

LXXII.—*On some Derivatives of Anthraquinone.*

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DURING some experiments on the sulphonic acids of anthraquinone it was observed that the sodium salts of these acids were decomposed in a somewhat remarkable way when submitted to dry distillation. As the compounds formed appeared to be of considerable interest, we have investigated them more closely.

The sodium salt employed in the following experiments was the so-called "silver salt" which is produced in such large quantities in alizarin factories, and which consists of nearly pure sodium anthraquinonemonosulphonate.

The specimen used was soluble in water, forming a clear neutral solution, which gave no coloration with caustic soda, and thus showed the absence of hydroxyanthraquinone-derivatives. Dried at 120° and ignited with nitrate of ammonia, 0.2005 gram gave 0.0467 gram $\text{Na}_2\text{SO}_4 = 23.29$ per cent.; calculated for $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{SO}_3\text{Na} = 22.97$.

The dry distillation of this salt was carried out in an iron tube $8'' \times 2''$ welded together at one end. A piece of gas piping, bent at a right angle, was screwed into the aperture of this tube, and its open end passed through a loose wooden lid into a large cylindrical copper vessel which served as a condenser. The retort was charged with about 150 grams of salt, and heated over an ordinary fire. After a few minutes, yellowish-brown vapours were evolved which easily condensed in the receiver, and these continued to come off until the end of the operation, the whole distillation usually occupying about half an hour.

The distillate was a brownish, fluffy mass, mixed with a small quantity of a slightly acid liquid containing sulphur in suspension. On unscrewing the connecting tube it was usually found to contain a small quantity of long yellow needles easily recognisable as anthraquinone.

The yield of distillate was small—on an average only about 20 per cent. of the weight of salt employed. From 55—60 per cent. of residue remained in the retort as a hard, brittle, carbonaceous mass; this, when extracted with water, yielded a strongly alkaline, green solution, which was found to consist almost entirely of sodium sulphide containing a little ferrous sulphide.

The distillate, which proved to be a mixture of several compounds, was digested for some time with boiling baryta-water. A portion dissolved, producing a blood-red solution which was separated from

the insoluble residue by filtration. The filtrate, after standing for some time, was again filtered, and then treated with dilute hydrochloric acid, which caused the precipitation of a small quantity of a straw-coloured, gelatinous substance.

This was thrown on a filter, well washed with water, and dried. After repeated recrystallisation from coal-tar naphtha, it was obtained pure in the form of pale-yellow needles, which on analysis gave the following numbers:—

0.2058 gram substance gave 0.0693 H_2O and 0.5641 CO_2 .

	Found.	Theory: $\text{C}_{14}\text{H}_8\text{O}_3$.
C	74.75 per cent.	75.00 per cent.
H	3.74 ,,	3.57 ,,
O	21.51 ,,	21.43 ,,

It was therefore metahydroxyanthraquinone, the compound produced by fusing anthraquinonemonosulphonic acid or metabromoanthraquinone with potash (Graebe and Liebermann, *Annalen*, **160**, 141), and agreed in properties with this compound in every respect. It melted at about 300° (metahydroxyanthraquinone 302°), and gave an easily soluble barium salt (distinction from orthohydroxyanthraquinone).

The residue insoluble in baryta-water was repeatedly extracted with boiling glacial acetic acid, until the extracts became of a pale, yellowish colour. These extracts, when filtered from the insoluble residue and cooled, deposited a dirty yellowish substance, which was separated from the mother-liquors, well dried, and sublimed. The sublimate, which appeared to consist chiefly of anthraquinone, was extracted with small quantities of hot coal-tar naphtha, in order to free it from traces of a more soluble substance, and the residue repeatedly recrystallised from the same solvent. On analysis it gave the following numbers, showing it to be anthraquinone:—

0.1207 gram substance gave 0.0448 H_2O and 0.3554 CO_2 .

	Found.	Theory: $\text{C}_{14}\text{H}_8\text{O}_2$.
C	80.30 per cent.	80.77 per cent.
H	4.12 ,,	3.84 ,,
O	15.58 ,,	15.39 ,,

This compound crystallised in yellow needles, melting at 271 — 273° (anthraquinone melts at 273°). On heating it in a test-tube it sublimed in the beautiful way so characteristic of anthraquinone, and had, moreover, all the properties of that compound.

On evaporating the mother-liquors from the above crystals they deposited a small quantity of metahydroxyanthraquinone which had

escaped extraction in the first instance. The residue, after having been extracted a few times with glacial acetic acid as described above, was digested with large quantities of glacial acetic acid and filtered, this operation being repeated until the whole was dissolved. On cooling the solutions thus obtained a yellowish-red substance separated out, which under the microscope was seen to consist for the most part of minute crystals. By carefully recrystallising this substance several times from the same solvent, it was obtained pure in the form of a spongy mass of minute reddish-yellow needles, which sometimes had a silky lustre. The greatest care was necessary in order to obtain this substance well crystallised, the method found to give the best results being the following:—A saturated solution in boiling acetic acid was filtered into a flask standing on a sand-bath and containing a small quantity of boiling acid, the funnel being so arranged that the greater portion was heated by the vapour evolved. After filtration the lamp was removed, and the whole allowed to stand in a place free from draught. The separation of the substance, which commenced after several minutes, was peculiar, reminding one somewhat of a fungoid growth. It started at the bottom of the vessel in small spongy tufts which gradually grew until the whole liquid was filled with crystals. If the solution be quickly cooled, or agitated during cooling, the substance is deposited in a more or less gelatinous condition. The following numbers were obtained on analysis, each sample being from a different preparation.

I.	0.1248	gram substance gave	0.0390	H ₂ O	and	0.3425	CO ₂ .
II.	0.1745	„ „	0.0526	H ₂ O	„	0.4815	CO ₂ .
III.	0.1358	„ „	0.0420	H ₂ O	„	0.3728	CO ₂ .
IV.	0.1415	„ „	0.0437	H ₂ O	„	0.3899	CO ₂ .
V.	0.1354	„ „	0.0418	H ₂ O	„	0.3740	CO ₂ .

	Found.							
	I.	II.	III.	IV.	V.		C ₂₈ H ₁₄ O ₆ .	C ₁₄ H ₈ O ₃ .
C..	74.84	75.25	75.19	75.16	75.33	p. c.	75.34	75.00 p. c.
H..	3.46	3.35	3.43	3.29	3.43	„	3.14	3.57 „
O..	21.70	21.40	21.38	21.55	21.24	„	21.52	21.43 „

This compound therefore appears to have the formula C₂₈H₁₄O₆, rather than that of C₁₄H₈O₃, which is also borne out by its properties. It is practically insoluble in all the usual solvents in the cold, and only very sparingly soluble in boiling acetic acid, from which it seems to crystallise best. For ordinary purposes it is therefore only necessary to extract the crude product from the destructive distillation of the sodium anthraquinonemonosulphate with alcohol or acetic acid

until the more soluble portion has been removed, and to use for further reactions the sparingly soluble residue, which consists of the compound $C_{28}H_{14}O_6$ in an almost pure state. On distillation with zinc-dust, the compound $C_{28}H_{14}O_6$ gave anthracene—recognised by its melting point (215°), and from the fact that it gave anthraquinone on oxidation. When heated, it melts at a temperature much above 300° , to a reddish-black liquid, which on further heating sublimes as a reddish powder, only a small quantity of charcoal being left. It dissolves in concentrated sulphuric acid in the cold, forming an intense magenta-coloured solution, from which on the addition of water it is precipitated unchanged in the form of a transparent yellow jelly. When heated to a high temperature with fuming sulphuric acid, it dissolves, forming an orange-coloured solution resembling anthraquinonesulphonic acid, with which, however, it is not identical. At very high temperatures a small quantity of a colourless, crystalline sublimate was obtained. This readily dissolved in a hot solution of sodium carbonate, and on addition of acid, extraction with ether, and evaporation of the ethereal extract, colourless needles were obtained, which were easily recognised as phthalic acid.

A boiling mixture of nitric and sulphuric acids dissolves it, and on addition of water a white substance is precipitated, which separates in an amorphous condition from its boiling solution in ordinary solvents. The compound $C_{28}H_{14}O_6$ is, curiously enough, absolutely insoluble in alkalis. When fused with caustic soda it dissolves, forming a violet mass, which has the properties of sodium alizarate, and which, on solution in water and treatment with acid, gives a yellow precipitate; this dyes mordanted cloth in a way perfectly analogous to alizarin.

As it was important to be sure of the formation of alizarin, a quantity of the red body was heated with a strong solution of caustic soda in an iron tube at 180° , and the sodium alizarate, after dilution with water and filtering, purified by conversion into the lime salt. On acidifying this salt with hydrochloric acid, a yellowish mass was precipitated, which after being collected, well washed with water, and recrystallised, was found to melt at 277° (alizarine melts at 275°). The identity of these two substances was further proved by the similarity of the spectra of their solutions.

Heated with zinc-dust and caustic soda the compound $C_{28}H_{14}O_6$ dissolves, and forms a blood-red solution, which on exposure to the air is decolorised, the original compound being reprecipitated. In this respect the substance very much resembles anthraquinone.

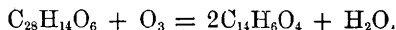
Oxidation of the Compound $C_{28}H_{14}O_6$.

If a boiling saturated solution of this substance in glacial acetic acid be treated with chromic acid, a violent reaction sets in, and, on cooling, a whitish substance separates. As it was thought that the examination of this reaction might give some clue to the constitution of the compound $C_{28}H_{14}O_6$, it was carried out on a large scale in order to obtain the white substance in sufficient quantity for analysis. For this purpose the boiling solution of the red compound was treated with chromic acid, in small quantities at a time, until it was no longer reduced. The boiling was then continued for a short time, and the solution allowed to cool. After standing for some hours, the green solution had deposited a quantity of a white crystalline substance, which was collected, well washed with water, and dried at 100° . After being purified by several crystallisations from coal-tar naphtha, it was obtained in the form of colourless transparent plates melting at $292-295^\circ$. On analysis the following numbers were obtained:—

- I. 0.1546 gram substance gave 0.0439 gram H_2O and 0.3988 gram CO_2 .
 II. 0.1196 gram substance gave 0.0327 gram H_2O and 0.3096 gram CO_2 .

	Found.		Theory. $C_{14}H_6O_4$.
	I.	II.	
C	70.35	70.59 per cent.	70.59 per cent.
H	3.15	3.03 ,,	2.52 ,,
O	26.50	26.38 ,,	26.89 ,,

The compound has therefore the formula $C_{14}H_6O_4$, and is formed from the compound $C_{28}H_{14}O_6$ according to the equation—



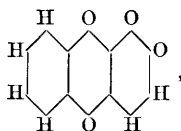
It is almost insoluble in boiling benzene, slightly soluble in boiling coal-tar naphtha and acetic acid, more soluble in boiling aniline; on cooling, it separates from the latter, in the form of transparent needles. It is quite insoluble in alkalis, and can therefore contain no hydroxyl-group.

When heated it first melts to a straw-coloured liquid, and then sublimes almost without decomposition. It yields anthracene when distilled with zinc-dust. On warming with phenylhydrazine it yields a red substance, which, however, has not been obtained in sufficient quantity for analysis. The hot alcoholic solution of the compound $C_{14}H_6O_4$ gives, on the addition of ferric chloride, a reddish-brown coloration. When heated with strong alcoholic potash, a violet solution is first

obtained, which, however, again becomes colourless on shaking with air. If the heating be repeated, a reddish-brown solution is obtained.

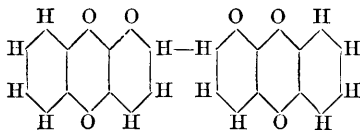
If the substance is heated with aqueous potash and a trace of zinc-dust, a violet solution is produced, which on the addition of more of the reducing agent changes to olive-green. On agitating with air, the solution becomes first violet and then colourless, the original compound being reprecipitated. With zinc-dust and ammonia a violet solution is produced, which becomes colourless in contact with the air.

From the study of these properties, it seems that the compound $C_{11}H_6O_4$ must have the following formula:—



it being an orthoquinone of anthraquinone.

The red substance $C_{28}H_{14}O_6$ has therefore probably the constitution—



being a derivative of di-anthracene.

These formulæ, however, require further experimental proof before they can be looked upon as being definitely settled. It is also intended to investigate the behaviour of the α - and β -salts of anthraquinone-disulphonic acid when submitted to dry distillation.