchanged. The solution was now evaporated, at first over pieces of hydrate of potash, and afterwards over sulphuric acid *in vacuo*. As soon as most of the water was gone, small needles, radiating from a common centre, began to form, and at last the whole of the contents of the evaporating-basin appeared one mass of crystals, which were found to be soaked with a syrupy mother-liquor, and to be so easily soluble in the ordinary means of solution, that all attempts at further purification were abandoned. A solution of glyoxylate of lime comports itself like glyoxylic acid when acted upon by sulphuretted hydrogen; it apparently remains unchanged; but on allowing a part of it to evaporate at ordinary temperatures *in vacuo*, a brittle, transparent and amorphous compound is obtained.

In order to avoid the inconvenience of evaporation *in vacuo*, the rest of the glyoxylate-of-lime solution, after having been treated with sulphuretted hydrogen, was mixed with a little more than its bulk of alcohol. Nearly the whole of the new compound separated as a precipitate, which was collected on a filter and washed with spirit of wine.

Thus prepared, the substance easily dissolved in water, forming a solution of a pale pink colour. The liquid, after the evaporation of the water *in vacuo*, left a transparent amorphous and nearly colourless substance. This compound is the lime-salt of an acid which bears a similar relation to glyoxylic acid that thiactic acid does to acetic acid. In the state of powder it exhibits a striking property when brought in contact with water; it becomes as viscous as glass when rendered red-hot by means of a Bunsen's burner, and may be drawn out in long threads. By degrees the water dissolves the viscous mass, and forms a solution which shows the following properties with reagents:—A white precipitate is formed by the addition of acetate of zinc or corrosive sublimate; acetate of lead or nitrate of silver throws down a yellow precipitate; and sulphate

of copper causes the immediate separation of a black substance, which is probably sulphuret of copper. Both the silver and the lead precipitates turn black, the silver after the lapse of some time at ordinary temperatures, and the lead at once on exposure to a temperature of 100° C. Hydrochloric acid produces no perceptible change in the aqueous solution of the compound; ammonia causes the formation of a white precipitate; and lime-water the same result as it does with glyoxylate of lime. The brown colour of iodine immediately disappears, as it does in solutions of other sulphur compounds, such as xanthate of potash. Sesquichloride of iron acts like iodine. The solution of this sulphur compound, when boiled, decomposes; it turns yellow; a crystalline powder of oxalate of lime separates; and a lime-salt, which could not be obtained in crystals, remains in solution. The compound burns on a hot piece of platinum foil like tinder, and evolves, when heated in a glass tube which is sealed at one end, an odour like that of mercaptan.

In order to obtain some guarantee for the homogeneous nature of the substance, a powdered quantity of it was well mixed and digested for a long time with such a quantity of very dilute spirit of wine as was required to dissolve about half of it. The undissolved portion will be called S, the dissolved part S'. S' was obtained by evaporating the solution wherein it was contained; both S and S' were prepared for analysis by being dried over sulphuric acid *in vacuo*.

The analysis of S gave the following results:—

0.731 gm., burnt with chromate of lead, gave 0.508 gm. of carbonic acid and 0.186 gm. of water.

0.423 gm., boiled with nitric acid and precipitated with chloride of barium, gave 0.39 gm. of sulphate of baryta.

The analysis of S' gave the following results:—

0.274 gm., burnt with chromate of lead, yielded 0.192 gm. of carbonic acid and 0.074 gm. of water.

The results of the analysis of S+S' were as follows:—

0.557 gm. from another preparation furnished 0.381 gm. of carbonic acid.

0.4 gm., oxidized with chlorate of potash and hydrochloric acid, gave 0.357 gm. of sulphate of baryta.

0.49 gm., precipitated with oxalate of ammonia, gave 0.192 gm. of carbonate of lime.

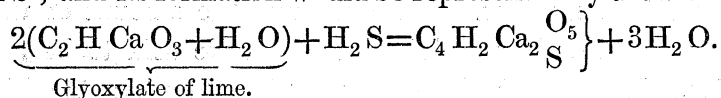
According to these determinations, 100 parts contain—

	S.	S'.	S+S'.
Carbon . . .	18.95	19.11	18.65
Hydrogen . .	2.82	3.00	—
Calcium . . .	—	—	15.67
Oxygen . . .	—	—	—
Sulphur . . .	12.67	—	12.26

The formula $C_4H_2Ca_2\left\{\begin{smallmatrix} O_5 \\ S \end{smallmatrix}\right\} + 3H_2O$ requires—

Carbon	4	48	18.75
Hydrogen	8	8	3.12
Calcium	2	40	15.62
Oxygen	8	128	—
Sulphur	1	32	12.5

The homogeneity of the substance may be considered as proved by the identity in composition of S and S'; and its formation would be represented by the following equation:—



The crystalline derivative from sulphuretted hydrogen and glyoxylic acid just mentioned is probably represented by the formula $C_4H_4\left\{\begin{smallmatrix} O_5 \\ S \end{smallmatrix}\right\}$.

Neither the salts prepared from this acid, nor the compounds obtained by exchanging the calcium in $C_4H_2Ca_2\left\{\begin{smallmatrix} O_5 \\ S \end{smallmatrix}\right\} + 3H_2O$ for other metals could be obtained in crystals; and therefore I did not pursue the investigation of these bodies.

Action of Zinc on Glyoxylic Acid.

A concentrated solution of this acid dissolves pure zinc without evolution of hydrogen gas, and the liquid at the same time becomes perceptibly warm; the reaction very soon ceases. Even if metal and acid be left in contact for a day or two at ordinary temperatures, the liquid will still contain a considerable portion of unchanged glyoxylic acid. The process may be accelerated, and may in fact be completed in the course of eight or ten hours, by exposing the reacting substances to a temperature of about 80° C. The previously colourless liquid will then have assumed a yellow colour, and does no longer contain glyoxylic acid or glyoxylate of zinc. The pieces of undissolved zinc are found to be covered with a small quantity of a white crystalline powder. Glyoxylic acid thus saturated with zinc was mixed with pure carbonate of lime and treated with sulphuretted hydrogen: the zinc precipitated as sulphuret of zinc, and the liberated acid dissolved carbonate of lime and formed a lime-salt. The filtrate from the Zn_2S and the excess of Ca_2O , CO_2 furnished, on evaporation, only one kind of crystals, which possessed the form of glycolate of lime. After purification by recrystallization from boiling water, they were dried over sulphuric acid and analysed, with the following results:—

I. 0.371 grm. lost at 125° C. 0.078 grm. of water, and gave 0.154 grm. of carbonate of lime.

II. 0.194 grm. of another preparation lost at 108° C. 0.041 grm. of water, and yielded by the usual treatment 0.08 grm. of carbonate of lime.

The compound therefore contained in 100 parts—

	I.	II.
Calcium	16·5	16·49
Water	21·02	21·13

The formula of glycolate of lime, $2(C_2H_3CaO_3) + 3H_2O$, requires—

Calcium	16·3
Water	22·1

The percentage of water as found by experiment differs to the amount of nearly 1 per cent. from the theoretical number. I always found the amount of water contained in glycolate of lime which has been dried over sulphuric acid to be a little below the calculated quantity. If, however, from the quantity of carbonate of lime found in the above analysis the amount of calcium contained in 100 parts of the anhydrous substance be calculated, the number thus obtained agrees with the theoretical percentage of calcium in anhydrous glycolate of lime.

	I.	II.	Theory.
Calcium	21·03	20·9	21·05

The substance is therefore glycolate of lime. In order to prove the identity of the glycolic acid obtained by the oxidation of alcohol by means of nitric acid with the acid formed by reducing glyoxylic acid with zinc, the solubility in water of their respective lime-salts was determined.

A = lime-salt of the glycolic acid prepared from alcohol.

B = lime-salt prepared from the acid obtained by the action of zinc on glyoxylic acid.

A. 3·073 gram. of solution, saturated at 12° C., evaporated at 100° C., left 0·027 gram. of residue.

B. 1·767 gram. of solution, saturated at the same temperature, left 0·016 gram. of residue.

3·206 gram. of solution, prepared at 7° C., gave 0·028 gram. of residue.

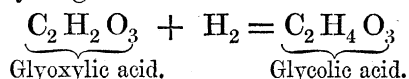
100 parts of water therefore dissolve—

	12° C.	7° C.
A.	0·886	—
B.	0·913	0·881

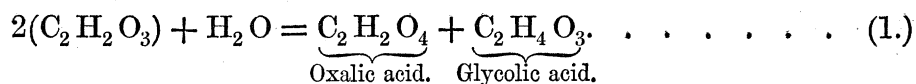
The lime-salts A and B, and consequently the acids contained therein, may therefore be considered to be identical—a conclusion which is supported by the other properties of A and B.

Glycolic acid can be obtained from glyoxylic acid by at least two different ways.

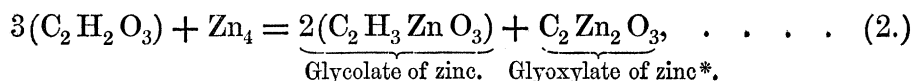
1. By direct addition of hydrogen:—



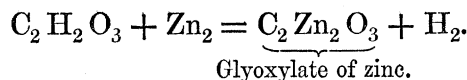
2. By the decomposition represented in the following equation:—



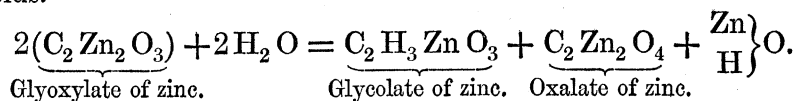
Under the influence of zinc the following reactions could take place:—



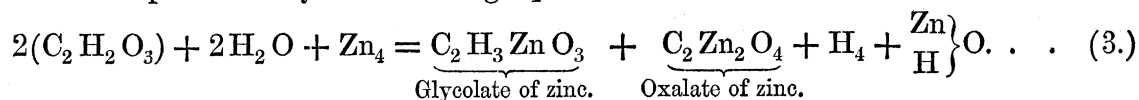
or



Glyoxylates which contain more than one atom of metal decompose easily at the temperatures at which the experiments were made, and form compounds of glycolic and oxalic acids.



By combining this and the preceding equation, the action of zinc on glyoxylic acid may at once be represented by the following equation:—



If the reaction takes place according to (2.), then by the side of five atoms of glycolate only one atom of oxalate of zinc can be produced; but if according to (3.), for every five atoms of glycolate five atoms of oxalate of zinc ought to be formed, and twenty atoms of hydrogen be liberated.

The relative quantities of oxalic acid and glycolic acid formed by the action of zinc on glyoxylic acid were therefore first determined. An unknown quantity of the acid was treated with zinc until the action was complete, and the filtrate from the undissolved metal was divided into two parts. In one part the oxalic acid was determined by the usual method, and the glycolic acid in the other by converting the glycolate of zinc into glycolate of lime, and by evaporating and drying the latter at 100° C.; this could be done because no other substance was present in the liquid. In this way 0.98 gm. of glycolate of lime†, and 0.005 gm. of carbonate of lime from the oxalate were obtained.

A white crystalline powder has been mentioned which settles on the zinc during its action on glyoxylic acid; this powder would contain oxalate of zinc. From its solution in ammonia a precipitate of oxalate of lime was obtained, which gave after ignition 0.095 gm. of carbonate of lime. The whole of the Ca₂O, CO₂ obtained from the

* Proceedings of the Royal Society, vol. ix. p. 711. LIEBIG, Ann. vol. ex. p. 326.

† This glycolate of lime contained 21.4 per cent. of calcium, whereas theory requires 21.05 per cent.

oxalate weighed therefore 0.1 gm., which corresponds to 0.09 gm. of oxalic acid, $C_2H_2O_4$; the above-mentioned 0.98 gm. of glycolate of lime contain 0.784 gm. of glycolic acid, and therefore for every atom of oxalic acid we obtain 10.3 of glycolic acid.

Another experiment conducted on the same plan gave 0.122 gm. of carbonate of lime and 0.876 gm. of anhydrous glycolate of lime, or

1 atom of oxalic acid : 7.5 atoms of glycolic acid.

A third experiment yielded nearly the same result as the second.

The action of zinc on glyoxylic acid takes place therefore according to equation (2.).

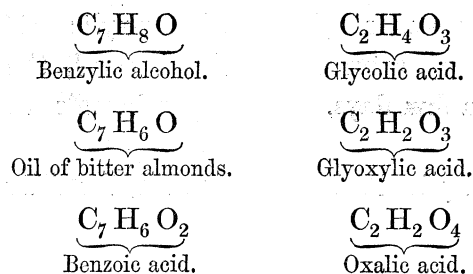
0.906 gm. of glyoxylic acid gave 0.876 gm. of glycolate of lime, corresponding to 0.7 gm. of glycolic acid, and 0.122 gm. of carbonate of lime, corresponding to 0.109 gm. of $C_2H_2O_4$. If we suppose none of the glyoxylate of zinc, formed according to (2.), to be decomposed, then no oxalic acid and only 0.62 gm. of glycolic acid ought to have been obtained; if, however, all the glyoxylate of zinc had been decomposed into glycolate and oxalate of zinc, 0.775 gm. of glycolic acid and 0.183 gm. of oxalic acid ought to have been found. The actual numbers are intermediate between these two extremes, and consequently half of the glyoxylate of zinc formed from 0.906 gm. of glyoxylic acid, according to equation (2.), underwent the decomposition represented in equation (1.). The action of zinc on glyoxylic acid may therefore be explained as follows:—zinc dissolves and forms glyoxylate of zinc, $C_2Zn_2O_3$; the hydrogen instead of being liberated combines with other glyoxylic acid and zinc and produces glycolate of zinc; a quantity of $C_2Zn_2O_3$, dependent on time and temperature, decomposes into glycolate and oxalate of zinc.

The following experiment proves that no hydrogen is liberated in this reaction. 0.906 gm. of glyoxylic acid and a few pieces of zinc were placed in a flask and the vessel nearly filled with water; a perforated cork holding a bent glass tube was then attached to the mouth of the flask, the other end of the tube being placed under a graduated receiver filled with mercury. The flask was then warmed to nearly $100^\circ C.$, and kept at this temperature for ten hours, after which time no more gas was given off. The apparatus was found to be air-tight both before and after the experiment. The quantity of the gas which was collected, when measured at $11^\circ C.$, was 10 cub. centims.; it possessed the properties of atmospheric air. If one atom of hydrogen had been set free for each atom of glyoxylic acid which was taken, the 0.906 gm. of acid ought to have liberated 0.0122 gm. of hydrogen; this quantity measures 135 cub. centims. at $0^\circ C.$ and 0.76 in. pressure.

Some years ago I directed attention to the following considerations*.

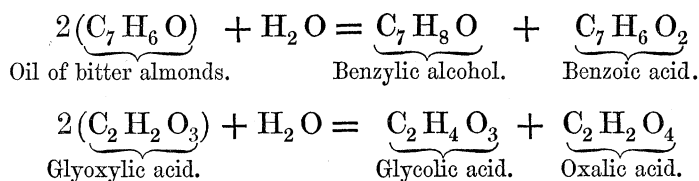
Among the products formed by the action of nitric acid on alcohol, which remain after the more volatile substances have been evaporated on the water-bath, are three acids, glycolic acid, glyoxylic acid, and oxalic acid. These bodies show the same differences in composition as benzylic alcohol, oil of bitter almonds, and benzoic acid.

* Quarterly Journal of the Chemical Society, vol. xii. p. 234.

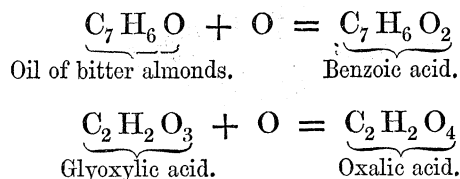


They comport themselves with different reagents like the members of the benzoyl series. Hydrate of potash decomposes glyoxylic acid into glycolic and oxalic acids, and oil of bitter almonds into benzylie alcohol and benzoic acid; dilute nitric acid oxidizes glyoxylic acid to oxalic acid, and oil of bitter almonds to benzoic acid.

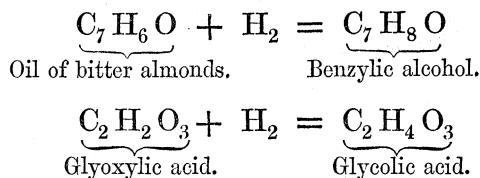
a. Decomposition with potash:—



b. Oxidation with nitric acid:—



According to FRIEDEL, oil of bitter almonds unites with hydrogen and forms benzylie alcohol; and the experiments described in this paper show glyoxylic acid to enter into combination with this element, forming glycolic acid.



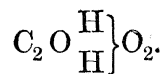
Glycolic acid may therefore be termed the alcohol of oxalic acid, and glyoxylic acid the aldehyde of both; in fact glyoxylic acid possesses other properties which are generally only found in connexion with aldehydes. Amongst these are the great affinity of glyoxylates for sulphites (whereby well-defined and beautifully crystallizing compounds are formed), the exchange of the oxygen of the acid for the sulphur of sulphuretted hydrogen, and, finally, the production of compounds with ammonia.

Glyoxylic acid may likewise be compared with various other bodies; it has, for instance, in many respects a resemblance to sulphurous acid.

KEKULÉ'S interesting experiments with fumaric and maleic acids induced me to

examine the action of bromine on a solution of glyoxylic acid. If the two bodies be left in contact at ordinary temperatures in a closed vessel, the colour of the bromine disappears in the course of a few days. Only hydrobromic and oxalic acids, however, resulted from this reaction.

If a rational formula be required for glyoxylic acid, the following expression may be adopted:—



It indicates the diatomic nature of the acid as well as its intermediate position between glycolic and oxalic acids. Two atoms of hydrogen added to the radical C_2O produce the radical of glycolic acid, and one atom of oxygen the corresponding radical of oxalic acid.