XXXV. *On some of the Products of the Destructive Distillation of Boghead Coal.*—Part II.

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The first part of this paper contained the results of the examination of those hydrocarbons found in the distillate from the Torbane-hill mineral which were remarkable for their resistance to the action of monohydrated nitric and sulphuric acids. It was shown that, when in a state of purity, they possessed the composition, boiling-point, and density in the fluid and gaseous states, of the radicals of the ethylic class of alcohols. The present communication enters on the study of a group of substances as distinguished by the mobility, as the former are by the fixity of their hydrogen atoms. The examination of them has involved more labour than was experienced with their companion hydrocarbons; and the quantities obtained being necessarily small, even when working on a considerable scale, it has been impossible, at present, to do more than determine their constitution. The study of their combinations and decompositions is therefore necessarily deferred.

Up to the present time we have been unacquainted with methods for the proximate analysis of complex mixtures such as that under study. It was necessary, therefore, to devise some plan for the purpose. The presence of benzole and its homologues was almost a matter of certainty, as they appear to be formed in all processes where coaly or bituminous matters are subjected to destructive distillation. In order to separate the hydrocarbons, the following method was adopted. Four ounces of bromine being placed in a large and well-stoppered flask, about eight volumes of water were added. The naphtha boiling in the fourteenth rectification between 71° and 77° Centigrade, was then added in very small portions, the whole being violently agitated after each addition. As the bromine, from its superior density, lay at the bottom of the water and the naphtha at the top, it will be seen that combination could not take place until the flask was shaken, at which time they united with a sharp hissing sound and a rise of temperature. The entire quantity of naphtha was absorbed by the bromine, forming a dense oil, becoming paler and at last colourless as the hydrocarbon increased in quantity. To ensure a definite product more bromine was used, so as to obtain a red oil, the excess being afterwards removed by agitation with mercury. During the process some substance is generated, acting powerfully on the eyes and causing a flow of tears; it is always present in the brominated oil, even when every trace of free bromine is removed. If the brominated oil be kept for some time in contact with water, it will be found that a third layer will make its appearance beneath the oil; this will be described hereafter.

On the crude bromine compound being separated and distilled, all the benzole and radicals will distil away, leaving the brominated oil, the boiling-point of which is much higher. We are not acquainted with any process for separating benzole from the radicals in such a manner as to yield the former pure, but by treatment with fuming nitric acid, in the manner described in Part I., the benzole is transformed into the nitrocompound, from which the propyle may be obtained by distillation on the water-bath.

It was necessary to ascertain whether the nitrocompound obtained by treating with nitric acid the fluid distilling away from the brominated oil, contained any substance (save nitrobenzole) capable of forming alkaloids by reduction. On treatment by BÉCHAMP's process, it yielded a considerable quantity of base having all the characters of aniline, and distilling at 182°.

To confirm this result a portion was dissolved in hydrochloric acid, and to the solution was added about a third of the quantity of bichloride of platinum necessary to precipitate the whole of the base in the state of platinum salt. The precipitate being filtered off, a fresh quantity of the bichloride was added, and so on until three precipitates were obtained. They were washed with a mixture of alcohol and ether previous to drying.

I. ·5197 gramme of the first precipitate gave ·4726 carbonic acid and ·1359 water.
II. ·2980 gramme of the first precipitate gave ·0972 platinum.
III. ·5196 gramme of the second precipitate gave ·4668 carbonic acid and ·1359 water.
IV. ·3408 gramme of the second precipitate gave ·1112 platinum.
V. ·3447 gramme of the third precipitate gave ·1128 platinum.

Or, per cent.—

	Experiment.			Calculation.		
	1st precip.	2nd precip.	3rd precip.			
Carbon . . .	24·5	24·5	.....	C^{12}	72·0	24·0
Hydrogen . .	2·9	2·9	.....	H^{8}	8·0	2·7
Nitrogen . . .	.....	.....	.....	N	14·0	4·7
Chlorine . . .	.....	.....	.....	Cl^{3}	106·5	35·6
Platinum . .	32·6	32·6	32·7	Pt	99·0	33·0
					299·5	100·0

It is evident, therefore, that the aniline procured in this manner is almost pure, the only admixture being a small portion of toluidine; and it may with safety be concluded that benzole is the only hydrocarbon (distilling away from the brominized oil) which forms a nitrocompound capable of reduction by protacetate of iron.

If the bromine compound obtained from the naphtha boiling between 71° and 77° be distilled, a thermometer being in the tubulature of the retort, no constant boiling-point will be obtained until a temperature of 123° is reached. This arises from the tenacity with which the oil retains benzole and the radicals. It was only after much labour and numerous analyses that this source of difficulty was discovered, and precautions taken to prevent its interfering with the isolation of the hydrocarbons to be presently described. If the heat be very gradually applied to the retort, ebullition will commence at about 80°, the mercury rapidly rising until 123° is reached, after which the rise becomes very slow. When the propyle and benzole have distilled away, and the point of ebullition of the fluid is elevated to 150° or upwards, rapid evolution of hydrobromic acid takes place, accompanied by a vapour acting powerfully on the eyes. The distillate at this point acquires a fine blue colour. It being plain from these phenomena that the hyperhalyde produced by the action of bromine could not be prepared in a state fit for analysis, the residue in the retort was mixed with a strong alcoholic solution of potash, in order to obtain a halyde capable of being distilled without decomposition. On mixing the two fluids there was a great rise of temperature, and a large quantity of bromide of potassium crystallized out. Sometimes the bromine compound and the alcoholic potash were cohobated together, at others the halyde was prepared by mere digestion of the ingredients and subsequent precipitation of the oil by water; even cohobation over solid hydrate of potash produced the same result. The brominated oil thus prepared was colourless, very dense, and had a powerful odour, somewhat resembling iodide of amyle. Although the hyperhalyde was prepared from a fraction of almost constant boiling-point, and purified carefully by distillation on the oil-bath, all coming over below 130° being rejected, yet the halyde produced from it was not homogeneous, its boiling-point varying from 80° to 150°.

MM. Berthelot and De Luca have shown in their memoir on iodized propylene the great difficulty of obtaining pure products of this class, owing to the simultaneous formation of other substances, both fixed and volatile; and it is evident that if such a difficulty is found with that substance, it must exist to a much greater extent with a homologue having so comparatively high an atomic weight as that yielding the compound under consideration. In order to lessen the sources of error, the bromine compound was fractionated previous to analysis, but, despite every precaution, numerous and perfectly concordant analyses showed the impossibility of obtaining it free from oxygen. This arose from the mode of preparation. The formula of the brominated oil was, originally, $C^{12} H^{11} Br$, but oxidation had proceeded so far as to make the composition almost agree with the expression $C^{12} H^{11} BrO$. The cause of the oxidation of the monobrominated caproylene or hexylene will become apparent from the following experiments.

It has been said that when the hydrocarbons were treated with bromine in presence of water, the fluid separated after a time into three layers, the upper being water containing a small quantity of hydrobromic acid, the middle the brominated oil, and a lower stratum. The latter, on separation by a tap-funnel, proved to be highly acid and perfectly soluble in water. It distilled, with very little evolution of acid fumes, at 127°. A piece of paper moistened with it and held near the fire, became jet-black at the spot touched. Excess of precipitated carbonate of lime was added, and, as soon as effervescence had ceased, the whole was boiled for a few minutes and filtered. The solution evaporated to dryness yielded a white and highly deliquescent mass, a qualitative analysis of which indicated the presence of bromine and calcium. A portion was heated to redness, rapidly cooled in a platinum crucible with a well-fitting lid, and the percentage of calcium estimated.

·2872 gramme of substance gave ·1447 of carbonate of lime.

	Experiment.	Calculation.
Bromine	79·85	Br 80
Calcium	20·15	Ca 20
	100·00	100

The ignited salt, on being moistened with warm water, became extremely hot, and hissed like hot metal when quenched.

The preceding salt being deliquescent, and consequently not convenient for analysis, I digested a fresh portion of the acid upon carbonate of baryta, the latter being in excess; the solution was boiled, filtered and evaporated to dryness on the water-bath. After two hours' desiccation at 100°, it gave on a determination of the barium 43·67 per cent., corresponding to the formula Ba Br, HO; requiring 43·53. By ignition the per-centage of barium was raised to 46·8. Ba Br requires 46·16. During ignition the salt became grey, but regained its original appearance when moistened with water.

A determination of the per-centage of dry hydrobromic acid in the fluid was next made.

I. 2·0624 grammes of acid gave 1·7782 of bromide of silver.

II. 1·1190 gramme of acid gave ·9720 bromide of silver.

	I.	II.
Or, per cent.—	37·2	36·96

The specific gravity of the fluid obtained in this singular manner was 1·320 at 18°. The small quantity of fumes evolved during the distillation points to the existence of a definite hydrate; H Br+15HO would contain 37·5 of hydrobromic acid, a number not far from that found by experiment. The reason for examining thus minutely the lower layer of liquid, was to trace the nature of the reaction resulting in the production of the oxidized fluid. It is plain that water was decomposed by the excess of bromine; the oxidation therefore resembled that produced by the halogens generally.

The examination of the bromine compounds was not pursued further because their products of decomposition appeared more interesting.

The results detailed render it evident that the only method of studying satisfactorily the $C^n H^n$ group as it existed in the oily fluid would be by means of its derivatives. It is well known that bodies of this class must, after the action of alcoholic potash, be regarded as bearing the same relation to the negative that the hydriodic ethers do to the positive radicals. Like them, the halogen compounds, when decomposed by metals, yield hydrocarbons, having, for four volumes of vapour, double the number of atoms of carbon and hydrogen existing in the iodides, bromides, &c., and these hydrocarbons or radicals, as they are still called, have consequently a higher boiling-point than if the number of carbon and hydrogen atoms remained the same. Thus propylene, $C^6 H^6$, is a gas, while allyle, the negative radical, $C^{12} H^{10}$, is a fluid boiling at 59°. It was therefore probable that the hydrocarbon, $C^{12} H^{12}$, would, by treatment of the bromine compound with sodium, yield a derivative boiling at about 116°.

For the purpose of acting on the bromine compound with sodium, a small glass retort was used, into the tubulature of which a large pipette was fastened by means of a cork. The neck of the retort was closed. The pipette being removed and the bromine compound introduced, some freshly-cut fragments of sodium were added. The pipette being returned to its place, the whole was allowed to remain until the action of the sodium, at first energetic, became sluggish in consequence of a coating of bromide covering the metal. Gentle heat was then applied, upon which the fluid entered into ebullition, but the vapours condensing in the pipette constantly returned to the retort. During the reaction the sodium acquired a superb blue colour, reminding us of the phenomena observed by M. Bouis when acting on chloride of capryle with the same metal. The addition of the sodium was continued until no more action occurred, upon which the pipette was removed and the fluid distilled over. To ensure absence of bromine, it was once more rectified over sodium, but the metal remained perfectly brilliant until the end of the operation.

The fluid thus procured was not the only product, for the bromide of potassium in the retort was mixed with greasy and carbonaceous matters. The hydrocarbon submitted to a fractional distillation, came over at 71°, instead of 116°, as would have been the case if the bromine had reacted with sodium in an analogous manner to iodized propylene. The following are the analyses of this fluid:—

I. ·1677 gramme yielded ·5251 of carbonic acid and ·2164 water.

II. ·1703 gramme yielded ·5354 carbonic acid and ·2178 water.

	Experiment.		Mean.	Theory $C^n H^n$.
Carbon	85·4	85·7	85·6	85·7
Hydrogen . . .	14·3	14·2	14·3	14·3
				100·0

The bromine compound is therefore decomposed by sodium in a manner totally different to iodide of allyle. To determine the value of *n*, I determined the density of the vapour of the fluid. The operation was performed in an apparatus permitting the experiment to be made at any desired pressure. It was originally intended to ascertain the density at several pressures; the experiment was consequently commenced with an extra column of 205·5 millimetres of mercury, the atmospheric pressure being 759·2. The elastic force of the vapour was therefore equal to a column of mercury 964·7 millimetres in height. On consideration, the idea of making more than one experiment with the vapour of this hydrocarbon was abandoned until its formation had been repeated several times.

Corrections made.

Weight of substance	·4240 grm.
Volume of vapour	116·5 cub. cent.
Atmospheric pressure	759·2 mm.
Extra pressure	205·5 mm.
Temperature of vapour	98°·0
Density	3·02

The formula $C^{12}H^{12}$ requires—

$$\begin{array}{lr} \text{12 volumes of carbon vapour} \;.\;. & =0{\cdot}8290\times12=9{\cdot}9480 \\ \text{24 volumes of hydrogen} \;.\;.\;.\;. & =0{\cdot}0692\times24=1{\cdot}6608 \\ & \dfrac{11{\cdot}6088}{4}=2{\cdot}9022 \end{array}$$

The excess is partly due to the extra pressure*, but chiefly to the presence of a little $C^{14}H^{14}$.

The fluid procured in this manner is therefore caproylene or hexylene. Its formation by the process detailed is interesting, because it is an instance of the regeneration of a hydrocarbon by means of a complex decomposition similar to that found by MM. BERTHELOT and DE LUCA to occur with propylene. The hexylene is not therefore a mere product of decomposition in the ordinary sense of the term, but is identical in kind with the fluid in the naphtha which yielded the bromine compound. This is proved by the identity of boiling-point. The naphtha distilled between 71° and 77°, and the hexylene produced from it boiled at 71°.

Hexylene was discovered by FREMY† among the products of the distillation of hydroleic and metoleic acids.

BOUIS found that chloride of capryle treated with sodium in the cold yielded capryle, but that if the reaction took place with heat, caprylene resulted. It appearing probable from this that the products of the action of sodium on the bromine compounds would vary with the temperature, I repeated my experiments with the necessary precautions.

With the view of obtaining the next homologue of hexylene, the fraction boiling between 82° and 88° was selected. About twelve ounces of bromine were saturated with naphtha in the same manner as before, but, during the treatment of the brominated oil with sodium (after the action of alcoholic potash), all rise of temperature was carefully avoided, the apparatus being constantly covered with cold water. The decomposition is of course more gradual than when heat is applied, but it is quite as perfect.

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* I have been occupied at intervals during the last two years in ascertaining the amount of influence exercised by pressure on vapour volume, and also in endeavouring to improve the processes generally used for determining the densities of vapours. I hope before long to communicate these results to the Society. In the meantime some values obtained with propyle are annexed, to give an idea of the extent to which the density is increased by pressure.

Vapour-density of Propyle at various pressures.

Theory 2·976=4 volumes.

Temperature.	Pressure.	Density.
100·0°	772·1	2·963
97·0	870·6	3·005
97·0	943·8	3·022
98·7	1013·0	3·032

† Ann. de Chim. et de Phys. lxv. 139.

On redistilling the hydrocarbon, fractions were obtained from 82° to 104°. They were analysed as follows:—

I. ·1390 gramme gave ·4366 carbonic acid and ·1785 water.
II. ·1667 gramme gave ·5254 carbonic acid and ·2161 water.
III. ·1532 gramme gave ·4800 carbonic acid and ·1953 water.
IV. ·1862 gramme gave ·5850 carbonic acid and ·2348 water.

Or, per cent.—

	I.	II.	III.	IV.	Mean.	Theory $C^n H^n$.
Carbon	85·7	86·0	85·5	85·7	85·7	85·7
Hydrogen . . .	14·3	14·4	14·2	14·0	14·2	14·3

The first of these analyses was made on a fluid boiling at 85°, the second and third at 90°, and the fourth at 99°. In order to find the value of *n*, the vapour-density of each of these fractions was determined by GAY-LUSSAC'S method.

Boiling-point.	Weight of liquid.	Volume of vapour.	Difference of level.	Barometer.	Temperature of vapour.	Pressing col. of oil in mm. of mercury.	Density.
85°	0·0977	35·75	87·3	755·1	100°	21·7	3·19
90	0·1292	47·50	36·0	732·5	121	20·3	3·22
99	0·1117	43·25	55·0	742·0	146	21·0	3·32

The fraction boiling at 99° has therefore the composition and condensation of œnanthylene or heptylene, the olefiant gas of the œnanthylic alcohol, which requires the following numbers:—

$$\begin{array}{lr} \text{14 volumes of carbon-vapour} = 0{\cdot}8290 \times 14 = & 11{\cdot}6060 \\ \text{28 volumes of hydrogen} \quad = 0{\cdot}0692 \times 28 = & 1{\cdot}9376 \\ \hline & \dfrac{13{\cdot}5436}{4} = 3{\cdot}3859 \end{array}$$

The specific gravity of heptylene, in the fluid state, was 0·7184 at 17°.

From these results it is evident that the products of the action of sodium do not vary with the temperature. They also fully confirm the statement, made in another part of this paper, to the effect that the hydrocarbons produced by the processes detailed are identical with those existing in the Boghead naphtha. It will be remembered that the naphtha, from which the bromine compound yielding the heptylene was obtained, boiled between 82° and 88°, and the hydrocarbon produced by the action of sodium on the bromine compound came over between 85° and 99°.

The decomposition which the bromine compound undergoes is by no means simple, large quantities of difficultly combustible charcoal separating, with production of small but distinct traces of fatty acids.

Little is known with regard to the true boiling-points of the $C^n H^n$ series. Those which have been most examined, and consequently appear best adapted for standards with which to compare the boiling-points of the other homologues, do not agree with each other. The boiling-point of amylene, according to Frankland, is 35°; that of octylene was determined by Cahours to be 108°, while Bouis found it 125°. For convenience of reference the following Table is appended, showing some of the physical properties of the best-known members of the $C^n H^n$ family.

Table of the Physical Properties of some of the $C^n H^n$ series.

	Observer.	Formula.	Boiling-point.	Density.	Density of vapour.	
					Experiment.	Theory.
Amylene............	Frankland.	$C^{10} H^{10}$	35°	....	2·386	2·422
Hexylene	Fremy[*].	$C^{12} H^{12}$	55	....	2·875	2·904
Hexylene	C. G. Williams.	$C^{12} H^{12}$	71	....	3·020	2·904
Heptylene	C. G. Williams.	$C^{14} H^{14}$	99	0·718 at 17°	3·320	3·386
Octylene............	Bouis[†].	$C^{16} H^{16}$	125	0·723 at 17°	3·900	3·875
Octylene............	Cahours[‡].	$C^{16} H^{16}$	108	0·708	3·920	3·875
Nonylene	Fremy[*].	$C^{18} H^{18}$	110	....	4·488	4·359

It results from the experiments detailed in the first and second parts of this investigation, that Boghead naphtha consists of a mixture of hydrocarbons belonging to three series, namely,—

The radicals of the alcohols.
Homologues of benzole.
Homologues of olefiant gas.

APPENDIX.

Since the reading of the above, I have seen some experiments recently published by Limpricht on the action of perchloride of phosphorus on œnanthole[§]. He finds the product to be chloride of œnanthylene, $C^{14} H^{14} Cl^2$. By treatment with sodium he obtains œnanthylene (heptylene), boiling at 95°. By first treating the chloride with alcoholic potash to obtain $C^{14} H^{13} Cl$, and then with sodium, he expected, as I did, to obtain $C^{14} H^{13}$, or rather (for 4 volumes of vapour) $C^{28} H^{26}$. The resulting fluid, however, boiled at 95°, and had all the properties of heptylene. One not very satisfactory analysis agreed better with $C^{14} H^{13}$ than $C^{14} H^{14}$, but he admits that the properties of the hydrocarbon agreed so exactly with œnanthylene, that he could not insist on the accuracy of $C^{14} H^{13}$ as the true formula. My experiments, by proving the regeneration of œnanthylene by the action of sodium on $C^{14} H^{13} Br$, show the true nature of M. Limpricht's result. M. Limpricht states $C^{14} H^{13} Cl$ to be without action on sodium at ordinary temperatures; this difference between the chlorine and bromine compounds is curious and worthy of examination.

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[*] By distillation of hydroleic and metoleic acids.

[†] By action of sulphuric acid on octylic alcohol.

[‡] By distilling pelargonic acid with potash-lime.

[§] Chemical Gazette, March 15th 1858.