XXXI.—*On the Constitution of Anthracene or Paranaphthaline, and some of its Products of Decomposition.* By THOMAS ANDERSON, M.D., F.R.S.E., Professor of Chemistry in the University of Glasgow.

(Read 29th April 1861.)

The solid compounds of carbon and hydrogen form a class of substances to which chemists have scarcely, as yet, paid that attention which their importance and interest appear to merit. With the exception of naphthaline, very little is known regarding them, and it is remarkable that the numerous and varied products of decomposition obtained from that singular substance should not have induced a more minute examination of the kindred compounds, whose existence has been indicated by different chemists. The interest attaching to these compounds is all the greater because, according to their discoverers, several of them are isomeric, or at least polymeric, with naphthaline; and a more careful examination of them might be expected to throw some light on their intimate constitution, and relations to that body.

Not less than five substances said to be polymeric with naphthaline have been described. These are paranaphthaline or anthracene, metanaphthaline or retisterene, pyrene, and two substances not yet named, which occur along with benzine and benzophenone among the products of the destructive distillation of benzoate of lime, and are apparently quite distinct from one another and the other three. All of these substances, except naphthaline, have hitherto been obtained in small, and some of them in very minute quantity, so that their constitution has been in most instances fixed by analysis alone; and the difficulties attending the analysis of highly carbonaceous compounds at the time they were made, as well as the absence of any control derived from the examination of their products of decomposition, have naturally occasioned some doubts as to the accuracy of the formulæ assigned to them.

Paranaphthaline or anthracene, which was discovered by DUMAS and LAURENT in the year 1832,* is the only one of these substances whose examination has extended beyond the mere analysis; and the determination of its vapour density by the former chemist gave for it the formula $C_{30}H_{12}$, which the examination of some of its decomposition products by the latter was supposed to confirm. A critical examination of LAURENT'S experiments by no means bears out this opinion. They are in many respects extremely imperfect, have obviously been

* Annales de Chimie et de Physique, vol. l. p. 187.

made on a very small quantity of material, and the formulæ (mostly deduced from a single analysis) are so improbable, that there can be but one opinion as to the necessity for submitting the subject to a further investigation.

Anthracene, as is well known from the observations of DUMAS and LAURENT, is met with only among the latter portions of the distillation of coal-tar. It has been little seen by chemists, because hitherto the distillation has not generally been pushed so far as to yield it in quantity; but during the last few years, the demand for the asphalt and the higher oils having increased, the distillation has been carried further, and it has been found abundantly in some of the products, and even been used in the manufacture of machinery grease. I have availed myself of the opportunity which a large supply afforded of extending the examination of anthracene, and with the result of showing that its constitution differs from that attributed to it by its discoverers, and that it is not polymeric with naphthaline.

Before entering on the details of my own experiments, it may be advisable to recapitulate shortly the history of the substance. As already stated, it was discovered by DUMAS and LAURENT, working in concert, in 1832, and described by the former chemist, who attributed to it the formula $C_{30}H_{12}$, with which his results corresponded very closely. In 1835 LAURENT* described, under the name of paranaphthalese, a compound for which he gives the formula $C_{30}H_8O_4$, and he appears to have considered it to be a direct product of the action of nitric acid on anthracene. In a subsequent paper† he extends his investigation in this direction, and describes no less than five different nitro-compounds, and assigns to them very problematical formulæ. In this paper he again refers to paranaphthalese, but under the name of anthracenuse, giving for it the formula $C_{30}H_7O_5$, and stating that it is not a product of the direct action of nitric acid on anthracene, but formed by the decomposition of a nitro-compound, in a manner precisely similar to that in which naphthase is obtained from nitronaphthaline. He mentions that a substance of similar properties is obtained from several of the nitro-compounds he prepared, but leaves it an open question whether it is in all cases the same, or whether it differs in constitution according to the nitro-compound from which it is produced. He also describes a chlorine substitution product, and adopts the name of anthracene; a change even then advisable, and which the results of my investigation show to be quite indispensable.

Crude anthracene is in the form of a soft yellow mass, not unlike palm oil, but with a greenish tinge and harder consistence; in this state, it contains a little naphthaline and a considerable quantity of oil of high boiling point, which causes it to leave a greasy stain on paper, and to melt easily when rubbed between the fingers. It has a decided though not a strong smell, due partly to the naphthaline,

* Annales de Chemie et de Physique, vol. lx. p. 220.

† *Ibid.*, vol. lxxii. p. 415.

but still more to the oil with which it is contaminated, and which it loses on purification. It is soluble, though not abundantly, in alcohol, but dissolves with tolerable facility in ether, turpentine, and still better in benzole. Methylated spirit was in the first instance used for its purification, and the first solution, on cooling, deposited thick oily globules, along with a small quantity of crystals; but after several successive quantities of spirit had been used, crystals were deposited free from oil, but still retaining the yellow colour of the original substance, and apparently, owing to the removal of the oil, they were much less soluble in new quantities of spirit. By repeated crystallisations, it was found possible to obtain the anthracene quite colourless; but the process was too tedious to be employed for preparing it on the larger scales. Other solvents, and more particularly benzole, were likewise tried; but, though preferable, the complete removal of the colouring matter is difficult with them also, and it was found necessary to commence by distilling the crude substance in a small iron still. The first portions which passed over during the process contained much naphthaline and oil, but they were quite free from colour. As the distillation proceeded, however, the colour gradually increased, and at the end a small quantity of a dark green substance remained in the retort. The first portions of the distillate were pressed to remove the oil, and the last portions redistilled so as to get rid of the colour as completely as possible, and the purification finished by repeated crystallisation from benzole, and sometimes by sublimation.

Anthracene is deposited from its solutions in perfectly colourless scales, generally of very small size even when large solutions have been allowed to cool. Those obtained from spirit are generally the best, and when suspended in the solution have a fine satiny lustre, which they lose to some extent when dried. From benzole its crystals are somewhat granular, and less brilliant in appearance. By sublimation, it is got in thin plates resembling those of naphthaline, but smaller and of inferior lustre. When quite pure it has no smell, but it is apt to retain a trace of oil, which communicates to it a faint empyreumatic odour. It is entirely devoid of taste. It is not volatile at ordinary temperatures, but is slowly volatilised in the water bath. At higher temperatures it sublimes freely. It melts at 416° F. into a transparent colourless fluid, which, on cooling, solidifies into a foliated crystalline mass, and at a higher temperature distils unchanged. It is insoluble in water, sparingly soluble in alcohol, but more so in ether, benzole, and the volatile oils. The alkalies are without action upon it, but sulphuric acid dissolves it, and acquires a green colour, with the formation of a sulpho-acid; and nitric acid, even when moderately dilute, acts rapidly upon it. Chlorine and bromine form substitution products.

The analysis of anthracene at first presented some difficulties. When oxide of copper was employed in the usual way, the carbon was always deficient, while chromate of lead gave an accurate result with that element, but a marked excess

on the hydrogen.* Oxide of copper and chlorate of potash were therefore resorted to, and with success. The results are:—

- I. { 4·715 grains of anthracene gave
16·250 grains of carbonic acid, and
2·435 grains of water.
- II. { 4·546 grains of anthracene gave
15·720 grains of carbonic acid,
2·420 grains of water.
- III. { 4·975 grains of anthracene gave
17·180 grains of carbonic acid, and
2·650 grains of water.

	Experiment.			Mean.	Calculation.		
	I.	II.	III.				
Carbon, . . .	94·00	94·31	94·18	94·16	94·38	C ₂₈	168
Hydrogen, . . .	5·74	5·91	5·92	5·85	5·62	H ₁₀	10
	99·74	100·22	100·10	100·01	100·00		178

The results correspond exactly with the formula C₂₈ H₁₀. This is precisely the constitution of a substance described some years since by FRITSCHÉ† as a new carbo-hydrogen, obtained from coal-tar, with which also its properties closely agree. A careful comparison of the two substances made by Professor FRITSCHÉ and myself, during a visit he paid to Glasgow some time since, satisfied us that his substance really is anthracene. The picric-acid compounds of the two are completely identical, and have a fine ruby-red colour, which distinguishes it from those obtained from the other carbo-hydrogens. An analysis of the compound obtained from anthracene gave—

- { 5·120 grains of picrate of anthracene gave
11·016 grains of carbonic acid and
1·629 grains of water.

	Experiment.	Calculation.		
Carbon,	58·71	58·97	C ₄₀	240
Hydrogen,	3·54	3·17	H ₁₃	13
Nitrogen,	...	6·88	N ₃	42
Oxygen,	...	30·98	O ₁₄	112
	100·00			407

This corresponds with the formula C₂₈ H₁₀ + C₁₂ H₂ (NO₄)₃ O₂, which is that given by FRITSCHÉ for his compound.

* I have had frequent occasion to observe, that in the analysis of carbo-hydrogens with chromate of lead a considerable excess of hydrogen is often obtained. I at first attributed this to impurities in the chromate, but analyses made with a pure material, specially made for the purpose, showed the same excess. I have not examined into the cause of this phenomenon.

† Erdmans Journal für Practische Chemie, vol. lxxiii. p. 282.

Action of Nitric Acid on Anthracene.

Anthracene is but little acted on by cold nitric acid, but the boiling acid, even when moderately dilute, attacks it with considerable rapidity, and the products depend upon the strength of the acid and the length of time during which the action is continued.

Oxanthracene.—When anthracene is boiled for some days with nitric acid of SG. 1·2, red fumes are evolved, and a resinous mass is obtained, which becomes hard and gritty in cooling. The same change may be more rapidly effected with acid of SG. 1·4, but the product is then liable to be contaminated with some other compounds. The substance was washed with water, and purified by crystallisation from alcohol or benzole. It is then obtained in crystals, which, when deposited from alcohol, are long silky needles, but from benzole are shorter and more compact. They have a light buff colour, have neither taste nor smell, and are insoluble in water, sparingly soluble in alcohol, and more so in benzole. They are completely soluble in boiling nitric acid of SG. 1·4, and are deposited unchanged on cooling. Concentrated sulphuric acid in the cold dissolves them with an orange colour, which becomes deep red on heating, and on dilution with water the oxanthracene is deposited unchanged. It sublimes when heated, and is deposited unaltered in fine needles of considerable length. It may be distilled without decomposition over quick-lime. Its volatility may be taken advantage of as a means of preparing it, as it is only necessary to boil anthracene in a retort with nitric acid, and to continue the heat until the acid has distilled over and the oxanthracene sublimes, any other compounds formed at the same time being decomposed. It contains no nitrogen, and analysis gave the following results:—

- I. { 4·600 grains of oxanthracene gave
13·525 grains of carbonic acid and
1·670 grains of water.
- II. { 4·987 grains of oxanthracene gave
14·770 grains of carbonic acid and
1·760 grains of water.
- III. { 4·600 grains of oxanthracene gave
13·600 grains of carbonic acid and
1·650 grains of water.

	Experiment.			Calculation.		
	I.	II.	III.			
Carbon, . .	80·19	80·77	80·63	80·77	C ₂₈	168
Hydrogen, . .	3·99	3·92	3·99	3·85	H ₈	8
Oxygen, . .	15·82	15·31	15·38	15·38	O ₄	32
	100·00	100·00	100·00	100·00		208

Its formula, therefore, is C₂₈ H₈ O₄, and it is derived from anthracene by the
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removal of two equivalents of hydrogen, and the addition of four of oxygen. It belongs to a class of substances of which there are very few examples, and for which we have no satisfactory system of nomenclature. I have given it the provisional name of Oxanthracene, as recalling its mode of formation.

Binitroxanthracene.—When anthracene was boiled for a long time with nitric acid, with occasional additions of fuming acid, red fumes continued to be given off, and a resinous substance was gradually produced. The substance was washed with water and dried. It appeared to be a mixture of some of the last substance with a new compound, which was obtained by heating it with a small quantity of alcohol, and cooling. It is deposited as a red powder which shows but little disposition to crystallise. A combustion gave—

4.907 grains of nitro-binitroxanthracene gave
10.558 grains of carbonic acid, and
1.210 grains of water.

Experiment.					
Carbon,	. . .	58.66	56.37	C ₂₈	168
Hydrogen,	. . .	2.73	2.02	H ₆	6
Nitrogen,	. . .	...	9.40	N ₂	92
Oxygen,	. . .	...	32.21	O ₁₂	32
			100.00		298

This is a distant approximation to the formula C₂₈ H₅ (NO₄)₂ O₄, and it is probable that this is its constitution; but as its properties showed nothing of interest, I did not prosecute its purification further.

Anthracenic Acid.—When the nitric acid and the washings of the preceding compound are carefully evaporated in the water-bath, a yellow crystalline acid, to which I give this name, is obtained. It is very soluble in water, and gives crystallisable salts with ammonia and potash, and precipitates the salts of lead and baryta. I reserve the further investigation of this substance for a future communication.

Action of Bromine on Anthracene.

Bromine acts somewhat slowly upon anthracene in the cold. When mixed together, they concrete into a resinous-looking mass, the interior of which is not completely saturated with bromine, and it was found most convenient to expose the anthracene in a thin layer under a bell glass, along with a capsule containing bromine. After a day or two's exposure, the anthracene has agglutinated into a mass which must be removed, reduced to powder, and reintroduced; and this is repeated as long as bromine is absorbed. This mass, which has a brown colour, dissolves in benzole, and on cooling deposits hexabrom-anthracene in crystals, which are purified by solution in benzole or ether. It is thus obtained in small hard white granular crystals, apparently rhomboidal. They are sparingly soluble in alcohol, ether, and benzole. Nitric acid acts upon them but slightly. When

heated with strong sulphuric acid they fuse, and bromine and hydrobromic acid are expelled. On digestion with alcoholic potash they immediately become yellow, and are converted into another compound. When heated to 348° F. they become brown, and at 361° fuse and give off bromine. Analysis gave the following results:—

	Experiment.				Calculation.		
	I.	II.	III.	IV.			
Carbon, . . .	25·62	25·84	25·62	...	25·53	C ₂₈	168
Hydrogen, . . .	1·59	1·59	1·72	...	1·52	H ₁₀	10
Bromine, . . .	...	...	...	72·33	72·95	Br ₆	486
					100·00		658

The formula is C₂₈ H₁₀ Br₆, and the substance is produced by the direct absorption of six equivalents of bromine.

Quadribrominated Anthracene.—When the preceding compound is treated with an alcoholic solution of potash, it swells up considerably and acquires a bright sulphur-yellow colour, and the solution contains bromide of potassium. This change occurs in the cold, but it is more convenient to heat the solution. The yellow powder is collected on a filter, washed, dried, and crystallised from boiling benzole. It is thus obtained in long yellow needles, having a fine silky lustre. It is very sparingly soluble in cold alcohol, ether, and benzole—more so when hot. Boiling benzole is its best solvent, but even of this it requires above a hundred times its weight. It fuses at 460°, and gives a dark coloured mass, which has undergone partial decomposition. The portions used for analysis were crystallised from benzole, and then washed with ether:—

I.	{	5·110 grains of quadribrominated anthracene gave
		6·400 grains of acid, and
		0·780 grains of water.
II.	{	5·021 grains of quadribrominated anthracene gave
		6·250 grains of carbonic acid, and
		0·750 grains of water.
III.	{	5·271 grains of quadribrominated anthracene gave
		6·560 grains of carbonic acid, and
		0·792 grains of water.

	I.	II.	III.			
Carbon, . . .	34.16	33.94	33.95	33.87	C ₈	168
Hydrogen, . . .	1.39	1.66	1.66	1.61	H ₈	8
Bromine, . . .	...	...	...	64.52	Br ₄	320
				<hr/>		
				100.00		496

This gives for the constitution of the compound C₂₈ H₈ Br₄, a somewhat unusual formula, differing from that of most similar compounds. In general, when a bromide or chloride of an organic compound is treated with potash, one half of the haloid is removed in combination with hydrogen, the remainder passing into the radical. In this case, however, only two equivalents of hydrogen are removed, and the formula of the compound ought in all probability to be written C₂₈ H₈ Br₂ + Br₂.

Action of Chlorine on Anthracene.

The examination of the compounds produced by the action of chlorine on anthracene is attended with some difficulty, the changes occurring being of a somewhat complicated kind; more than one substance being generally obtained, and the nature and proportion of the products depending very greatly on the circumstances of the experiment. Chlorine is readily absorbed by anthracene in the cold; and if the current is rapid it becomes warm, gives off hydrochloric acid in abundance, and is eventually converted into a hard cake. If the chlorine be passed through it in a slow current, the evolution of hydrochloric acid is greatly diminished, although it cannot be altogether avoided; and when this is done, and the chlorine is not continued too long, the principal product is bichloride of anthracene.

Bichloride of Anthracene.—The mass obtained by the action of chlorine dissolves readily in benzole, and on cooling, groups of radicated needles, often of considerable length, are deposited. The bichloride is readily soluble in alcohol, but only very sparingly in ether. When crystallised from alcohol, it is very liable to lose hydrochloric acid, and this change always takes place to some extent, which causes a slight excess of carbon and deficiency of chlorine in analyses:—

- I. { 5.074 grains of bichloride of anthracene gave
12.564 grains of carbonic acid, and
1.795 grains of water.
- II. { 4.614 grains of bichloride of anthracene gave
11.524 grains of carbonic acid, and
1.717 grains of water.
- III. { 4.474 grains of bichloride of anthracene gave
5.14 grains of chloride of silver.

	Experiment.			Calculation.		
	I.	II.	III.			
Carbon,	67.53	68.11	...	67.47	C ₂₈	168
Hydrogen,	3.93	4.13	...	4.02	H ₁₀	10
Chlorine,	...	...	28.40	28.51	Cl ₂	71
				100.00		249

corresponding very closely with the formula C₂₈ H₁₀ Cl₂.

Chloranthracene.—When anthracene is treated with a rapid current of chlorine continued for a short time only, this compound is produced. It may also be obtained by decomposing the preceding substance with alcoholic potash. It is soluble in alcohol, ether, and benzole, from the last of which solutions it is deposited in small hard scaly crystals. Analysis gave the following numbers:—

{ 4.285 grains of chloranthracene gave
12.375 grains of carbonic acid, and
1.720 grains of water.

	Experiment.		Calculation.	
Carbon,	78.74	79.06	C ₂₈	168
Hydrogen,	4.46	4.24	H ₉	9
Chlorine,	...	16.70	Cl	35.5
		100.00		212.5

The formula, therefore, is C₂₈ H₉ Cl.

When chlorine is passed over anthracene kept hot, it is absorbed in much larger quantity, and hydrochloric acid is abundantly evolved. The compounds thus obtained depend entirely on the length of time during which the current is continued, and products analysed at different periods were found to contain very different quantities of carbon and chlorine; and as the substances produced differ little in solubility, it was found difficult to effect their separation. When the chlorine is continued for about eight days, the product is semisolid, and the greater part dissolves easily in cold ether; and when this solution is evaporated, first an oily chloride and then crystals are deposited. The crystals are soluble in benzole, alcohol, and ether, and were found to have the following composition:—

5.558 grains of chlorine compound gave
9.680 grains of carbonic acid, and
1.280 grains of water.

	Experiment.		Calculation.	
Carbon,	47.50	47.39	C ₂₈	168
Hydrogen,	2.56	2.54	H ₉	9
Chlorine,	...	59.07	Cl ₅	177.5
		100.00		354.5

This agrees very well with the somewhat improbable formula C₂₈ H₉ Cl₅, but it is quite possible that it may be a mixture—a point which, owing to the small quantity of substance at my disposal, I was unable to determine. The oily chloride gives more than one crystalline substance when treated with alcoholic potash.

The facts now detailed are sufficient to fix the constitution of anthracene, and to show that its chemical relations are of considerable interest. Its formula connects it with certain substances derived from oil of bitter almonds; and more especially with stilbene, the carbo-hydrogen discovered by LAURENT, from which it differs by two equivalents of hydrogen. A similar relation exists between oxanthracene and benzil, as is seen by the following comparison of their formulæ:—

These relations merit a further examination, and I propose to return to the subject in a subsequent paper, which will also include the results of a further investigation of the anthracene compounds.