

## XX.—*Interaction of Glycerol and Oxalic Acid.*

By FREDERICK DANIEL CHATTAWAY.

ALTHOUGH the interaction of glycerol and oxalic acid is no longer employed to prepare formic acid on a large scale, it is still the simplest process for obtaining a small quantity in the laboratory, and is a practical exercise habitually performed by students. The more complicated decomposition which takes place when the initial product is heated to a higher temperature is by far the most convenient source of allyl alcohol, and is invariably used for its preparation.

The explanations, which are given in most textbooks, of these familiar reactions are fundamentally incorrect.

Oxalic acid reacts with glycerol as it does with other alcohols, both an acid and a normal oxalate being produced.

The former,\* like all such compounds, is unstable at a slightly

\* This explanation of the production of formic acid has been suggested as an obvious alternative in Wade's and Richter's text-books, but no evidence in support of it is brought forward.

elevated temperature, and decomposes when this is reached into carbon dioxide and monoformin. The oxalic acid subsequently added displaces the formic acid from the monoformin, and the cycle of operations is repeated.

That this is the correct explanation of the reactions leading to the production of formic acid is shown by the observations that glycerol and oxalic acid interact readily at temperatures below that at which carbon dioxide begins to be evolved, and that, although the acid oxalate which must be formed has not yet been isolated, the products of its interaction with aniline and with ammonia, oxanilic acid, and oxamic acid respectively are readily obtainable.

That the whole course of the reaction is as above stated is rendered practically certain by the fact that a precisely similar cycle of operations can be carried out with ethyl alcohol and oxalic acid when the products can easily be isolated at every stage.

As is well known, ethyl hydrogen oxalate, which is formed when ethyl alcohol and oxalic acid are heated together, and which can be distilled under diminished pressure, decomposes into carbon dioxide and ethyl formate when heated under ordinary atmospheric pressure, this being the source of the ethyl formate always obtained in such quantity when the product of heating together oxalic acid and ethyl alcohol is distilled.

Oxalic acid, when heated with ethyl formate, displaces the formic acid, producing ethyl hydrogen oxalate.

It is possible, although it seems unlikely, that the peculiar decomposition of monoformin, invariably stated in textbooks to be the source of allyl alcohol, can occur to a very limited extent, but the chief, if not the sole, source of the allyl alcohol is the normal oxalic ester, dioxalin,

$$\begin{array}{c} \text{CH}_2 \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ | \qquad \qquad | \\ \text{O} \cdot \text{CO} \cdot \text{CO} \cdot \text{O} \end{array}$$
 This on heating decomposes

into carbon dioxide and allyl alcohol.

The presence of this compound in the reaction mixture, after the first evolution of carbon dioxide has ceased, is shown by the production of oxamide or oxanilide when ammonia or aniline is added. These can only be produced from a normal ester of oxalic acid, and the more complicated esters in which two glyceryl residues are united by two oxalyl residues, although they may exist, are unlikely to be produced in large amount.

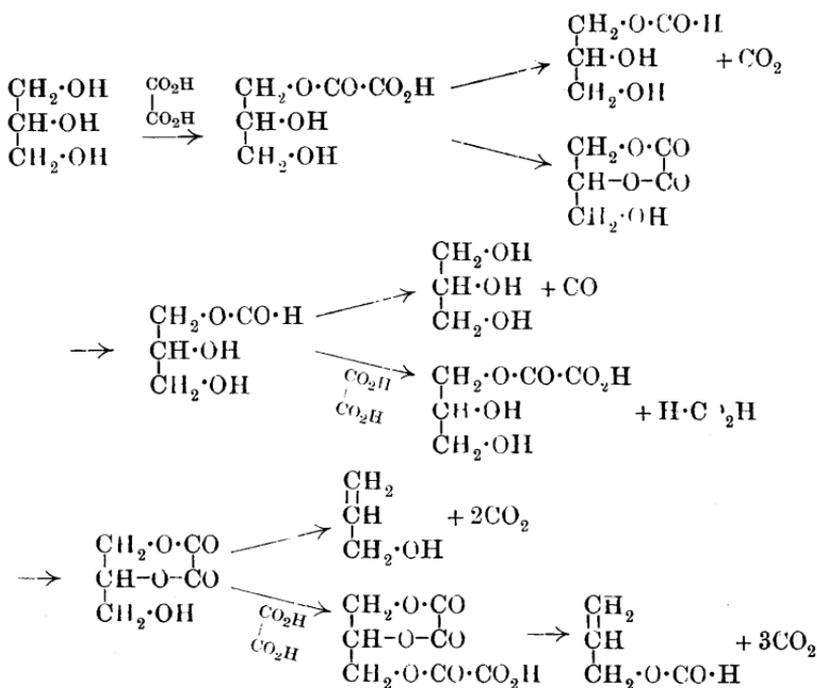
As the quantity of oxamide obtainable always corresponds, within the limits of experimental error, with the amount of allyl alcohol obtainable, the correctness of this theory of the process is established.

The allyl formate, a little of which is always obtained as a by-product, results from a similar decomposition of monoformo-

dioxalin,  $\begin{array}{c} \text{CH}_2 \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CHO} \\ | \quad | \\ \text{O} \cdot \text{CO} \cdot \text{CO} \cdot \text{O} \end{array}$ , which is produced from monoformin by the action of oxalic acid or from dioxalin by the formation and decomposition of an acid oxalate.

The small amount of acrolein and the large quantity of carbon monoxide which also are formed as by-products in the reaction result from the decomposition of glycerol and monoformin respectively by heat, the latter yielding carbon monoxide and glycerol, as formic acid yields carbon monoxide and water, when heated.

The main reactions, resulting in the production of formic acid, allyl alcohol, allyl formate, and carbon monoxide respectively, should therefore be formulated thus\*:



#### *Action of Anhydrous Oxalic Acid on Ethyl Formate.*

One hundred grams of ethyl formate (2 mols.) were heated to boiling for five hours with 60 grams (1 mol.) of anhydrous oxalic acid. Eleven grams of oxalic acid, which crystallised out on cooling, were filtered off, and as much as possible of the unchanged ethyl formate distilled off under the ordinary pressure on a water-bath.

\* In the first action, either the  $\alpha$ - or the  $\beta$ -hydroxyl group may interact, the first only is represented as acting. Di- and possibly tri-formin may also be similarly produced in small quantity and react similarly.

The mobile, strongly acid, pungent-smelling residue, which weighed 71 grams and still contained some ethyl formate, was fractionated under diminished pressure, when 12 grams of formic acid, 20 grams of ethyl hydrogen oxalate, and 12 grams of ethyl oxalate were obtained.

*Action of Anhydrous Oxalic Acid on Glycerol.*

Nine grams of finely-powdered anhydrous oxalic acid (1 mol.) were thoroughly mixed with 184 grams (20 mols.) of glycerol (D 1.2638), and the acid dissolved by warming to about 50° for a short time. The liquid was then allowed to remain for three months at the laboratory temperature, small weighed quantities being removed from time to time, and the free acid titrated with *N*/10-potassium hydroxide. The titre fell rapidly at first, and more slowly afterwards, until it became practically constant at about 54 per cent. of its original value. No recognisable amount of carbon dioxide was at any time given off.

An excess of concentrated aqueous ammonia was added to a quantity of the final product, when a copious precipitate consisting of oxamide and ammonium oxamate was formed. The addition of concentrated aqueous ammonia to a similar quantity which had been neutralised as rapidly as possible by *N*/10-potassium hydroxide gave no oxamide, showing that the normal ester is very rapidly partly hydrolysed to a salt of the acid ester.

When concentrated aqueous ammonia is added to precipitate the oxamide this partial hydrolysis takes place to a considerable extent, so that a much larger yield of oxamide with a correspondingly smaller yield of ammonium oxamate is obtained when a saturated alcoholic solution of ammonia is used.

When the product obtained as above by the interaction of oxalic acid and glycerol is warmed for some hours to about 90° with excess of aniline, a mixture of oxanilic acid and oxanilide is produced, which can easily be separated on account of the sparing solubility of the latter.

The fall of the titre and the production of these compounds show that an acid ester and a normal ester are formed without evolution of carbon dioxide when glycerol and oxalic acid interact.

If such a mixture is heated until the first evolution of carbon dioxide ceases and is then allowed to react with alcoholic ammonia or aniline, although oxamide or oxanilide is obtained as before, neither oxamic acid nor oxanilic acid is produced, showing that during the first evolution of carbon dioxide the acid oxalic ester is decomposed.

In the normal ester the oxalyl residue must be attached in the

manner shown in the formula  $\begin{array}{c} \text{CH}_2 \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{OH}, \\ | \qquad \qquad | \\ \text{O} \cdot \text{CO} \cdot \text{CO} \cdot \text{O} \end{array}$  or in some similar way. This normal ester decomposes during the second evolution of carbon dioxide, for if the product left when the disengagement of gas has ceased is treated with ammonia no oxamide is obtained.

In order to prove experimentally that the allyl alcohol is formed by the decomposition of this normal ester, it is necessary to show that the amount of the latter formed corresponds with the amount of allyl alcohol obtainable by further heating the product.

Sixty-three grams of anhydrous oxalic acid and 252 grams of glycerol, the relative proportions found most advantageous by Tollens and Henninger, were mixed and heated for a few hours to 80—90° on a water-bath, and then under diminished pressure until the temperature of the liquid reached 180°. The product thus obtained weighed 280 grams. A tenth of this (28 grams) was cooled, mixed with a cold saturated solution of ammonia in absolute alcohol, and a rapid stream of dry ammonia passed through the liquid for some minutes. The heavy, white precipitate of oxamide which was deposited was collected, well washed with hot water and alcohol, and dried. It was found to weigh 1·8 grams. The remainder (252 grams) was then heated under the ordinary atmospheric pressure until the temperature of the liquid reached 270°. The distillate, which weighed 24·5 grams, was allowed to remain over dry potassium carbonate, then separated, the potassium carbonate washed with a little ether, and the mixed liquids fractionated, using a distilling column. Nine grams of allyl alcohol of correct boiling point were obtained.

The amount of oxamide precipitated from the one-tenth shows that in the remainder which was distilled there must have been 26·8 grams of the normal ester, which should have yielded 10·6 grams of allyl alcohol.

The result is within the limits of experimental error considering the conditions of the experiment, and proves that the formation of allyl alcohol is due to the decomposition of the normal ester. The quantity of allyl formate produced was too small to be isolated satisfactorily; if its amount could have been determined the approximation would have been somewhat closer.

On treating with alcoholic ammonia, the residue left after heating to 270°, from which no more allyl alcohol could be obtained, no oxamide was precipitated.

The carbon monoxide so freely liberated during the later stages of the heating is formed by the decomposition of the mono- and possibly di-formin produced during the first evolution of carbon

dioxide, whilst the acrolein also produced is due to a decomposition of the glycerol itself at the high temperature of the reaction. The whole of the monoformin is not destroyed at the temperature at which the normal ester decomposes, and if the residue, even after heating to 250—260°, is distilled in a current of steam a small quantity of formic acid can be obtained.

In conclusion, the author desires to express his thanks to Mr. Dalziel, General Manager of Price's Candle Company, who kindly supplied him with the specially distilled glycerol (D 1·2638) with which the work was carried out.

UNIVERSITY CHEMICAL LABORATORY,  
OXFORD.

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