LXXIII.—*Oxidation of Tartaric Acid in presence of Iron.*

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WHEN tartaric acid in aqueous solution interacts with certain oxidising agents in presence of a trace of a ferrous salt, a solution is obtained which gives a beautiful violet colour on the addition of caustic alkali. I observed this change some years ago, and proposed it as a distinguishing test for tartaric acid. Tartaric and racemic acids are the only substances yet examined which behave in this way, citric, malic, succinic, oxalic, and a variety of other acids having been tried with negative results. The solution to be examined is mixed with a drop of ferrous sulphate solution, followed by a drop of hydrogen peroxide, and then made alkaline with caustic soda or potash. Acids destroy the colour, but alkalis restore it. Excess of ferrous salt or of oxidising agent prevents or destroys the effect.

It was observed subsequently that the iron may be removed from the acid solution by precipitation with a ferrocyanide; the filtered liquid has very powerful reducing properties, and, with ferric chloride and alkali, gives a violet colour, which is changed to a transient emerald-green by dilute mineral acids. The effects are very similar to those given by ferric chloride with pyrocatechin or with phloroglucin.

Chlorine water, hypochlorites, barium peroxide, sodium peroxide, or potassium permanganate may be employed as oxidising agents in place of hydrogen dioxide, but the results are not so good.

Nitric and nitrous acids are inactive in this respect, as also, apparently, is ozone. If, however, ozonised air is passed into ether, it becomes strongly active; this is, perhaps, due to the formation of ethyl peroxide.

If moist ferrous tartrate, prepared by precipitation, is exposed to the air for about 10 minutes and then treated with excess of caustic

alkali, a faint violet coloration is produced, and from comparative experiments it would appear that fresh external air is more active than the air of a room. I hope, shortly, to make further experiments in this direction.

If a strongly alkaline solution of a tartrate, containing a trace of ferrous salt, be electrolysed, using platinum electrodes, beautiful violet striæ will appear round the anode, and a strong solution of the substance may be produced in this manner if the temperature is kept low. Or, if a strong solution of tartaric acid is electrolysed, using an iron anode, the liquid turns yellow round the anode, and on the addition of caustic alkali this changes to violet.

In order to throw some light on the nature of this reaction, experiments were made with standard solutions of tartaric acid, ferrous sulphate, and hydrogen peroxide. Measured volumes of these solutions were mixed in the order named, made alkaline with soda, diluted to the same volume in tall glasses, and the depths of violet colour compared. With equal quantities of tartaric acid and a fixed proportion of iron, it was observed that the depth of colour increased with increasing quantities of hydrogen peroxide up to a certain limit, beyond which the colour diminished as the peroxide increased, and beyond a certain point disappeared altogether. The maximum was always produced when the ratio was 1 mol. of tartaric acid to 1 atom, or slightly more, of available oxygen; and the complete disappearance of colour occurred when the ratio was 1 mol. of tartaric acid to 5 atoms of available oxygen.

In the next series of experiments, the proportion of iron was varied from 1 atom to $\frac{1}{16}$ atom for 1 mol. of tartaric acid, and it was found that the ratio of oxygen to tartaric acid required to produce the maximum colour, and the discharge of colour, remained practically unchanged.

From these results, it seems probable that the iron acts in a manner usually termed "catalytic," a very small quantity of iron being sufficient to determine the oxidation in this direction of an almost unlimited amount of tartaric acid.

Ferric salts are quite inoperative in bringing about the change, but if, in the first instance, the quantity of ferrous salt is very small, the colour produced by the alkali is greatly intensified by adding a few drops of ferric chloride. It would appear that ferrous salt is essential in producing the compound, and that ferric salt gives the violet coloration with the compound produced.

Many attempts were made with a view of isolating this colour-giving substance, but, owing to the unstable character of the solution, the problem was an exceedingly difficult one. Exposure to the air, heating, or even evaporation in a vacuum, seem to destroy it.

Dialysis, in an inert atmosphere, fractional precipitation by various metallic salts, and extraction by various solvents under different conditions, were also tried without success. Subsequently, whilst experimenting with very strong solutions of ferrous tartrate and hydrogen peroxide, I observed that it was possible to extract a minute quantity of a substance which gave a violet coloration with ferric chloride and caustic alkali, but the quantity was too small for further examination. It seemed probable, from this result, that the substance divides itself very unequally between water and ether, and that the addition of a dehydrating agent would enable the ether to extract a larger quantity. This was tried with considerable success—strong sulphuric acid, dry hydrogen chloride, phosphorus pentoxide, alcohol, many dehydrated salts, and even finely divided silica, very greatly increased the quantity of substance which ether was able to extract. On evaporating the ether, a white powder was left, generally amorphous, but sometimes semi-crystalline; it was sparingly soluble in cold water, acted as a powerful reducing agent, and, with ferric chloride, gave the characteristic reaction mentioned above.

The substance prepared in this way gave somewhat variable results on analysis, and the yield was so small as to make the method almost prohibitive owing to the cost of production. Whilst engaged in these experiments, however, it was observed that, occasionally, a minute quantity of brilliant, white crystals appeared in the liquid on standing after addition of the dehydrating agent, and these proved, on examination, to be identical in reactions with the substance extracted by ether. Their production was at first very uncertain, but, recently, I have worked out the conditions by which they may be obtained with certainty and in considerable quantity. The method which gives the best result is as follows :—Tartaric acid is dissolved in the least possible quantity of hot water; finely-divided iron (*ferrum redactum*) is added, and the liquid boiled until all the iron has disappeared. The quantity of iron must be insufficient to cause a separation of ferrous tartrate when the action is finished; about $\frac{1}{250}$ part of the weight of tartaric acid employed answers well, but the final result does not appear to be much influenced by the proportion of iron in solution, at any rate, within considerable limits. The solution, filtered, if necessary, through cotton wool, is carefully cooled, surrounded by ice, and hydrogen peroxide (20 volume) added in small quantities at a time, allowing a few minutes to elapse between each addition. The first portions of the peroxide merely produce a yellowish colour, but, as the action proceeds, each addition produces a dark green or nearly black appearance, transient at first, but becoming more and more persistent. When this dark colour remains for two or three minutes, it is a rough guide that sufficient peroxide has been

added, although it is, perhaps, safer to calculate the quantity neces-
sary from the proportions indicated in the colour experiments men-
tioned above. Great care must be taken not to add an excess of the
peroxide, or the whole of the material will be wasted. Nordhausen
sulphuric acid is now added by means of a thistle funnel, drawn out
to a fine point, in very small quantities at a time, cooling carefully
between each addition, preferably by ice and salt. The quantity
added is a matter of importance, too much or too little giving an
indifferent yield of the substance; the best proportion is found by ex-
perience to be about $\frac{1}{10}$th of the total volume of the liquid operated on.
The mixture, still surrounded by ice, is put aside in a cold place, and
after a few hours crystals begin to form; the first deposit is often dis-
coloured and the crystals small, but the subsequent crops are beauti-
fully white and pure. If the experiment is properly conducted, and
the liquid kept sufficiently cool, crystals continue to form for several
days, but the greater part is deposited within about 24 hours.

The crystals are collected with the aid of a pump, carefully
drained, and washed repeatedly with small quantities of cold water.
After again thoroughly draining, they are spread on filter-paper and
air-dried. They appear to undergo no change in the air, even after
several weeks' exposure.

Properties.—The substance obtained in this manner has the appear-
ance of a shining crystalline mass with a pearly lustre. The crystals
are described by Mr. Solly as follows:—" Thin, orthorhombic,
diamond-shaped plates, $100 \wedge 110 = 52° 35'$. Cleavage perfect
parallel to 010. The plane of the optic axes probably parallel to 001,
the basal plane. The direction of greatest optic elasticity parallel
to 100,001."

The substance dissolves very sparingly in cold water, ether, or
acetic acid, but more readily in ethylic or methylic alchol, or in
warm water, or hot acetic acid. It may be recrystallised from hot
water, but with considerable loss, since decomposition, with evolution
of carbon dioxide, takes place rapidly at about 50—60°, and slowly
even at ordinary temperatures. The crystals give off water when
heated, or when placed in a vacuum over sulphuric acid, a white,
amorphous powder being left. If the dehydrated substance is dis-
solved in absolute alcohol, and a few drops of water added, a crystal-
line precipitate of the hydrated substance is thrown down. The
dehydrated substance begins to decompose, without melting, at about
155°.

The aqueous solution has a strongly acid taste, and gives an acid
reaction with indicators. It rapidly reduces silver, cupric, and mer-
curic salts, potassium permanganate, &c. *Ferric chloride* gives a
blackish colour, changing to a beautiful violet on the addition of

caustic alkali, and to a transient emerald-green when acidified with dilute sulphuric acid. *Lead acetate* gives a yellow precipitate, *barium chloride* a white crystalline precipitate, and silver nitrate a white precipitate quickly turning black. These precipitates all give the original substance on treatment with acids. Carbamide gives a white crystalline precipitate with the alcoholic solution.

Hydroxylamine hydrochloride gives a crystalline precipitate consisting of long, narrow, obliquely modified prisms; but its formation is somewhat uncertain, and the conditions have yet to be investigated.

Phenylhydrazine appears to give three distinct compounds, perhaps more. The first is obtained as a yellow, amorphous powder on adding a limited quantity of alcoholic phenylhydrazine to an excess of the dehydrated substance in alcohol. The second comes down slowly in beautiful silver-white, flat, oblique plates, when excess of phenylhydrazine in alcoholic or acetic acid solution is added to a cold dilute alcoholic solution of the hydrated substance; when collected by the aid of a filter-pump it has a very brilliant appearance, almost like that of metallic silver. The third compound is obtained in beautiful golden plates if the solutions are heated after mixing. The second silver-like compound seems to change spontaneously into this golden substance after a short time, but whether this is due to dehydration or to the action of light, &c., has not yet been made out.

In aqueous solution the substance slowly decomposes, giving off bubbles of gas, and after a few hours a weak solution has lost its original properties. When heated to about 60°, the decomposition is very rapid, carbon dioxide is evolved with effervescence, and the solution ceases to give the ferric chloride reaction after a few minutes. The solution which has been heated, leaves a gummy mass when evaporated in a vacuum over sulphuric acid; this acts as a powerful reducing agent, giving a silver "mirror" with ammoniacal silver nitrate, and reducing Fehling's solution in the cold; it also gives the "aldehyde reaction" with magenta decolorised by sulphurous acid, whereas the original acid does not.

If the solution is boiled, neutralised with chalk, filtered, aniline oxalate added, and the liquid, after filtering, heated, an orange colour and precipitate is produced (Perkin's reaction). With dimethylaniline and mercuric chloride a blue colour is produced after heating for some time (Böttinger). From these results, *glyoxylic acid* seems to be indicated, but later experiments show that the quantity of acid is very small, the neutralising power being insignificant as compared with the reducing power. The main product appears to be an aldehyde; the latter is now being investigated.

If the original substance is heated with a concentrated solution of

hydrogen iodide, a copious liberation of iodine takes place after a few minutes. Three or four grams of the original acid were heated with excess of fuming hydrogen iodide at about 100° in a stoppered bottle, and small pieces of phosphorus were added from time to time until the liquid became colourless. After heating on a water-bath until most of the hydrogen iodide was expelled, the liquid was evaporated to dryness, and, on heating the solid residue, white fumes were evolved which condensed upon a cold surface as a crystalline mass; this, on re-sublimation, yielded white, feathery crystals which melted at about 116°. These, after crystallisation from water, melted at 180—182°, and by optical examination and by the characteristic reaction with ferric chloride, were found to be *succinic acid*.

0·1806 gave 0·2666 CO_2 and 0·0782 H_2O. C = 40·25; H = 4·81.
Succinic acid requires C = 40·67 per cent.; H = 5·08 per cent.

In other experiments, it was observed that if the heating with hydrogen iodide were not continued too long, a crystalline substance separated as the liquid cooled; on recrystallisation from water, this was found to melt at about 191°. It gives no reaction with ferric chloride, but if treated with ferrous sulphate and hydrogen dioxide, in the manner described above, it gives the tartaric acid reaction. From its high melting point, *racemic acid* was suspected, and this has since been confirmed by a careful optical examination by Mr. Solly.

Analysis of the Original Crystals.—Thoroughly air-dried specimens gave the following results on combustion.

I. 0·2262 gave 0·2158 CO_2 and 0·0878 H_2O; C = 26·01; H = 4·31.
II. 0·1673 gave 0·1603 CO_2 and 0·0642 H_2O; C = 26·13; H = 4·26.
III. 0·2201 gave 0·2094 CO_2 and 0·0829 H_2O; C = 25·94; H = 4·18.

The specimens analysed in I and II were obtained as the third crop of crystals in the original preparation, and that in III was a specimen which had been recrystallised from hot water.

Estimation of Water.—The substance was placed in a vacuum over sulphuric acid until the weight was constant.

I. 0·5743 lost 0·1097 H_2O = 19·10 per cent.
II. 0·4932 lost 0·0948 H_2O = 19·22 per cent.

The weight became constant after two days or less, and no further loss took place even after four weeks.

Heated in a current of dry hydrogen until the weight was constant.

III. 0·5477 lost 0·1073 H_2O at 80° = 19·59 per cent.
IV. 0·1611 lost 0·0314 H_2O at 60° = 19·49 per cent.
V. 0·2041 lost 0·0399 H_2O at 90° = 19·54 per cent.

No further loss occurred at 100°.

It appears from these results that the substance cannot be completely dehydrated at ordinary temperatures in a vacuum over sulphuric acid.

Analysis of the Dehydrated Substance.—The residue from Experiment IV (0·1297 gram), on combustion, gave 0·1542 CO_2 and 0·0308 H_2O ; C = 32·40 ; H = 2·63 per cent.

The residue from Experiment V (0·1642 gram), on combustion, gave 0·1966 CO_2 and 0·0393 H_2O ; C = 32·65 ; H = 2·61 per cent.

The specimens dried in a vacuum, which were analysed in the first instance, gave an average of 30·8 per cent. C and 2·8 per cent. H.

Methylic Salt.—To prepare this compound, the original substance is dissolved in the least possible quantity of methylic alcohol (about 1 in 8) and dry hydrogen chloride passed into the solution. A white, amorphous substance begins to deposit as soon as the liquid is saturated with the gas, and continues to come down for some hours, after which it is deposited in a beautifully crystalline form. The liquid is then drained off by means of a pump, the solid washed with small quantities of cold methylic alcohol, and dried in a steam cupboard. It may then be recrystallised from boiling methylic alcohol, glacial acetic acid, or benzene. The crystals originally produced, and often on first recrystallising from methylic alcohol (*a*), consist of long, slender, oblique prisms. $\bar{a}$ makes with the long edges of the prism an angle of $37\frac{1}{2}°$. Optically *positive*. In convergent light gives an unsymmetric optic picture. When recrystallised a second time (*b*), the crystals are very different in habit; they consist of a number of very nearly square plates twined together, and built up in rows nearly at 90° apart. Optically *negative*. The first mean line is apparently perpendicular to the basal plane. The second mean line makes an angle of 17° with a prism edge.

Both these modifications give identical results on analysis, as will be seen below. The difference may possibly be caused by a trace of some impurity, but if so the quantity is too small to be detected. When heated to about 150°, the substance may be easily vaporised, and condensed upon a cold surface in crystals which are identical with those obtained by repeated recrystallisation (*b*). Heated in a capillary tube, these modifications all melt at about 151°, but the exact point is difficult to observe owing to the volatility of the substance. It is very sparingly soluble in cold acetic acid and ether, rather more so in cold methylic or ethylic alcohol, and fairly easily in these liquids when hot.

When treated with caustic alkalis, a lemon-yellow coloration is produced. If ferric chloride is added to the alkaline mixture no effect occurs at first, but after a few minutes the characteristic violet

colour is produced. This effect is evidently due to the gradual "saponification" of the ethereal salt.

I. 0·1619 gave 0·2386 CO_2 and 0·0644 H_2O; $C = 40·19$; $H = 4·41$.

II. 0·1506 gave 0·2249 CO_2 and 0·0568 H_2O; $C = 40·72$; $H = 4·18$.

III. 0·1824 gave 0·2733 CO_2 and 0·0729 H_2O; $C = 40·86$; $H = 4·44$.

IV. 0·2224 gave 0·3331 CO_2 and 0·0897 H_2O; $C = 40·84$; $H = 4·48$.

I was sublimed on a watch glass, II and III were the result of a first recrystallization, and IV of a second recrystallisation.

Ammonium Salt.—Aqueous ammonia is added to a solution of the acid in dilute alcohol until it is just alkaline to litmus paper. The salt begins to separate after a few minutes. The crystals consist of flat, nearly square, plates. Optically positive. The first mean line inclined to the basal plane, as only one optic axis with rings is seen. The second mean line is parallel to one of the prism edges.

The salt dried in a vacuum does not lose weight when heated in dry hydrogen at 90°.

0·2108 gave 0·2023 CO_2 and 0·1086 H_2O; $C = 26·17$; $H = 5·72$.

0·1751 gave 22·6 c.c. of nitrogen at 17° and 757·3 mm.; $H = 15·19$.

0·3495 gave 45 c.c. of nitrogen at 19° and 755·6 mm.; $N = 15·01$.

Sodium Salt.—This may be prepared either by adding alcoholic soda to a solution of the acid in dilute alcohol until alkaline, washing with a little water and then with alcohol, or by neutralizing the acid with sodium carbonate, when crystals separate after an hour or two if the solution is sufficiently strong. They are long, narrow, obliquely developed prisms. *a* parallel to long edge of the prism.

The salt is somewhat sparingly soluble in cold water. It does not appear to be altered in a vacuum over sulphuric acid, and the salt dried in a vacuum does not lose weight even at 140° in a current of dry hydrogen.

Analysis gave the following results.

I. 0·2269 gave 0·2031 CO_2 and 0·0260 H_2O; $C = 24·41$; $H = 1·27$.

II. 0·1985 gave 0·1441 Na_2SO_4; $Na = 23·51$ per cent.

III. 0·1453 gave 0·1043 Na_2SO_4; $Na = 23·25$ per cent.

IV. 0·2976 gave 0·2142 Na_2SO_4; $Na = 23·31$ per cent.

Barium Salt.—The crystalline precipitate, obtained by adding barium chloride to an aqueous solution of the acid, was dried under diminished pressure at $50-60°$ until the weight was constant.

0·8941 gave 0·5520 $BaCO_3$; $Ba = 42·93$ per cent.

Formula for the Acid.

The results of the above analysis agree closely with the empyrical formula, $C_2H_2O_3$, for the dehydrated acid, and $C_2H_2O_3,H_2O$ for the

crystals. It is evident, from the composition of the salts, that the number of carbon atoms in the molecule must be even, since two atoms of carbon are present for each atom of "replaceable" hydrogen. The direct production of the acid from tartaric acid, and the formation of succinic acid by interaction with hydrogen iodide, suggest the formula $C_4H_4O_6$, whereas some of the properties of the acid might lead one to expect a higher multiple. It was important, therefore, to obtain conclusive evidence as to its molecular weight.

Attempts were made, in the first instance, to determine the vapour density of the methylic salt. Hofmann's apparatus was employed, and the heating liquids tried were amylic alcohol, crude xylene, oil of turpentine, and aniline. With the two first named, the vaporization of the substance was so slow as to make the determination practically impossible, and with both turpentine and aniline there were signs of decomposition. The experiment had, therefore, to be abandoned for the time, since no liquid boiling at the required temperature was available in sufficient quantity. Dumas' method was also tried, using an oil bath at 150—155°, but owing to the slow rate of vaporization it was impossible to displace more than about $\frac{1}{2}$ of the air.

The next experiments were made by a vapour pressure method first suggested, I believe, by Ostwald, in the apparatus and after the manner recommended by Will and Bredig (*Ber.*, 1889, 1084).

A current of dry air is drawn first through the solution of the substance in absolute alcohol, and then through alcohol alone, the loss of weight of each being determined. The air after being thoroughly dried is led through (*a*) a leaden spiral, (*b*) a set of three potash bulbs sealed together containing the solution, (*c*) a similar set containing the solvent, (*d*) an empty ∪-tube, and lastly through a drying apparatus to the aspirator. The parts of the apparatus *a*, *b*, *c*, and *d*, are immersed together in a large bath through which a very gentle stream of water flows from a cistern. Will and Bredig use a motor to keep the temperature uniform, but the arrangement mentioned seemed to answer almost as well, and the temperature of the bath did not alter more then 2° during a determination. About 18—25 litres of air were drawn through the apparatus in each experiment at the rate of $\frac{1}{2}$ to 1 litre per hour. In some experiments the air was passed through alkaline ferrous tartrate and alkaline pyrogallol in the first instance, in order to avoid any risk of oxidation, but this precaution appeared to be unnecessary.

If $S_1 =$ the loss experienced by the solution containing W_1 grams of substance in W_2 grams of solvent, and $S_2 =$ the loss experienced by the solvent, it follows, from the relation $\dfrac{P - P_1}{P} = \dfrac{n}{N + n}$, that

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the molecular weight $= \dfrac{MS_1W_1}{S_2W_2}$, where $M =$ the molecular weight of the solvent.

The following results were obtained using the dried acid, with absolute alcohol as solvent.

$[M = 46]$.

	S_1.	S_2.	W_1.	W_2.	Mol. wt.
I.	0·8106	0·0213	3·8256	36·08	185
II.	1·9974	0·0339	5·3359	62·25	232
III.	1·2922	0·0313	4·2572	52·68	153
IV.	2·0130	0·0743	4·4163	41·70	131

It is not surprising that the results should differ considerably, since an error of a few milligrams in weighing the bulbs containing the solvent would make a very great difference in the result, and such an error is probable considering the bulky nature of the apparatus to be weighed, and the conditions of the experiments. Still the average number pointed clearly to the formula $C_4H_4O_6$. (Mol. wt. $= 148$.)

Freezing point determinations were hardly applicable to the acid itself owing to its very sparing solubility in cold acetic acid, water, benzene, melted phenol, naphthalene, stearin, &c.

The boiling point method was, therefore, next tried, in the apparatus recommended by Sakurai (Trans., 1892, **61**, p. 994). Absolute alcohol, dehydrated by copper sulphate and boiling at $78\cdot3°$, was used as the solvent, and the dried acid was examined.

In order to estimate the contents of the solution after the experiments I, II, and III, the weighed quantity of solution was diluted with water and titrated with soda, which had been standardized by the same dry acid. In experiment IV, the quantity was estimated by weighing in a vacuum the residue left on evaporation.

The following results were obtained.

	Boiling point.		Grams of substance.	Grams of solvent.	Mol. wt.
	Solvent.	Solution.			
I.	3·310	3·390	0·1503	10·4835	205
II.	3·555	3·805	0·5177	17·0695	139
III.	3·330	3·500	0·3047	10·5181	195
IV.	3·260	3·430	0·2311	12·3892	126

The alcoholic solution of the acid had rather a tendency to froth up on boiling, which made the experiments somewhat difficult.

The most satisfactory results, however, were obtained with the methylic salt; this substance, although very sparingly soluble in cold acetic acid, or benzene, dissolves fairly well in melted phenol or

melted naphthalene, so that it is possible to determine its molecular weight by the freezing point method.

The following were the results with phenol as solvent.

	Freezing point.		Grams of substance.	Grams of phenol.	Mol. wt.
	Solvent.	Solution.			
I.	3·200	3·015	0·0593	11·62	209
II.	3·200	2·560	0·1820	11·62	185
III.	4·640	4·355	0·1904	27·36	188
IV.	4·672	3·900	0·2758	15·14	179

and with naphthalene as solvent,

V.	4·075	3·735	0·1257	13·48	189

The "constants" for phenol and for naphthalene are taken as 76 and 69 respectively. The calculated value of the molecular weight for $C_4H_2(CH_3)_2O_6$ is 176.

The dry acid must, therefore, be represented as a bibasic acid having the formula $C_4H_4O_6$, and the original crystals as $C_4H_4O_6,2H_2O$.

In the following table, the results calculated from this formula are compared with those obtained by analysis. It will be observed that the agreement is everywhere very close except in the case of the sodium salt, where the results are somewhat low; it would seem, therefore, that it retains water, even at 140°. The barium salt agrees exactly with the calculated result if it be considered as the hydrated normal salt.

Original Crystals.

	Found.			Calculated for $C_4H_4O_6,2H_2O$.
	I.	II.	III.	
C	26·01	26·13	25·94	26·08 per cent.
H..........	4·31	4·26	4·18	4·02 ,,
H_2O.......	19·59	19·49	19·54	19·56 ,,

Dry Acid.

	Found.		Calculated for $C_4H_4O_6$.
	I.	II.	
C	32·40	32·65	32·43 per cent.
H.............	2·63	2·61	2·70 ,,

Methylic Salt.

	Found.				Calculated for $C_4H_2(CH_3)_2O_6$.
	I.	II.	III.	IV.	
C	40·19	40·72	40·86	40·84	40·99 p. c.
H..........	4·41	4·18	4·44	4·48	4·54 ,,

Ammonium Salt.

	Found.			Calculated for $C_4H_2(NH_4)_2O_6$.
	I.	II.	III.	
C	26·17	—	—	26·37 per cent.
H	5·72	—	—	5·48 ,,
N	—	15·19	15·01	15·38 ,,

Sodium Salt.

	Found.				Calculated for $C_4H_4Na_2O_6$.
	I.	II.	III.	IV.	
C	24·41	—	—	—	25·00 p. c.
H	1·27	—	—	—	1·04 ,,
Na	—	23·51	23·25	23·31	23·95 ,,

Barium Salt.

	Found.	Calculated for $C_4H_2BaO_6,2H_2O$.
Ba	42·93	42·94 per cent.

Titration of the Acid with Soda.—0·6481 gram of the original crystals dissolved in water, and titrated with soda (prepared from metallic sodium) containing 0·007268 gram Na per c.c., required 22·8 c.c. for neutralization, phenolphthaleïn being used as indicator. = 0·1657 gram Na. Theory for a bibasic acid of the formula $C_4H_8O_9$ = 0·1620 gram Na = 22·29 c.c.

The properties of these two acids are very different; dihydroxytartaric acid (Miller, *Ber.*, **22**, 2015) crystallises in prisms, melts and decomposes at 98°, is very easily soluble in cold water, and gives no reaction with ferric chloride.

The "constitution" of the acid might, of course, be easily conjectured from the results above recorded, but I prefer to leave the consideration of this point to a future communication, in which I hope to give an account of its phenylhydrazine and hydroxylamine compounds and of the interaction of the acid with acetyl chloride and other agents.

In conclusion, I wish to express my best thanks to Mr. R. H. Solly, M.A., Demonstrator of Mineralogy, for his kindness in examining and describing the various specimens of crystals.

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