II.—*On some Derivatives of Anthracene.*

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IN the "Chemical News" of the 22nd July last, I published a short note upon some new derivatives of anthracene, and referred more particularly to the products resulting from the action of sulphuric acid upon dichlor- and dibromanthracene. I now beg leave to lay before the Society a more detailed account of my experiments in this direction, with the addition of a few other observations relating to the history of anthracene.

DICHLORANTHRACENE.

I have found it convenient to prepare this substance by passing chlorine gas over benzole holding about one-fifth its weight of purified commercial anthracene in suspension, until the mixture becomes a crystalline pasty mass. The product is then thrown on a linen filter, drained, and well washed with cold benzole. It is then dried and further purified, first by distillation, and then by two or three crystallisations from benzole. Thus obtained it presents itself as golden-yellow coloured needles.

Analysis of this product gave the following numbers :—

- I. .3151 of substance gave
 .3624 of AgCl.
- II. .6258 of substance gave
 .7333 of AgCl.
- III. .3607 of substance gave
 .8974 of CO₂ and
 .1073 of H₂O.
- IV. .3143 of substance gave
 .7833 of CO₂ and
 .0957 of H₂O.

These numbers agree with the formula—

as the following comparisons show :—

Theory.		Experiment.			
		I.	II.	III.	IV.
C ₁₄	168 68·02	—	—	67·85	67·97
H ₈	8 3·24	—	—	3·30	3·38
Cl ₂	71 28·74	28·45	28·95	—	—
	<hr/> 247 100·00				

It will be observed that these results perfectly agree with those of Graebe and Liebermann.* Dichloranthracene, when gently heated, sublimes in beautiful needles, which may be obtained of considerable size. It is fluorescent in the solid state as well as when in solution.

* Ann. Chem. Pharm., Supp. vii, 259 (1870).

When a boiling solution of dichloranthracene in benzole is added to a similar solution of picric acid, the mixture assumes a dark orange-red colour, and on cooling becomes filled with small bright red needles. These consist of a compound of dichloranthracene and picric acid. A determination of the dichloranthracene in this body gave numbers closely approximating to those required by the formula—

DIBROMANTHRACENE.

The product used in my experiments was prepared by Graebe's process*. It was however purified first by distillation and then by crystallisation from benzole. Thus obtained it is of a golden-yellow colour. It gave on analysis the following numbers :—

·3205 of substance gave
·5864 of CO_2 , and
·0729 of H_2O .

These numbers closely agree with those required by the formula—

as the following comparisons will show :—

	Theory.		Experiment.
C_{14}	168	50·00	49·9
H_8	8	2·38	2·52
Br_2	160	47·62	—
	<hr/> 336	<hr/> 100·00	

Like dichloranthracene, this body produces a beautiful red compound with picric acid.

Action of Sulphuric Acid on Dichloranthracene.

Dichloranthracene when submitted to the action of fuming sulphuric acid dissolves, forming a bright green solution, and is at the same time converted into a sulpho-acid.

To prepare this acid, one part of dichloranthracene is added

* Ann. Ch. Pharm., Suppl. vii (1870).

to about five parts of fuming sulphuric acid, and the mixture heated for a short time on the water-bath. It is then gradually poured into several times its bulk of water and treated with baric carbonate until all the sulphuric acid is neutralized. The acid solution when filtered off from the baric sulphate is evaporated to a small bulk. When sufficiently concentrated, it becomes on cooling a slimy mass of minute orange-yellow coloured crystals which may be drained on a porous tile.

This acid has not been analysed, but from the composition of its salts evidently possesses the formula—

I therefore propose to call it—*Disulphodichloranthracenic Acid*.—It is easily soluble in water, from which it is precipitated upon the addition of a little concentrated sulphuric or hydrochloric acid. It possesses a strongly acid taste and character. The dilute solutions of this acid and its salts are remarkably fluorescent, but not so strongly as an alkaline solution of pure *Æsculine*. The colour of the fluorescence is blue.

Sodic Disulphodichloranthracenate.—This salt can be obtained by neutralizing the acid with sodic carbonate, or from the calcic or crude baric salt by double decomposition. To obtain it from the latter, the product of the action of sulphuric acid on dichloranthracene is entirely neutralized with baric carbonate. Sodic sulphate is then added in the proportion of about five parts of dry salt to every ten parts of dichloranthracene employed, and the mixture well boiled; it is then filtered and the filtrate concentrated. On standing for some time, the new sodic salt separates in small orange-red crystals. These are well pressed between bibulous paper and purified by one or two crystallisations; dried at 150° C., they gave the following numbers on analysis:—

I.	·2284	gram.	of substance	gave
	·0693	„	Na ₂ SO ₄ .	
II.	·3449	„	of substance	gave
	·4694	„	CO ₂ , and	
	·0559	„	H ₂ O.	

These numbers give percentages agreeing with those required by the formula—

as the following comparisons will show :—

	Theory.		Experiment.	
			I.	II.
C_{14}	168	37·25	—	37·11
H_6	6	1·33	—	1·80
Cl_2	71	15·74	—	—
Na_2	46	10·20	9·83	—
S_2	64	14·19	—	—
O_6	96	21·29	—	—
	<hr/> 451	<hr/> 100·00		

This salt dissolves easily in water, forming an orange-coloured solution.

Baric Disulphodichloranthracenate.—This salt is best obtained in the pure state by the addition of baric chloride to a solution of the pure sodic salt. It is then thrown down as a bright canary-yellow coloured precipitate, nearly insoluble in water. The analysis of this salt gave the following numbers :—

I.	·2023	gram. of substance gave
	·0859	„ BaSO_4 .
II.	·0845	„ of substance gave
	·0360	„ BaSO_4 .
III.	·1534	„ of substance gave
	·0658	„ BaSO_4 .
IV.	·4179	„ of substance gave
	·4637	„ CO_2 , and
	·0560	„ H_2O .
V.	·4117	„ of substance gave
	·4549	„ CO_2 , and
	·0571	„ H_2O .
VI.	·3059	„ of substance gave
	·3438	„ CO_2 , and
	·0448	„ H_2O .
VII.	·5936	„ of substance gave
	·6767	„ CO_2 , and
	·0878	„ H_2O .

These give percentages agreeing tolerably well with the formula—

The following is a comparison of the theoretical and experimental numbers:—

Theory.			Experiment.						
			I.	II.	III.	IV.	V.	VI.	VII.
C ₁₄	168	30.99	—	—	—	30.26	30.13	30.65	31.09
H ₆	6	1.11	—	—	—	1.48	1.54	1.62	1.64
Ba....	137	25.28	24.96	25.05	25.22	—	—	—	—
Cl ₂	71	13.10	—	—	—	—	—	—	—
S ₂	64	11.81	—	—	—	—	—	—	—
O ₆	96	17.71	—	—	—	—	—	—	—
	542	100.00							

If to a hot solution of sodic disulphodichloranthracenate, strongly acidified with hydrochloric acid, baric chloride be added, no change at first is observed, but on standing a short time the above baric salt separates as an orange-coloured crystalline precipitate.

The following numbers were obtained on analyzing a specimen prepared in this manner:—

•1723 of substance gave

•0742 of BaSO₄ = 25.32 per cent. of barium.

Strontic Disulphodichloranthracenate.—On adding a solution of strontic chloride to a solution of sodic disulphodichloranthracenate, no apparent change takes place; but if the solution be evaporated, the new strontic salt separates in yellow crusts, difficultly soluble in water. A specimen gave the following numbers on analysis:—

•3146 of substance gave

•1136 of SrSO₄ = 17.21 per cent. of strontium.

The formula

Calcic Disulphodichloranthracenate.—This salt may be obtained by neutralizing the product of the action of sulphuric acid on dichloranthracene with calcic carbonate, filtering

off the calcic sulphate, and evaporating the filtrate to dryness. The residue is extracted with water, filtered, and again evaporated. This salt is of a yellow colour, and easily soluble in water. It is useful for the preparation of the sodic salt by double decomposition with calcic carbonate.

Action of Sulphuric Acid upon Dibromanthracene.

Dibromanthracene dissolves in fuming sulphuric acid, forming a sulpho-acid. This has not, however, been prepared in a pure state, but from the examination of its salts it evidently possesses the formula—

and may therefore be called *disulphodibromanthracenic acid*. It is crystalline, and its dilute solutions are fluorescent, as also are its salts, but not nearly to the same extent as those of the corresponding dichloro-acid.

Sodic Disulphodibromanthracenate.—To obtain this salt one part of dibromanthracene is dissolved in the cold in about six or seven parts of fuming sulphuric acid, and the mixture allowed to stand for an hour or two. It is then gradually added to several times its bulk of cold water, well stirred, and neutralized with baric carbonate. Sodic sulphate is then added in the proportion of about five parts of dry salt to every twelve parts of dibromanthracene employed, and after boiling, the resulting sodic salt is filtered off from the baric sulphate, concentrated by evaporation over the water-bath, and set aside to crystallise. It is then well drained and pressed from the mother-liquor, and purified by two or three crystallisations from water.

Thus obtained, it is of a yellow colour, and crystallises in microscopic needles. It is easily soluble in water. It gave on analysis the following numbers:—

- I. 0.4676 of substance gave—
0.1256 of $\text{Na}_2\text{SO}_4 = 8.70$ p.c. sodium.
- II. 0.4809 of substance gave—
0.1311 of $\text{Na}_2\text{SO}_4 = 8.85$ p.c. sodium.

The formula

Baric Disulphodibromanthracenate.—This salt may be obtained in precisely the same manner as the corresponding disulphodichloranthracenate. It is obtained as a pale yellow precipitate. It gave on analysis the following result :—

·5565 of substance gave—

·2026 of $\text{BaSO}_4 = 21.41$ p.c. barium.

The formula

This salt is remarkable for its insolubility. If a boiling solution of the sodic salt be strongly acidified with hydrochloric acid, and baric chloride added, the mixture, which is for a few seconds perfectly clear, becomes rapidly turbid with the formation of this salt, which cannot be re-dissolved, even by vigorous boiling, notwithstanding the excess of hydrochloric acid present.

Oxidation of Disulphodichloro- and Disulphodibromanthracenic Acid.—These sulpho-acids, when subjected to the influence of oxidizing agents, rapidly decompose, exchanging their chlorine or bromine for oxygen, and are thus converted into disulphanthraquinonic acid.

An analogous result is also obtained by heating them with concentrated sulphuric acid, the following reactions taking place :—

A quantity of disulphanthraquinonic acid, prepared by heating disulphodichloranthracenic acid with concentrated sulphuric acid, was made into the baric salt,* and analysed. The following results were obtained :—

- I. ·2273 of substance gave—
 ·1040 of $\text{BaSO}_4 = 26\cdot90$ p.c. barium.
 II. ·3093 of substance gave—
 ·1415 of $\text{BaSO}_4 = 26\cdot89$ p.c. barium.

The formula

Graebe and Liebermann have shown that dichlor- or dibrom-anthracene, when oxidized, also exchange their chlorine or bromine for oxygen, yielding anthraquinone.†

Whilst making the foregoing experiments, I have often been struck with the remarkable fluorescence of many of the anthracene products, anthracene itself, when pure and in large crystals, being one of the most beautifully fluorescent solid bodies I know of, though curiously its solutions are comparatively poor in this respect.‡ As this hydrocarbon, and also its chlorine derivative, which is fluorescent both in the solid state and in solu-

* I may here remark, that the baric disulphanthraquinonate although more soluble than the baric salts of the sulpho-acids obtained from dichlor or dibromanthracene is, like them, precipitated from hot solution in the presence of an excess of hydrochloric acid, if the solution be not too dilute; a specimen, prepared in this manner, gave the following results upon analysis :—

·2135 grm. of substance gave
 ·0981 $\text{BaSO}_4 = 27\cdot01$ per cent.; theory, 27·23.

† When endeavouring to obtain some highly chlorinated anthracene derivatives, some time since, I came across a rather unexpected instance of this kind.

A quantity of dichloranthracene was suspended in glacial acetic acid and chlorine passed through the mixture. On allowing this to stand, a large quantity of a white product was obtained, which, when crystallised from benzole, was analysed, and gave of carbon 80·65 per cent., and of hydrogen 4·14 per cent. It was, in fact, anthraquinone, which requires of carbon 80·77, and of hydrogen 3·85, and had been formed owing to the presence of a small quantity of water in the glacial acetic acid, thus :—

‡ The anthracene used in these experiments was chemically pure, and gave the following numbers on analysis :—

	I.	II.	Theory.
Carbon	94·31	94·37	94·38
Hydrogen	5·68	5·78	5·62

tion are volatile, it appeared to me interesting to examine them in the state of vapour. So far as I have gone, however, my experiments seem to show that the vapour of anthracene or dichloranthracene is not fluorescent, and moreover, a ray of light sent through a length of about 4 inches of the vapour of either body still retained its power of rendering fluorescent solutions luminous.

On sealing up anthracene in a long vacuum tube with platinum poles, and allowing the discharge from an induction coil to pass through the tube, nothing particular is observed, except the beautiful fluorescence of the crystals of anthracene. On examination with the spectroscope, the light showed carbon and nitrogen lines, the latter arising from the presence of a little air in the tube. Upon heating the tube, however, somewhat strongly, so as to volatilise the hydrocarbon, the ordinary colour of the discharge changed to a magnificent deep azure blue, and what is remarkable is that this blue light, when examined with the spectroscope, is perfectly continuous, and consists of blue with a little green.

Dichloranthracene, when treated in a similar manner, gives an analogous result, but suffers a good deal of decomposition, anthracene changing but little. These curious results do not appear to be due to the fluorescent character of the substances employed, as naphthalene produces a similar effect, the blue light, though not so intense, being continuous. It must be observed, however, that this hydrocarbon undergoes considerable change, becoming brown and oily.

Anthraquinone, heated in a vacuum tube in the same way, gives a greenish blue light, showing faint carbon bands.

On exposing a solution of disulpho-dichloranthracenic acid to the light of one of the recent displays of the aurora borealis, it was very strongly illuminated, as might be expected: moonlight, on the other hand, had no perceptible effect either upon it, or an alkaline solution of æsculin.