3. Hydrolysis in alcoholic solution gives similar results; the percentage of nitrous acid is independent of experimental conditions, but nearly twice as much is formed as in the previous case.

4. The reason for this difference is discussed.

5. It was found that when alkali is excluded altogether, and a substance like sulfanilic acid added, which can take up nitrous acid as fast as formed, the production of nitrous acid is greatly increased.

6. The rate of formation of nitrous acid under the latter conditions was found to be monomolecular.

7. In the hydrolysis of nitric esters two processes occur independently of each other. One is the normal saponification into alcohol (or oxyacid) and nitric acid; the other is isomerization to a nitrous ester, which subsequently hydrolyzes into a carbonyl compound (aldehyde or ketone) and nitrous acid. Each of these reactions proceeds at its own rate under the given conditions.

8. The constant yield of nitrous acid obtained when, for example, aqueous alkali is employed is a false equilibrium. The real constant is the ratio of the rates of the two reactions.
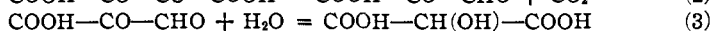
BERKELEY, CALIFORNIA.

DIHYDROXY-TARTARIC ACID.

BY ARTHUR LACHMAN.
Received May 18, 1921.

Dihydroxy-tartaric acid was first obtained by Gruber,[1] by the action of nitrous acid on protocatechuic acid. He found that it readily lost carbon dioxide, with formation of tartronic acid; he therefore named the compound carboxy-tartronic acid, and ascribed to it the following structure.

$$\text{COOH—C(OH)—COOH} = \text{COOH—CH(OH)—COOH} + CO_2 \qquad (1)$$

with a COOH group attached to the C(OH).
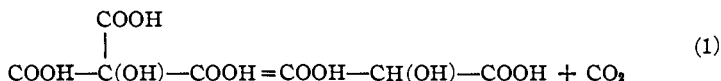
As the formation of an acid of this structure from the oxidation of a benzene ring appeared to support the prism rather than the hexagon formula, the subject was promptly investigated by Kekulé.[2] The latter obtained Gruber's acid from nitrotartaric acid, and was able to reconvert it into tartaric acid by reduction. He explained the formation of tartronic thus: first, loss of carbon dioxide and production of an aldehydo-acid, and second, rearrangement of the aldehydo-acid.

$$\text{COOH—CO—CO—COOH} = \text{COOH—CO—CHO} + CO_2 \qquad (2)$$
$$\text{COOH—CO—CHO} + H_2O = \text{COOH—CH(OH)—COOH} \qquad (3)$$

[1] Gruber, *Ber.*, **12**, 514 (1879).
[2] Kekulé, *Ann.*, **221**, 245 (1883).

Kekulé wrote these equations with the keto groups dehydrated, although as a matter of fact the free acid and its salts all hold at least two mols of water, and should be formulated

$$COOH—C(OH)_2—C(OH)_2—COOH \qquad (4)$$
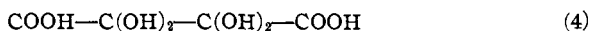
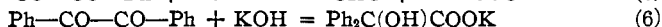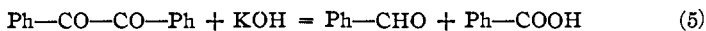as a true dihydroxy-tartaric acid.

Nearly 20 years later, Fenton[3] prepared glyoxyl-formic acid of the formula shown in Equation 2, and found that it did indeed readily pass over into tartronic acid on warming with alkalies, according to Equation 3.

Kekulé's explanation, however, fails to account for the fact that the *sodium salt* of dihydroxy-tartaric acid also loses carbon dioxide (and water) when heated in the *dry state*, and changes over into sodium tartronate. It is difficult to picture the movements of the sodium atoms in this reaction, on the basis of Equations 2 and 3. Kekulé must have felt this inadequacy, for he devoted much time to a study of the behavior of sodium dihydroxy-tartrate. On one occasion he heated the salt for over 800 hours, with more than 35 weighings. Fenton also made a painstaking investigation of this salt.[4]

A satisfactory explanation of the conversion of dihydroxy-tartaric acid into tartronic acid must, of course, explain equally well the entirely similar transformation of its salt. Such an explanation has been found by noting the similarity in structure between dihydroxy-tartaric acid and benzil.

Comparison of Dihydroxy-tartaric Acid and Benzil.

Benzil is an α-diketone; likewise, dihydroxy-tartaric acid is its dehydrated form (2). In fact, dihydroxy-tartaric acid reacts with phenylhydrazine, taking up two mols. Benzil, treated with moderately concentrated alkalies, undergoes two different reactions simultaneously, *viz.*, rupture into benzaldehyde and benzoic acid, and rearrangement into benzilic acid

$$Ph—CO—CO—Ph + KOH = Ph—CHO + Ph—COOH \qquad (5)$$
$$Ph—CO—CO—Ph + KOH = Ph_2C(OH)COOK \qquad (6)$$

In the course of the present work, it was found that dihydroxy-tartaric acid, when acted upon by alkalies, behaves quite similarly. Rupture occurs, with production of oxalic and glyoxalic acids; and tartronic acid is also formed together with carbonic acid. Analogy clearly points to a primary rearrangement, in this latter case, to *carboxy-tartronic acid*, which then loses carbon dioxide according to Equation 1.

$$COOH—CO—CO—COOH + H_2O = COOH—CHO + COOH—COOH \quad (7)$$
$$COOH—CO—CO—COOH + H_2O = (COOH)_2C(OH)COOH \qquad (8)$$
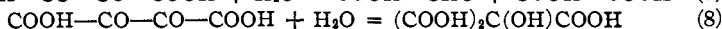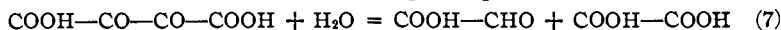
[3] Fenton and Ryffel, *J. Chem. Soc.*, **81**, 426 (1902).

Fenton, *ibid.*, **87**, 813 (1905).

[4] Fenton, *J. Chem. Soc.*, **74**, 71 (1898). Kekulé (Ref. 2) promised a further investigation, which never appeared in print.

The only essential difference between the behavior of benzil and dihydroxy-tartaric acid lies in the fact that the CO groups in the latter substance are hydrated (cf. 4), and consequently neither water nor alkali is required to be added, so that both rupture and rearrangement may take place upon simple heating, *as in fact they do*. The details will be found in the experimental section of this paper.

The view that the formation of tartronic acid, in the above reactions, is due to a primary rearrangement, finds confirmation in the behavior of diketo-butyric acid.[5] This acid is known only in the form of an ester; when the ester is hydrolyzed by alkali, methyl-tartronic acid results.

$$CH_3CO—CO—COOR + 2\ KOH = CH_3C(OH)(COOK)_2 + ROH \qquad (9)$$

It cannot be decided, in this case, whether methyl or carboxyl has shifted, the result being the same in either event. In the case of dihydroxy-tartaric acid, carboxyl is the only group that can shift. Nor is such a movement without analogy. Phenyl-oxypivalic ester, when heated with phosphorus pentoxide shifts a COOR group.[6]

When sodium dihydroxy-tartrate is heated, the shifting group is COONa

$$COONa—C(OH)_2\ C(OH)_2COONa = (COONa)_2\overset{\displaystyle OH}{\overset{\displaystyle |}{C}}—C(OH)_3 \qquad (10)$$
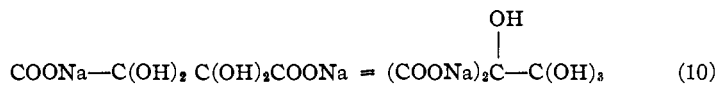
and we can thus understand why this salt loses carbon dioxide and water *simultaneously* when it is carefully heated (see experimental section). The carbon dioxide comes from the newly formed ortho-carboxyl group, $-C(OH)_3$, not from the pre-existing, neutralized groups.

The two characteristic reactions which dihydroxy-tartaric acid undergoes simultaneously, *viz.*, rupture and rearrangement (7 and 8), like all simultaneous reactions, may have their relative velocities profoundly influenced by experimental conditions. Weak alkali, acting without undue increase in temperature, gives chiefly rearrangement, and only about 6% of the acid is ruptured. Stronger alkali, aided by heat, will increase the velocity of the rupturing process so that 50% or more of oxalic acid may be found. Heat, without alkali, produces rupture only to the extent of about 1%.

It is a striking phenomenon that rearrangement should be the preferred mode of adjusting the valence or electronic strains in such a complex molecule. It is equally suggestive that rearrangement occurs without the aid or influence of reagents.

[5] Denis, *Am. Chem. J.*, **38**, 589 (1907).
Latham, *Chem. Zentr.*, [II] **1908**, 1050.
[6] Blaise and Courtot, *Bull. soc. chim.*, [3] **35**, 362 (1896). The same authors describe another case of carboxyl shift, *ibid.*, p. 969. Cf. Tiffeneau, *Rev. gen. sci.*, **18**, 588 (1907) for a discussion of this type of rearrangement.

Experimental Part.

Preparation of Sodium Dihydroxy-tartrate.—Crude nitro-tartaric acid, as obtained after filtration from the sulfuric acid mixture[7] is stirred into a thin paste with cracked ice, and solid sodium carbonate added until the solution is nearly neutral. If too much has been added, make slightly acid with acetic ácid. Under no circumstances must sodium *hydroxide* be used, as both nitro-tartaric and dihydroxy-tartaric acids are decomposed by it. The solution is allowed to stand, preferably immersed in cold water, for about 2 days. Sodium dihydroxy-tartrate deposits slowly, and may be filtered off from time to time. It should be thoroughly washed on the filter, and spread out in a thin layer for rapid drying. Yield, from 100 to 125% of the weight of tartaric acid taken.

As thus obtained, the salt is pure enough for all practical purposes. Previous investigators have failed to note the enormous tendency of this salt to occlude other salts, and their analytical data must therefore be regarded as uncertain. In fact, it may be doubted whether anyone has ever had a *pure* specimen of sodium dihydroxy-tartrate under observation. The best that I have been able to obtain was secured by redissolving 100 g. in just sufficient 3 N hydrochloric acid, and precipitating by an equal volume of 3 N sodium acetate; the precipitate was washed, first by decantation and then by suction, with 13 liters of water. The washing was continued long after the filtrates failed to give an opalescence with silver nitrate. The air-dried product contained 0.158% sodium chloride. When the hydrochloric acid was replaced by sulfuric, much larger amounts of sulfate were occluded.

Composition—The following data were obtained from the product just described, and have been corrected for sodium chloride content:

Loss on heating to ° C.		%.	Ignition residue (Na_2CO_3). %.
150	Very slow	37.85	39.97
150	Very slow	37.85	40.00
165	Slow	37.75	39.95
170	Rapid	37.78	40.02
75	5 hours	2.05	...
96–97	40 hours	2.00	...
96–97	40 hours	2.06	...
Calculated for $Na_2C_4H_4O_8 \cdot 2 H_2O.$			2.5 H_2O.
$3 H_2O + CO_2$		37.40	39.48
Na_2CO_3		40.43	39.10

These data agree well with a water content of 2 mols., and not with 2.5 mols as claimed by Fenton. The rate of loss in weight on heating is very irregular; samples heated side by side varied widely on intermediate weighings.

[7] THIS JOURNAL, **43,** 578 (1921).

Oxidation by Permanganate.—Fenton has proposed to use sodium dihydroxy-tartrate for the quantitative estimation of sodium, employing the potassium salt as reagent. The precipitated sodium salt is to be oxidized with permanganate. The method offers considerable advantages, as each atom of sodium requires 3 equivalents of oxygen. Fenton found, however, that the actual amount of oxygen consumed was always somewhat less than 3 equivalents. Part of this is accounted for by the occlusion referred to above. There are also irregularities in the action of the permanganate itself, and these were investigated during the present study.

It was found that these irregularities were caused entirely by partial formation of tartronic acid; for whereas solutions of dihydroxy-tartaric acid, freshly made and kept quite cold, used up exactly 3 oxygen equivalents, the same solutions after heating until all the dihydroxy acid had been converted into tartronic acid required but little more than two equivalents. This can be accounted for by the loss of some volatile product, such as formaldehyde or carbon monoxide. Formaldehyde was carefully sought for, but not found.

Quantitative and consistent results were obtained by first oxidizing with permanganate in alkaline solution, then completing in acid with excess of permanganate, using oxalic acid to secure the end point. As a reliable method of determining sodium will have considerable value, a few details will be given here; it is quite likely that the interference caused by occlusion can be minimized or obviated.

Using 0.5000 N permanganate solution, direct titration in cold acid solution gave, with samples of about 0.4 g. average weight, 99.8, 95.9, 94.7, 96.1, 93.0 and 94.3%.

Direct titration after boiling with dil. sulfuric acid, gave 62.0, 69.0, 63.7 and 73.5%.

Addition of sodium hydroxide, after boiling sample, before boiling, and together with permanganate followed by boiling respectively, then acidifying after excess of permanganate had acted hot, then finishing with oxalic acid, gave 100.1, 99.8 and 99.9%.

A final series was then made, using 0.1000 N permanganate with the following series of manipulations, in order: add dil. sodium hydroxide solution, heat, add excess of permanganate, boil for a few minutes, cool slightly, acidify with dil. sulfuric acid, add 0.1 N oxalic acid solution gradually, with boiling, until all of the manganese dioxide has gone into solution, cool slightly, and finish with permanganate. The sample (0.1059 g.) used 24.30- 24.35- 24.10- 24.20- 24.10 cc. of permanganate. Calculated, 24.25 cc.

Loss of Carbon Dioxide on Heating Sodium Dihydroxy-tartrate.—

It was shown above that the salt may be heated for nearly two days without any loss except absorbed moisture, below 97°. No carbon dioxide is given off. At or very near 100°, the substance loses weight again. Kekulé ran his tests "im dampfschrank." At this temperature weeks are required to reach constant weight. At 110° the process had not completed itself after 5 days. At 150° to 160°, a single hour suffices.

In all cases, carbon dioxide makes its appearance simultaneously with water, in agreement with Kekule's observations. In one test the salt was heated in a boat within a tube passing through a Freas air-bath; a current of washed, dried air traversed the tube and a trap containing lime water. A temperature equilibrium at 105° was established before introducing the boat. The lime water became turbid within 2 minutes.

Attempts were made to measure the ratio of loss of water to that of

carbon dioxide; but owing to the irregularity in the rate of total loss referred to above, no results of value were obtained.

Formation of Oxalic and Glyoxalic Acids.—If the rupturing process shown in Equation 7 accompanies the rearrangement of sodium dihydroxy-tartrate into sodium tartronate, the heated salt must be *acidic* in proportion to such rupture, since a new carboxyl group is formed.

Twenty-five g. of salt was heated to 160° for 1 hour, and required 5.5 cc. of 0.1 N sodium hydroxide solution to neutralize. This corresponds to 0.55% rupture. Twenty-five g. of salt was next boiled with 100 cc. of water until no more gas was given off; the mixture was allowed to cool and the volume restored, and boiled again. Twelve and one-tenth cc. of alkali was needed to neutralize the acid, equivalent to 1.2% rupture.

The two lots were combined, and phenylhydrazine acetate added. A yellow precipitate formed promptly, insoluble in dil. hydrochloric acid, soluble in sodium carbonate, slightly soluble in ether, easily soluble in alcohol, m. p. 137° (uncorr.), thus identifying it as the phenylhydrazone of glyoxalic acid.

The quantitative estimation of the amount of oxalic acid formed proved very troublesome. This was due to the presence of large amounts of tartronic acid, which also gives an insoluble calcium salt. After the details of the permanganate method for determining tartronic acid (see above) had been worked out, it was possible to use this method on a mixture of calcium tartronate and oxalate, and from the amount of oxygen consumed calculate the proportion of each salt present.

There were some additional difficulties. Calcium tartronate has a different composition when precipitated hot than when formed in the cold. It is also markedly soluble in excess of calcium chloride in the cold, and comes down very slowly when these solutions are boiled. It is therefore necessary to precipitate the mixed acids very slowly and carefully from boiling solutions, and to avoid excess of calcium chloride as much as possible. Nor is this all; the mixed precipitates must be dried at about 170–180°; but calcium oxalate, thus dehydrated, is enormously hygroscopic. Any water present in the sample will decrease the amount of permanganate required, and thus increase the apparent percentage of oxalate.

The results obtained may be summarized briefly. Two samples of sodium dihydroxy-tartrate were carefully warmed with a slight excess of 3 N sodium hydroxide solution until dissolved. The yields of oxalic acid were 5.9 and 6.4% respectively. Ten g. of salt was next dissolved in a slight excess of 3 N hydrochloric acid, and the solution added quickly and without cooling to a considerable excess of 6 N sodium hydroxide solution. The yield of oxalic acid was 9.4%.

Finally, 18 g. of nitrotartaric acid, dissolved in 50 cc. of alcohol, was slowly run into a solution of 15 g. of sodium hydroxide in 150 cc. of alcohol, with water cooling. A yield of 51% of oxalic acid was obtained.

From this last lot, it was possible to secure a small amount of glycolic acid as calcium salt.[8]

[8] Böttinger, *Ber.*, **13**, 1932 (1880), has shown that glyoxalic acid is unstable in the presence of alkalies, and goes over into a mixture of glycolic and oxalic acids. He states that the recovery of the glycolic acid is very difficult, which can be confirmed. Cf. Debus, *Ann.*, **338**, 322 (1905) for a careful study of this reaction.

Summary.

1.   Dihydroxy-tartaric acid, considered as a diketone, has a structural resemblance to benzil.

2.   This resemblance extends to the reactions of the two compounds.

3.   The conversion of dihydroxy-tartaric acid and its salts into tartronic acid is an analog of the rearrangement of benzil to benzilic acid.

4.   The composition and behavior of sodium dihydroxy-tartrate are discussed.

5.   Data are given which will help in the development of the method proposed by Fenton for the direct quantitative estimation of sodium.

BERKELEY, CALIFORNIA.

SPIRO-PYRIMIDINES. III. CONDENSATION OF CYCLOPROPANE-1,1-DICARBOXYLIC ESTER WITH UREAS.

By ARTHUR W. DOX AND LESTER YODER.

Received May 19, 1921.

The preparation of *spiro*-pyrimidines containing 4- and 6-membered hydrocarbon rings has been described in our previous papers.[1] The corresponding 3-membered ring with one of its carbon atoms identical with the 5-carbon atom of barbituric acid was cited as the simplest derivative of this type. Certain difficulties were encountered in preparing such derivatives, hence the discussion was reserved for a later paper. The condensation of cyclopropane-1,1-dicarboxylic ester with urea was readily effected, but the product was so entirely different in its properties from the corresponding cyclobutane and cyclohexane derivatives that it was thought advisable to repeat the work. It has now become evident that a very stable polymer is formed in this reaction, and although its constitution has not been definitely established, it seems advisable to publish the results thus far obtained, for the reason that further work along this line is not contemplated.

Preparation of Ethyl Cyclopropane-1,1-dicarboxylate.

This substance has been prepared by Perkin.[2]

In view of the tediousness of Perkin's process and the smallness of the yield, we undertook to apply the method by which we obtained good results in the preparation of cyclobutane-1,1-dicarboxylic ester. According to Perkin there is in this case, much less tendency toward the formation of the open chain tetracarboxylic ester.

[1] Dox and Yoder, THIS JOURNAL, **43**, 677–84, 1366–71 (1921).

[2] Perkin, *Ber.*, **17**, 54–9 (1884); *J. Chem. Soc.*, **47**, 808 (1885); *ibid.*, **51**, 849–53 (1887).