CCLXXXVIII.—*The Oxidation of Tartaric Acid by Solutions of Silver Salts.*

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It was shown by Claus (*Ber.*, 1875, **8**, 950) that when tartaric acid is oxidised with ammoniacal silver nitrate the resulting solution contains oxalic acid, and that the oxalic acid does not account for the whole of the tartaric acid used. It is now shown that when an excess (6—8 mols.) of silver nitrate is used the solution slowly deposits 6 atoms of silver per mol. of tartaric acid. In addition to the oxalic acid, formic acid, carbon dioxide, and water are formed in quantities agreeing with the equations

$$C_4H_6O_6 + 3Ag_2O \rightarrow 2(CO_2H)_2 + 6Ag + H_2O \quad . \quad . \quad . \quad . \quad . \tag{1}$$
$$C_4H_6O_6 + 3Ag_2O \rightarrow (CO_2H)_2 + H{\cdot}CO_2H + CO_2 + 6Ag + H_2O \tag{2}$$
$$C_4H_6O_6 + 3Ag_2O \rightarrow 2H{\cdot}CO_2H + 2CO_2 + 6Ag + H_2O \quad . \quad . \tag{3}$$

The quantity of oxalic formed varies considerably according to the conditions. Temperature and dilution have no very marked effect, but the chief variation is caused by the concentration of alkali. The concentration of ammonia cannot be varied greatly, since it is restricted, on the one hand by the amount necessary to effect solution, and on the other by the fact that too much ammonia makes the reaction inconveniently slow. In the experiments in Table I the reaction mixture consisted of 20 c.c. of *N*/10-sodium tartrate and 63 c.c. of *N*/10-silver nitrate, to which was added the volume of *N*-ammonia shown in the table. The last column gives the number of mols. of oxalic acid obtained from one mol. of tartaric acid.

TABLE I.

Expt.	C.c. of *N*-ammonia.	Mols. of oxalic acid.
1	8	0·4150
2	12	0·5139
3	13	0·5885
4	15	0·7260
5	16	(Incomplete after one week.)

TABLE II.

Expt.	C.c. of *N*-NaOH.	C.c. of *N*-NH_3.	Mols. of oxalic acid.
3	—	13	0·5885
6	1	14	0·8932
7	2	19·5	1·318
8	4	23·5	1·410
9	6	24	1·468
10	8	28·3	(Incomplete.)

The alkalinity of the solution can be further increased by the addition of caustic soda. This causes the precipitation of silver oxide and necessitates the addition of larger quantities of ammonia. The reaction takes place readily, however, in the presence of quantities of ammonia which would inhibit it in the absence of the caustic soda. The marked increase in the quantity of oxalic acid produced in this way is shown in Table II.

The increase in the yield of oxalic acid is due more to the caustic soda than to the ammonia. This is demonstrated by Expts. 4 and 6 : each had 15 c.c. of *N*-alkali, but in Expt. 6 the substitution of 1 c.c. of caustic soda for 1 c.c. of ammonia caused an increase of 23% in the yield of oxalic acid.

The Course of the Reaction.

The first attack of the tartaric acid might take place by :

(*a*) Splitting off one terminal carbon atom.
(*b*) Splitting off the two terminal carbon atoms symmetrically.
(*c*) Symmetrical rupture at the central bond.

(*d*) Oxidation to and subsequent rupture of dihydroxytartaric acid.

(*a*) With α-hydroxy-acids generally, oxidation with ammoniacal silver nitrate takes place readily, giving rise to carbon dioxide and the lower acid. When mandelic acid was used in this way, there was a distinct odour of benzaldehyde, showing that the aldehyde of the lower acid is an intermediate stage. It appears that with α-hydroxy-aldehydes oxidation with silver salts splits off the terminal carbon atom as formic acid. This is shown with aldoses such as glucose, where formic acid is the chief product of the reaction (Tollens, *Ber.*, 1883, **16**, 921). Then with an αβ-dihydroxy-acid we should expect the following changes :

$$\begin{aligned} R\cdot CH(OH)\cdot CH(OH)\cdot CO_2H &\longrightarrow R\cdot CH(OH)\cdot CHO + CO_2 \\ &\longrightarrow R\cdot CHO + H\cdot CO_2H + CO_2. \end{aligned}$$

In this way, tartaric acid would give carbon dioxide, formic acid, and glyoxylic acid. Glyoxylic acid in this reaction is found to give oxalic and formic acids and carbon dioxide, the last two being in equimolecular proportions. The complete change following this course would agree with equations (2) and (3).

(*b*) If the tartaric acid were split as above at both ends of the molecule, we should have

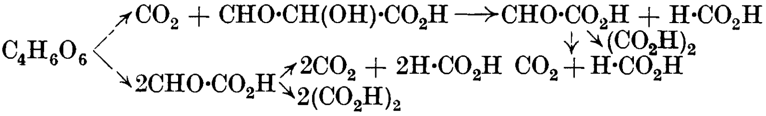
$$C_4H_6O_6 \longrightarrow CHO\cdot CHO + 2CO_2.$$

Glyoxal was tried in the reaction, however, and required 4 mols. of silver nitrate, producing no oxalic acid but equimolecular quantities of formic and carbonic acids. This would require the deposition of 8 atoms of silver instead of 6 for the complete reaction.

(*c*) Symmetrical rupture at the central bond, without previous oxidation to dihydroxytartaric acid, would probably first give 2 mols. of glyoxylic acid, each of which would oxidise, partly to oxalic acid, and partly to formic and carbonic acids : this would agree with equations (1) and (3).

(*d*) If dihydroxytartaric acid were an intermediate stage in the reaction, its further oxidation should require 2 mols. of silver nitrate; it was found, however, to deposit quantities of silver varying from 2·3 to 5·4 atoms per mol. of the acid used.

Hence changes (*b*) and (*d*) are ruled out, leaving as the possible courses of the reaction :



$$\begin{tikzcd}
 & CO_2 + CHO\cdot CH(OH)\cdot CO_2H \arrow[r] & CHO\cdot CO_2H + H\cdot CO_2H \arrow[d] \arrow[dr] & \\
C_4H_6O_6 \arrow[ur] \arrow[dr] & & CO_2 + H\cdot CO_2H & (CO_2H)_2 \\
 & 2CHO\cdot CO_2H \arrow[r] \arrow[dr] & 2CO_2 + 2H\cdot CO_2H & \\
 & & 2(CO_2H)_2 &
\end{tikzcd}$$

EXPERIMENTAL.

The substance to be oxidised was generally used in $N/10$-solution. The required quantity of the solution was mixed with the silver nitrate and ammonia in a conical flask which was connected to a long U-tube containing mercury to prevent loss of ammonia during the reaction. The flask was heated in a water-bath, usually at 60—62°. In most cases, 48 hours sufficed to complete the reaction, but when a large excess of ammonia was used the heating had to be continued for a further two or three days.

Analysis.—The silver deposited was filtered off and washed, first with water, then with ammonia, to remove any silver oxide or oxalate; thereafter it was dissolved in nitric acid and estimated with standard potassium thiocyanate. The filtrate and washings from the silver were treated at the boiling point with calcium nitrate solution. The precipitated calcium oxalate was dissolved in dilute sulphuric acid and titrated with standard permanganate.

To estimate the formic acid it was found necessary to remove the excess of silver left in the solution. This was done by adding sulphuric acid to the filtrate from the calcium oxalate and saturating the acid solution with hydrogen sulphide. The silver sulphide was filtered off and washed, and the filtrate and washings were left on the water-bath at about 70° until all the hydrogen sulphide had been driven off. Sodium carbonate was then added in excess, and the heating continued on the steam-bath until all the ammonia had been removed. A known excess of standard permanganate was then added (sufficient to give a purple solution), and the mixture left on the water-bath for 20 minutes. After acidification with sulphuric acid, the excess of permanganate was estimated by means of standard oxalic acid. Test experiments carried out with formic acid solutions of known strength showed that this method gave results usually 1—2% low, some formic acid probably escaping during the expulsion of the hydrogen sulphide. It was necessary to remove ammonia before the oxidation of the formic acid, otherwise the results varied between wide limits.

An estimation of carbon dioxide was carried out to show that the products of the reaction are formed in quantities agreeing with equations (1), (2), and (3). The reaction mixture consisted of 40 c.c. of $N/10$-tartaric acid, 125 c.c. of $N/10$-silver nitrate, and 23·1 c.c. of N-ammonia. All solutions were made with boiled-out water and the ammonia was freshly prepared by distillation from strong ammonia solution to which lime had been added. After the completion of the reaction, the solution was filtered as quickly as possible and made up to 250 c.c. In 100 c.c. of this solution, the oxalic and formic acids were estimated as described above. Another 100 c.c. portion was acidified with sulphuric acid and distilled into 20 c.c. of standard caustic soda. Carbon dioxide and some formic acid passed over in the distillate. The total acid distilled was estimated by titrating the excess of caustic soda with standard sulphuric acid. The indicator used was the minimum quantity of phenolphthalein dissolved in boiling water without alcohol. The formic acid was estimated by alkaline oxidation with permanganate, as described above. One mol. of tartaric acid gave 0·8859 mol. of oxalic acid, 1·099 mols. of formic acid, and 1·118 mols. of carbon dioxide. [For equations (1), (2), and (3), 0·8859 mol. of oxalic acid require 1·1142 mols. each of formic acid and carbon dioxide.]

Glyoxal.—A solution of glyoxal (B.D.H.) was made containing approximately 0·1 mol. per litre. This solution was estimated with alkaline permanganate as in the case of formic acid (Found : oxalic acid, nil; Ag, 3·889, 4·149 atoms per mol. of glyoxal).

Glyoxylic Acid.—The calcium salt was prepared by the method of Debus (*Annalen*, 1856, **100**, 2). It was treated with sulphuric acid and distilled in steam. The acid in the distillate was estimated with baryta. Oxidation with ammoniacal silver nitrate gave, per mol. of glyoxylic acid : Silver, 1·997 atoms; oxalic acid, 0·1712 mol.; formic acid, 0·8165 mol.

Dihydroxytartaric Acid.—The sodium salt was washed ten times with water, well pressed, and dried in a vacuum desiccator. The dried salt was weighed out and mixed with water in a measuring flask. The mixture was well cooled and sufficient nitric acid added to dissolve the salt. When it was treated with ammoniacal silver nitrate, a black precipitate formed immediately. The mixture was left for some hours at the temperature of the laboratory in order to avoid heating unchanged dihydroxytartaric acid. The reaction was completed by heating for 2 days at 65°. The quantity of silver deposited varied considerably, but in each case was greater than 2 atoms per mol. of the original salt. Found, per mol. of dihydroxytartaric acid :

Silver	5·44	2·4	4·2 atoms.
Oxalic acid	0·226	1·895	0·435 mols.

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