XXXI.—*On the Formation of Anthrapurpurin.*

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WHEN alizarin was first prepared from anthraquinone by treating it with sulphuric acid and decomposing the resulting product with caustic alkali, its formation was naturally believed to be due to the decomposition of a disulpho-acid of anthraquinone. This is now generally known to be incorrect, experience having shown that it is the monosulpho-acid which yields the colouring matter.

Graebe and Liebermann (*Ann. Chem. Pharm.*, clx, 121) some years ago showed that the result of treating the monosulpho-acid of anthraquinone with caustic alkalis, was in the first place the formation of monoxyanthraquinone—

And in the second place, that this substance when further treated with alkalis, becomes oxidised and converted into alizarin—

But at that time it was believed that the disulpho-acid was the proper compound to employ for the preparation of alizarin, the reaction

* This hydrogen is not evolved, but reduces a part of the products back to anthraquinone or hydroanthraquinone. This is avoided on the large scale by the introduction of a small quantity of potassium chlorate.

appearing more simple than the above, and practically a mixture of both sulpho-acids was used on the large scale. It is now known, however, that the disulpho-acid yields anthrapurpurin and not alizarin: hence the artificial product at first manufactured was invariably a mixture of these two colouring matters, but they are now sent into the market separately as well as mixed.

But how is the formation of anthrapurpurin from the disulpho-acid to be accounted for?

It is known that, by the action of caustic alkalis on this acid, monosulphoxyanthraquinonic acid is formed (*Jour. Chem. Soc.*, vol. xxiii, p. 139)—

This when further treated with caustic alkalis, changes into what was originally supposed to be alizarin, but is really anthrapurpurin.

Since I first became acquainted with the fact, I have been under the impression that an intermediate body must exist, having the composition of alizarin, and formed simply by the replacement of the (SO₃H) group by (OH) in the monosulphoxyanthraquinonic acid.

Dr. Schunck and H. Roemer (*Deut. Chem. Ges. Ber.*, 1875, p. 1628) have published an account of a substance isomeric with alizarin, obtained from some bye-products sent by me to Dr. Schunck several years ago. Some time since I also obtained this body myself from a portion of the same bye-product, and have since been engaged in experiments on its direct formation from the disulpho-acid of anthraquinone. It is, I believe, the intermediate product just referred to.

I have succeeded in obtaining it directly by heating a salt of the disulpho-acid with a dilute solution of caustic potash. I used a five per cent. solution, and only sufficient to contain an amount of alkali a little in excess of that required by theory; the mixture was placed in a strong mercury bottle, the plug being well luted and tightly screwed down, and then heated in an oil-bath to 180°—190° C. for six or seven hours. In this way scarcely any anthrapurpurin was formed, the product being a red-brown solution. On treating this with acids, large quantities of sulphurous anhydride were given off, and a yellow precipitate was formed; this was collected on a filter and washed. On treating it with cold baryta-water, it mostly dissolved. The solution when concentrated deposited a dark-coloured product, apparently crude baric anthraflavate, leaving a dark-red solution

which, when acidified, gave a greenish-yellow precipitate, containing a large quantity of this new isomeride of alizarin *Isoanthraflavic acid*.* This was purified by repeated crystallisations from glacial acetic acid, in which it is difficultly soluble. Dried at 180° C. it gave the following numbers on analysis:—

- I. ·2395 of substance gave—
 ·6184 of CO₂ and
 ·0726 of H₂O.
 II. ·2558 of substance gave—
 ·6611 of CO₂ and
 ·0799 of H₂O.

Theory for C ₁₄ H ₈ O ₄ .		Experiment.	
		I.	II.
Carbon	70·0	70·41	70·48
Hydrogen	3·33	3·42	3·47

The crystals when heated in the air-bath lose their lustre. They dissolve easily in baryta-water, forming a dark-red solution, and in concentrated sulphuric acid forming also a red solution; in fact, the compound possesses all the properties described by Dr. Schunck and H. Roemer.

When strongly heated it sublimes in leaves of a golden or orange colour, a good deal being carbonised. This sublimed product, when crystallised from glacial acetic acid, is deposited in orange-yellow needles, differing in this respect from the unsublimed, which is of a yellow colour; its composition and properties however remain unchanged. It gave on analysis the following numbers:—

- 2465 of substance gave—
 ·6353 of CO₂ = 70·28 p.c. carbon, and
 ·0759 of H₂O = 3·42 of hydrogen.

With fuming nitric acid it gives a crystalline nitro-acid, but no phthalic acid could be obtained.

On heating it with acetic anhydride to 160°—170°, a pale yellow solution was obtained. On distilling off part of the anhydride, the residue deposited on cooling pale yellow crystals of the acetylic derivative: these were pressed and dried. The specimen used in analysis I was made with sublimed isoanthraflavic acid; that used for II was unsublimed—

- I. ·2617 of substance gave—
 ·6413 of CO₂ and
 ·0856 of H₂O.

* Since reading this paper before the Society, Dr. Schunck and H. Roemer have published a second paper on the same subject, and given this name, which I have adopted to avoid confusion (*Deut. Chem. Ges. Ber.*, 1876, p. 379).

854 PERKIN ON THE FORMATION OF ANTHRAPURPURIN.

II. .2724 of substance gave—
 .6688 of CO₂ and
 .0909 of H₂O.

Theory for C ₁₄ H ₆ (C ₂ H ₃ O) ₂ O ₄ .		Experiment.	
		I.	II.
Carbon	66.66	66.83	66.96
Hydrogen.....	3.70	3.63	3.70

This diacetisoanthraflavic acid is difficultly soluble in alcohol and benzol, but more soluble in glacial acetic acid. Its fusing point appears to be easily influenced; for example, if the crystals which separate from acetic anhydride be examined, the fusing point is found to be about 175° C., but if this product be recrystallised from glacial acetic acid or alcohol, its fusing point will be found to be about 180°. Schunck and Roemer, in their second paper, do not appear to have obtained a definite fusing point for this substance.

Isoanthraflavic acid, when heated to about 180°—185° with an excess of caustic alkali for some time, is entirely changed, yielding a black-looking product which dissolves in water with a beautiful purple colour. On acidifying this, a yellow precipitate is obtained which, when washed with water, dyes mordanted cloth the same colour as anthrapurpurin. Its solution in sodic carbonate does not colour freshly-precipitated alumina, and its potassic solution gives the characteristic bands of anthrapurpurin, with which in fact I have no doubt it is identical.

Dr. Schunck kindly sent me a specimen obtained by himself and Mr. Roemer, and on treating it with alkali it gave the same results.

It appears, then, that in the formation of anthrapurpurin from disulphanthraquinonic acid, there are three successive reactions.

Firstly, the formation of sulphoxyanthraquinonic acid.

Secondly, the formation of isoanthraflavic acid, and

Thirdly, the formation of anthrapurpurin by the oxidation of this latter substance, thus—

isoanthraflavic acid standing to anthrapurpurin as oxyanthraquinone does to alizarin.

I have endeavoured to reverse the process and prepare isoanthraflavic acid from anthrapurpurin by the process by which Liebermann and Fischer (*Deut. Chem. Ges. Ber.*, 1875, xiii, 974) obtained purpuroxanthin from ordinary purpurin.

Anthrapurpurin when heated with ammonia produces an amide derivative, as observed some time since (*Jour. Chem. Soc.*, xxvi, 432). This, when dissolved in boiling alcohol and treated with nitrous acid, yielded a product which when sublimed and crystallised from acetic acid, was obtained in golden needles, and yielded a colouring matter when heated with alkali, dyeing mordants the same colour as anthrapurpurin. I have not had sufficient of this substance to examine it more fully, but, being still engaged with the subject, I hope shortly to be able to give a more detailed account of my results in this direction.

In alizarin, undoubtedly, both hydroxyls are in the same benzene group.

But it would appear that in the disulpho-acid of anthraquinone the replacement occurs in both groups.

This would account for the non-production of alizarin from this substance when it is heated with an alkali, the resulting product being an isomer :

Anthrapurpurin being produced from a substance of this nature evidently has the constitution :

At any rate, it cannot have the three hydroxyls in one benzene group, otherwise it should give phthalic acid on treatment with nitric acid.

It is probable that a number of isomeric anthrapurpurins may be obtained from the many isomerides of anthraflavic acid now known. Liebermann has already obtained one of these from chrysazin. Moreover, both anthraflavic acid and anthraflavone give colouring matters when heated with alkalis.