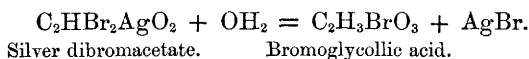
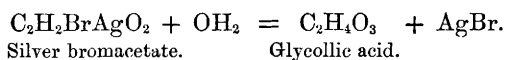


IX.—*On Dibromacetic and Glyoxylic Acids.*

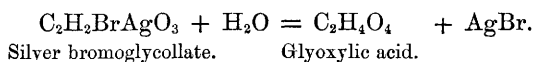
By W. H. PERKIN, F.R.S.

SEVERAL years since (*Journ. Chem. Soc.*, xi, 22), in conjunction with the late Mr. Duppa, I gave an account of bromo- and dibromo-acetic acids and some of their derivatives; amongst these were the products obtained by the decomposition of their silver salts when heated with water, that of the former acid yielding silver bromide and glycollic acid, that of the latter silver bromide and an acid which we believed to be bromo-glycollic acid.

Our reasons for believing this to be bromoglycollic acid were various; one was from the apparent analogy of the reaction by which it is formed from silver dibromacetate, to that by which glycollic acid is produced from silver bromacetate, thus—



A second reason was because its silver salt when boiled with water yielded silver bromide and glyoxylic acid apparently, thus—



From the difficulty of preparing dibromacetic acid in large quantities at that time, we were prevented from investigating this matter very fully; nor did we consider it important to do so, as we had no reason to doubt the correctness of the conclusions we had arrived at.

Since then new processes for the preparation of bromo- and dibromo-acetic acids have been discovered, by which they can be obtained

more easily; I therefore thought it would be interesting to make a more complete examination of this so-called bromoglycollic acid.

The process adopted for the preparation of dibromacetic acid consisted simply in the use of acetic anhydride in the place of glacial acetic acid for the production of the bromacetic acid required; the anhydride being readily acted upon by bromine, the use of sealed tubes is thus avoided. The bromacetic acid so obtained was converted into the dibromo acid by treatment with bromine in sunshine whilst heated to its boiling point as previously described. Considerable quantities were thus prepared, and the acid was usually in the crystalline state. A portion converted into the silver salt gave the following results on analysis:—

·6695 of substance gave
·3833 of AgBr = 32·87 p. c. Ag.

Theory for $C_2HBr_2AgO_2$ requires 33·23 p. c. Ag.

Decomposition of Silver Dibromacetate when heated with Water.

Having obtained a supply of dibromacetic acid, a considerable quantity of its silver salt was prepared, and a portion of it boiled with water until silver bromide ceased to be formed. The decomposition takes place with considerable energy when quantities of about 20 grams of silver salt are used, the ebullition continuing for some time after the removal of the source of heat. The resulting dilute acid liquid was separated from silver bromide by filtration, concentrated over the water-bath, nearly neutralised with sodium carbonate, and converted into the silver salt by precipitation with silver nitrate. It was then washed and dried in a vacuum. A silver determination gave the following numbers:—

·2447 of substance gave
·177 of silver bromide = 41·55 p. c. Ag.

The calculated percentage for silver bromoglycollate, $C_2H_2BrAgO_3$, is 41·22 p. c. Ag.

This result appeared to confirm the correctness of the equation already given; but by experimenting under different conditions very variable results were obtained. For example, when dilute solutions of the acid product obtained by boiling silver dibromacetate with water were used for the preparation of a silver salt, the resulting compound always contained a smaller percentage of silver than when strong and neutralised ones were employed.

To get a clue to this unexpected result fractional precipitation was resorted to, which soon showed that the product was not a definite body, but a mixture, the first crops giving low, and the last ones high

percentages of silver. The following is an example selected from several experiments :—

First crop contained 33·06 p. c. silver.
Third ,, 45·86 ,,

It was soon remarked that the first crops often gave percentages of silver closely corresponding with those required by silver dibromacetate, viz., 33·23 p. c., and on examining them they were found to consist of that substance.

Having established this curious fact, it was necessary to find out the nature of the product which accompanied the dibromacetic acid in this decomposition. After making several experiments it was believed to be *glyoxylic acid*.

To determine this, about 18 grams of dibromacetic acid were made into its silver salt, and decomposed by boiling with water, and the resulting acid solution was neutralised with calcium carbonate and filtered. On cooling, the solution was inclined to gelatinise, but on leaving it in a vessel surrounded by hot sand, so as to cause it to cool slowly, it deposited about 3 grams of crystals, and when further concentrated a further small quantity was deposited. These were undoubtedly *calcium glyoxylate*. Nevertheless a calcium determination was made.

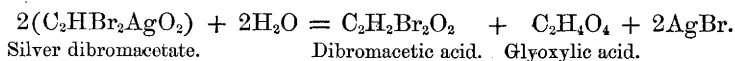
·292 of substance gave

·1795 of $\text{CaSO}_4 = 18\cdot07$ p. c. calcium.

The formula $\text{C}_4\text{H}_6\text{Ca}''\text{O}_8$ requires 18·0 p. c.

The mother-liquors from these crystals contained nothing but calcium dibromacetate.

From these results it is evident that silver dibromacetate when boiled with water yields only dibromacetic and glyoxylic acids, thus—



As this decomposition is remarkable, it was thought desirable to see if the products were really produced in the ratios indicated by the above equation.

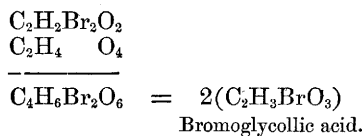
For this purpose recourse was had to the well known decomposition of glyoxylic acid into oxalic and glycollic acids when treated with calcium hydrate, it having been found previously from experiment that dibromacetic acid did not yield oxalic acid under these circumstances. The following quantitative experiment was made :—

4·586 grams of silver dibromacetate were boiled until silver bromide ceased to form, and the solution after filtration mixed with an excess of pure calcium hydrate. It was then heated until it boiled, and afterwards acidified with acetic acid. The calcium oxalate which had

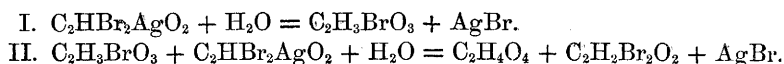
been produced was collected, washed, ignited, &c. In this manner '363 gram of calcium carbonate was obtained, equivalent to 7.1 per cent. of oxalic acid from the silver dibromacetate used.

Now as two molecules of glyoxylic acid are required to produce one of oxalic acid, it follows from the above equation that four molecules of silver dibromacetate would be necessary to produce one of oxalic acid. This, if calculated, is found to be in the proportion of 100 parts of silver salt to 6.9 parts of oxalic acid, which closely corresponds with the above experiment, and therefore proves the correctness of the equation.

These experiments show how the mistake occurred in supposing that bromoglycollic acid resulted on boiling silver dibromacetate with water, because a mixture of dibromacetic acid and glyoxylic acid in the proportions produced in this reaction has the composition of that substance.



It is difficult to understand the manner in which silver dibromacetate yields these products when boiled with water. It may perhaps be that bromoglycollic acid is first formed as the salt is decomposing, and being unstable is immediately acted upon by the undecomposed portions of the silver dibromacetate, thus:—



Decomposition of Silver Dibromacetate when heated with Alcohol.

Perfectly dry silver dibromacetate when heated to 100° C. with absolute alcohol quickly decomposes with formation of silver bromide. On filtering this off and allowing the alcoholic fluid to evaporate gently, a product is obtained which consists of an ethereal liquid and an acid. The latter was removed from the oily product by means of water, and when converted into a silver salt gave the following numbers:—

·0979 of substance gave
 ·0574 of AgBr = 33.68 p. c. silver.

showing it to be dibromacetic acid.

The ethereal product was distilled and was found to boil at about 193—195°. It was analysed, but no definite results were obtained. It contained from 32 to 33 p. c. bromine. It is probably a mixture of dibromacetic and diethylglyoxylic ether, for when treated with

ammonia it yields dibromacetamide, and on evaporating the mother-liquors from this brilliant plates like diethylglyoxylamide are obtained.

Decomposition of Silver Dibromacetate when heated with Dry Ether.

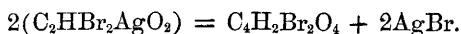
When heated to 100° C. in a sealed tube with ether the perfectly dry salt decomposes with formation of silver bromide, a small quantity of carbonic acid being also produced. On filtering off the ethereal fluid and evaporating, a thick oily product is left behind. It appears to be impossible to obtain this product in a perfectly pure state, as it cannot be distilled without decomposition. It is generally contaminated with a small quantity of a substance having a very irritating odour; this is removed partially by passing dry air through it whilst heated to 100° C. In order to purify it further it was redissolved in ether and kept over dry sodium carbonate for several hours, filtered, the excess of ether distilled off, and further separated by passing dry air through the oily product whilst heated in the water-bath. On analysis it did not give very satisfactory numbers. The following are the best obtained:—

- I. .2950 of substance gave
 .4017 of AgBr.
 II. .3495 of substance gave
 .2293 of CO₂ and
 .0558 of H₂O.

The formula C₄H₂Br₂O₄ requires the following percentages:—

	Calculated.		Found.
C ₄ =	48	17·72	17·89
H ₂ =	2	·73	1·77
Br ₂ =	160	58·39	57·94
O ₄ =	64	23·36	—
	<hr/>		
	274	100·00	

The above formula represents this substance as formed by the decomposition of two molecules of silver dibromacetate with separation of two molecules of silver bromide.



This formula is also confirmed by the products of decomposition of this body. If a quantity be mixed with alcohol and a little sulphuric acid, on dilution an oil separates having an irritating odour, which when treated with ammonia gives dibromacetamide, showing it to be dibromacetic ether.

If left in contact with water it gradually dissolves, forming an acid solution. On fractionally precipitating this with silver nitrate the first crop gave the following numbers:—

·2926 of substance gave
·1765 of AgBr = 34·68 p. c. silver,

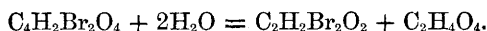
evidently silver dibromacetate containing a small quantity of glyoxylyate.

Another portion was dissolved in water and the solution neutralized with calcium carbonate; after concentration a crop of crystals of calcium glyoxylyate separated. A calcium determination of this gave the following results:—

·0424 of substance gave
·0262 of CaSO₄ = 18·18 p. c. calcium.

calcium glyoxylyate requires 18·01 p. c.

Therefore this oily substance, when decomposed with water, is resolved into dibromacetic and glyoxylic acids, thus:—

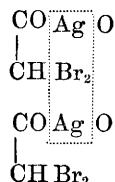


When distilled it is decomposed, yielding carbonic oxide and dibromacetic acid; a quantity of a gummy product is also formed somewhat like tartaric anhydride.

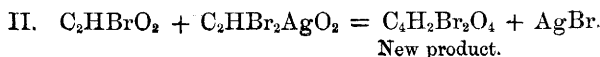
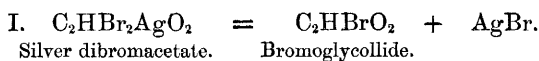
The first part of this decomposition may be represented thus:—



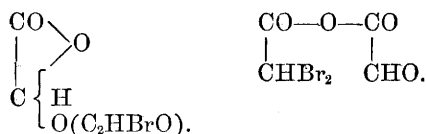
The formation of this substance from silver dibromacetate is difficult to understand; half only of the dibromacetyl contained in the silver dibromacetate used being decomposed, the rest remaining unchanged; thus:—



This curious reaction may perhaps be explained if we assume that a bromoglycollide is first formed, and as quickly as it is produced reacts upon the undecomposed silver dibromacetate, thus:—



This new product appears to possess the properties of an anhydride, and may be written either as a dibromacetoglyoxyllide or as a double anhydride, thus:—



Silver dibromacetate undergoes decomposition spontaneously when kept, and the decomposed salt when treated with water yields a solution of dibromacetic and glyoxylic acids.

Glyoxylic Acid.

Being desirous of making a further examination of glyoxylic acid and some of its derivatives, it was necessary to prepare a quantity of this substance, and the following process was employed:—

Forty or fifty grams of silver dibromacetate were boiled with water until decomposed, and the resulting solution of dibromacetic and glyoxylic acids filtered from the bromide of silver formed. Carbonate of silver was then carefully added to the clear solution until it was no longer acted upon, and the resulting mixture of silver salt boiled until silver bromide ceased to be formed. After this latter substance had been separated by means of a filter the acid liquid was concentrated on the water-bath. It usually contained a small quantity of silver in solution, owing to the addition of a slight excess of silver carbonate in the previous operation. This was not found to be injurious, and in fact was useful in removing the last traces of bromine, which it separated as the solution concentrated. When the product was reduced to a somewhat small bulk, hydrochloric acid was carefully added just in sufficient quantity to remove the last traces of silver; and after filtration the solution was further concentrated under a bell jar over sulphuric acid. In the course of a week or so the liquid, which had become syrupy, gradually deposited crystals; these slowly increased in quantity; when a considerable crop had formed, the thick mother-liquor was decanted and the crystals afterwards pressed strongly between bibulous paper, the resulting crystalline cake was then broken up and dried in a vacuum over sulphuric acid. The mother-liquors were again placed under a bell-jar over sulphuric acid, and in the course of a week or so became a nearly solid mass of crystals.

The following combustions were made of the product after drying for fourteen days in a vacuum:—

- I. ·29405 of substance gave
- 2814 of CO_2 and
- 1149 of H_2O .

II. .2428 of substance gave
 .2317 of CO₂ and
 .0970 of water.

These numbers show that the crystals were pure glyoxylic acid, having the formula, C₂H₄O₄.

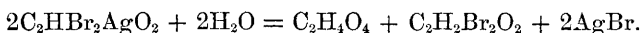
		Calculated.		Found.	
				I.	II.
C ₂	=	24	26.08	26.09	26.02
H ₄	=	4	4.34	4.34	4.43
O ₄	=	64	69.58	—	—
		92	— 100.00		

Several preparations were made of this acid, and it was always obtained in the crystalline condition.

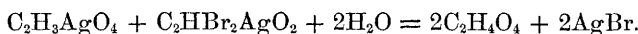
Pure glyoxylic acid crystallises apparently in oblique rhombic prisms; it is, however, very difficult to observe the form of the crystals, as they are small and rather confused, and also produced in a very thick fluid, in which it is only possible to view them, because when removed they deliquesce very rapidly. This acid is very soluble in water and alcohol. It tastes very like tartaric acid. When heated it melts to a syrupy liquid; it cannot be distilled without decomposition.

Its aqueous solution if quickly evaporated over sulphuric acid in a vacuum, does not usually crystallise, but becomes a gummy mass; if, however, the vacuum be dispensed with, so that the evaporation takes place slowly, crystals are obtained.

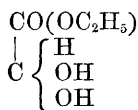
The process for the preparation of this acid is easily understood by the following equations:—



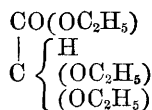
The resulting mixture of dibromacetic and glyoxylic acids being then converted into silver salts by the silver carbonate, decomposes as follows:—



A portion of crystallised glyoxylic acid was heated with absolute alcohol in a sealed tube for five hours, at 120°—130°, in the hope of obtaining the ether—



The product was a colourless liquid, which gave numbers showing it to have the composition—



The following are the numbers obtained :—

- I. ·1983 of substance gave—
 ·3900 of CO_2 , and
 ·1625 of H_2O .
 II. ·2929 of substance gave—
 ·5758 of CO_2 , and
 ·2357 of H_2O .

	Calculated.		Found.	
			I.	II.
$\text{C}_8 =$	96	54·54	53·63	53·61
$\text{H}_{16} =$	16	9·09	9·10	8·94
$\text{O}_4 =$	64	36·37	—	—
	176	100·00		

Although these results are not so good as could be desired, they undoubtedly show that the product is diethylglyoxylate of ethyl, any other possible ethylic derivative requiring much lower percentages of carbon. The amount of product at my disposal being small, I was unable to purify it so thoroughly as I could have wished; otherwise I have no doubt better numbers would have been obtained.

Sodium Glyoxylate.—A solution of crystallised glyoxylic acid, when neutralised with sodium carbonate and concentrated, yields a hard crystalline sodium salt. This, when recrystallised and dried at 100°C ., gave the following numbers on analysis :—

- I. ·3038 of substance gave—
 ·1928 of $\text{Na}_2\text{SO}_4 = 20·55$ p. c. sodium.
 II. ·232 of substance gave—
 ·146 of $\text{Na}_2\text{SO}_4 = 20·38$ p. c. sodium.

Theory for $\text{C}_2\text{H}_3\text{NaO}_4 = 20·17$ p. c.

Potassium Glyoxylate.—This salt prepared as the above, but substituting potassium for sodium carbonate, is obtained as an easily soluble crystalline salt. It cannot be dried at 100° , as it swells up and decomposes at that temperature. Dried in a vacuum it gave the following numbers on analysis :—

- I. ·2658 of substance gave—
 ·1776 of $\text{K}_2\text{SO}_4 = 29·95$ p. c. potassium.

- II. ·2046 of substance gave—
 ·1375 of K_2SO_4 = 30·12 p. c. potassium.
- III. ·236 of substance gave—
 ·155 of K_2SO_4 = 29·44 p. c. potassium.

Theory for $C_2H_3KO_4$ = 30·0 p. c.

Glyoxylic acid and Ammonia.—The product obtained by Dr. Debus, by the decomposition of calcium glyoxylate with ammonium oxalate, and generally known as ammonium glyoxylate, being the compound that most favours the formula $C_2H_2O_3$ for glyoxylic acid, and C_2HRO_3, H_2O for the glyoxylates, is necessarily of considerable interest; further experiments were therefore made to determine whether or no it be a true salt.

I. A quantity of calcium glyoxylate obtained from the acid produced by oxidizing alcohol with nitric acid, was dissolved in water, and the theoretical quantity of a neutral solution of ammonium oxalate added, both solutions being cold. On filtering off the calcium oxalate, a clear neutral fluid was obtained. This was evaporated over sulphuric acid in a vacuum, but it was observed that it gradually became acid to test-paper, the acidity increasing until crystals separated out. The crystals were washed with cold water, but when dissolved in cold water were still found to be decidedly acid. They were dissolved and recrystallised again by evaporation in a vacuum, but were still acid to test-paper.

II. Another quantity of this product was prepared in the same manner, using calcium glyoxylate prepared from dibromacetic acid, and the solution before evaporation in a vacuum, rendered slightly alkaline with ammonia. The crystalline product was also in this case acid to test-paper.

III. A quantity of a solution of crystallised glyoxylic acid was neutralised slowly with dilute ammonia and evaporated in a vacuum; the solution gradually became acid, and deposited crystals, which were acid to test-paper, even after recrystallisation.

As this derivative of glyoxylic acid dissolves but slowly in cold water, its acidity is most readily seen by placing a little of it in powder, on wet, blue litmus paper. With ammonia it behaves like an acid, inasmuch as it dissolves in it with great facility.

The following analyses were made of different specimens of this substance :—

- *I. ·2389 of substance gave—
 ·2311 of CO_2 .

* The hydrogen was lost.

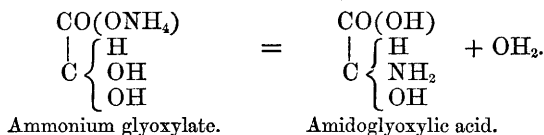
- II. ·1480 of substance gave—
 ·1416 of CO₂, and
 ·0753 of H₂O.
- III. ·2115 of substance gave—
 ·2020 of CO₂, and
 ·1082 of H₂O.

	Theory for C ₂ H ₅ NO ₃ .	Found.		
		I.	II.	III.
Carbon	26·37	26·38	26·09	26·04
Hydrogen	5·49	—	5·58	5·68

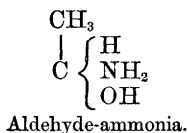
These numbers correspond with those obtained by Dr. Debus, but as they agree almost equally with an acid ammonia salt and also glyoxylic acid, it was thought desirable to determine the nitrogen in this body. Dr. Frankland kindly had a determination made for me by the process he employs for water analysis, and the ratio of carbon to nitrogen was found to be practically as 2 : 1; therefore the above formula is evidently the correct one for this substance.

Seeing that the glyoxylates, as those of potassium and sodium, are neutral to test-paper, and also that the freshly prepared solution of the ammonium salt obtained by double decomposition is also neutral, some change must evidently take place in this salt during its evaporation in a vacuum over sulphuric acid, seeing it becomes acid, without loss of nitrogen. This would indicate that the ammonium left the CO(OH) group for some other. At first sight this may appear strange, but we must remember that Dr. Debus has already shown that neutral glyoxylates will remove ammonia from its salts.

From these considerations I am led to infer that this so-called ammonium glyoxylate is not a true salt, but a product resulting from its decomposition. The change which the ammonium salt, which is undoubtedly at first formed, undergoes, may perhaps be as follows:—



This last compound would be a substance analogous to aldehyde-ammonia in which CH₃ is replaced by CO(OH)—



A portion of the ammonia derivative of glyoxylic acid was mixed with dilute ammonia, in which it is very readily soluble, far more so than in water. The solution was evaporated in a vacuum. It dried up to a glassy uncrystalline mass, and on analysis gave the following numbers :—

·200 of substance gave
 ·2040 of CO₂ and
 ·1147 of H₂O,

showing it to contain 27·81 per cent. of carbon and 6·37 per cent. of hydrogen.

A determination of carbon and nitrogen showed it to contain these elements in the ratio of 4 : 3. The nearest formula corresponding with these numbers is—



or a compound of amido- and diamido-glyoxylic acid; but the substance was of too indefinite a nature to form any decided conclusions from.

The following derivative obtained with aniline and glyoxylic acid favours the view that the ammonia derivative of this acid has the constitution assigned to it, namely, that it is an amido acid. This substance has already been referred to in the paper by Mr. Duppa and myself.

If instead of using ammonium oxalate in the preparation of the so-called ammonium glyoxylate, oxalate of aniline be employed, calcium oxalate separates; and on filtering this off a clear solution is obtained, doubtless glyoxylate of aniline. It, however, quickly changes, becomes yellow, and deposits an orange-coloured powder. This peculiar substance does not possess the properties of a salt, but is both an acid and a base, so that the aniline must have left the COOH group.

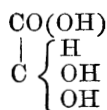
This substance is easily soluble in ammonia, and when the solution is evaporated in the water-bath it forms an orange glassy substance which is a soluble ammonia salt. With nitrate of silver a solution of the compound forms an amorphous pale yellow bulky silver salt which can be washed only on a vacuum filter. Several specimens were analysed, but the results were not very concordant, the percentage of silver generally being between 32 and 36 per cent.

It also dissolves in dilute hydrochloric acid, and when evaporated to dryness the solution leaves a soluble hydrochloride containing about 20 per cent. chlorine. This gives with platinum tetrachloride a platinum salt containing about 18 per cent. platinum.

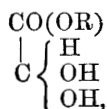
This peculiar aniline derivative does not crystallise; a great many analyses of it have been made, but no satisfactory conclusions as to its

formula have as yet been obtained. When distilled with strong potassium hydrate it decomposes and aniline distils over.

From the foregoing results and considerations it appears that undoubtedly the formula of glyoxylic acid is—



and its anhydrous salts—



and, therefore, it contains two hydroxyls in union with one atom of carbon. The substance—

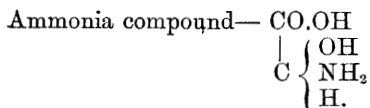
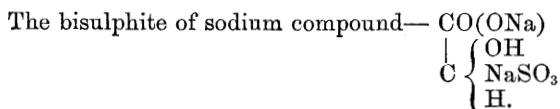


is at present unknown, though its existence is of course probable.

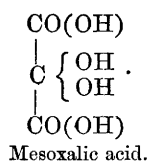
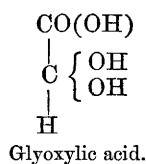
We have the following lists of substances confirming this view :

Glyoxylic acid	$\text{C}_2\text{H}_2\text{O}_4$
Sodium glyoxylate.....	$\text{C}_2\text{H}_3\text{NaO}_4$
Potassium glyoxylate	$\text{C}_2\text{H}_3\text{KO}_4$
Calcium ,,	$\text{C}_4\text{H}_6\text{CaO}_8$
Silver ,,	$\text{C}_2\text{H}_3\text{AgO}_4$
Ethyl-diethylglyoxylate.....	$\text{C}_2\text{H}(\text{C}_2\text{H}_5)_3\text{O}_4$
Diethylglyoxylamide.....	$\text{C}_2\text{H}_3(\text{C}_2\text{H}_5)_2\text{NO}_3$.

The compound of sodium bisulphite and glyoxylic acid and the ammonia derivative might also be added :



It is very possible that mesoxalic acid has the formula $\text{C}_3\text{H}_4\text{O}_6$, and not $\text{C}_3\text{H}_2\text{O}_6$; its so-called ammonium salt being possibly a product of decomposition like that of glyoxylic acid. This appears not improbable, as mesoxalic acid may be considered as glyoxylic acid with one atom of hydrogen replaced by CO(OH) :



The metallic derivatives of this acid and apparently its ether favour this view. The ammonia derivative being the only exception. This may, however, be constituted thus—

