View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

XLV.—*The Bases contained in Scottish Shale Oil. Part I.*

By FREDERIC CHARLES GARRETT and JOHN ARMSTRONG SMYTHE.

ALTHOUGH many workers have examined the basic substances contained in coal tar, very few have investigated those found in the crude oil obtained by the distillation of bituminous shale. Greville Williams examined the tar from Dorsetshire shale in 1855 (*Q. J. Chem. Soc.*, **7**, 97), and G. Carr Robinson obtained some quinoline bases from Scottish shale oil (*Trans. Roy. Soc. Edin.*, 1879, **28**, 561; 1880, **29**, 265 and 273), but in 1897, George Beilby (*J. Soc. Chem. Ind.*, 1899, **16**, 886) pointed out that practically nothing is known on this subject, and that in view of the fact that from seven to ten million

View Article Online

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

gallons of "basic tar" are obtained in Scotland alone during the year, it is very desirable that this tar should be fully investigated.

The "crude oil" obtained by distilling the shale undergoes a second distillation in large iron retorts, and the distillate is divided into two portions known as "green naphtha" (the more volatile portion) and "green oil" (the less volatile portion); towards the close of the distillation, a red heat is attained and a considerable quantity of "still coke" is left in the retort. The oils are then treated with strong sulphuric acid (about two per cent.), which gives a thick, black tar, and removes almost the whole of the nitrogenous compounds from the oil; after washing to remove the excess of sulphuric acid, this tar is either burnt under the boilers or thrown away as rubbish. In the extraction of the pyridine bases from coal tar, the best results are obtained by washing the "light oil" with dilute sulphuric acid, and we therefore asked Mr. D. R. Steuart of Broxburn—whom we have to thank for the great trouble he has taken in order to supply us with whatever material we have needed—to have some of the "green naphtha" treated in this way. Some 200 gallons of "green naphtha" were washed with weak sulphuric acid (one volume of acid in nine of water), giving about 5 gallons of a thin, brown-red, foul-smelling liquid of sp. gr. 1·13. This acid liquor was heated almost to boiling and steam blown through for 6 to 12 hours to remove small quantities of a dark oil having a most offensive smell; it was then made strongly alkaline by solid caustic soda (200 grams per litre), and superheated steam blown through until all the volatile bases had been driven over. The distillation proceeded rapidly at first, but slowly afterwards, and a considerable volume of distillate was obtained; from this, the basic oil was separated as completely as possible, and the aqueous portion distilled until about one-fourth had passed over; this second distillate was then made strongly alkaline by caustic soda, the bases removed and added to the first portion, and the whole dried over caustic potash. The yield amounted to about 120 grams per litre of acid liquor, about 3 kilograms being obtained in all. The mixture of bases was then fractionally distilled, using a "rod and disc" still head of twenty discs, the receiver being changed as a rule every five degrees, and the whole quantity being worked over seven times.

The yield was as follows:

Below 120°	0·3	per cent.
120—160	13·4	,,
160—200	43·2	,,
Above 200	43·1	,,
	100·0	,,

View Article Online

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

It was thought desirable to compare the bases obtained from the "green naphtha" with those from the "green oil," and therefore 20 gallons of each liquid were treated with dilute sulphuric acid (1 lb. of vitriol in 1 gallon of water) and worked up as already described, the bases, however, being fractionally distilled only twice.

The "green naphtha" yielded 226·3 grams of base, of which 63 per cent. boiled below 200°, whilst the "green oil" only gave 120 grams, of which 40 per cent. boiled below 200°. We are indebted to Mr. Arnold Merrick and Mr. W. Saunderson for their assistance in making this comparison.

Only those portions boiling below 164° have been examined as yet, the plan adopted being to refractionate each fraction two or three times, and then to treat each with mercuric chloride, a solution of the bases in hydrochloric acid being added to a hot 10 per cent. solution of mercuric chloride. It was generally found most convenient to use 2 mols. of mercuric chloride to one of base, as the salts obtained usually contain that amount of mercuric chloride, although occasionally more complex salts were found. The mercury salts were then recrystallised from water slightly acidified with hydrochloric acid until their melting points became tolerably constant and analysis showed them to be fairly pure. The base was next regenerated by removing the mercury either by caustic soda or by hydrogen sulphide, and if found to be impure the treatment with mercuric chloride repeated. There are very great discrepancies between the boiling points of the bases recorded by different observers, partly because of the difficulty of obtaining them in the pure condition, and partly because of the great influence of variations in the height of the barometer; we have determined all boiling points with "short scale" thermometers of very good quality, the column of mercury being completely immersed in the vapour.

The following bases have been isolated:

Pyridine	B. p. 115—116°.
2-Methylpyridine (α-picoline).........	B. p. 129·5° (763 mm.)
2 : 6-Dimethylpyridine	B. p. 142·5° (760 mm.)
2 : 4-Dimethylpyridine	B. p. 159—159·5°.
2 : 5-Dimethylpyridine	B. p. 154—155°.
2 : 4 : 6-Trimethylpyridine	B. p. 170·5° (763 mm.)

Pyridine.

Three attempts were made to isolate pyridine by Mohler's method of precipitation with a strong solution of potassium ferrocyanide (*Ber.*, 1888, **21**, 1015), but without success, as the base recovered from the precipitate showed no constant boiling point, but distilled between

View Article Online

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

115° and 130°. Apparently this method may be advantageously used for freeing pyridine from small quantities of its homologues, but not for separating small quantities of the base from larger amounts of picoline, &c.

The base (about 10 grams) recovered from these experiments was therefore boiled with excess of potassium permanganate solution, and the liquid distilled; from the distillate, 3 grams of base boiling almost entirely between 115° and 116° were recovered; it gave a yellow, crystalline platinichloride melting at 228—230° without decomposition. On analysis:

0·2665 gave 0·0915 Pt. Pt = 34·33.

$(C_5H_5N)_2,H_2PtCl_6$ requires Pt = 34·33 per cent.

2-*Methylpyridine* (*a-Picoline*).

From the lower fractions was isolated a fair quantity of a mercuric compound of 2-methylpyridine crystallising in small plates melting at 151°:

0·6330 gave 0·4390 HgS. Hg = 59·79.
0·5490 „ 0·3800 HgS. Hg = 59·67.

$C_6H_7N,HCl,2HgCl_2$ requires Hg = 59·61 per cent.

This salt yielded a base which was a colourless liquid, easily soluble in water, with a powerful pyridine-like odour, boiling at 129·5° under 763 mm. pressure. Its platinichloride formed orange-red crystals melting at 194° with decomposition, and on analysis gave 32·65 per cent. of platinum (calculated 32·72 per cent.). The base was oxidised by potassium permanganate, and after removal of manganese and potassium salts, treated with copper acetate, when it gave the beautiful violet-blue, crystalline copper salt characteristic of picolinic acid. From this copper salt, the acid was obtained; it crystallised from a mixture of alcohol and ether in thin, colourless needles melting at 134°.

2 : 4-*Dimethylpyridine.*

This base was isolated from the fractions boiling between 150° and 165° by means of its mercurichloride, and is a colourless liquid, easily soluble in cold, but sparingly so in hot water; it has a characteristic cucumber-like odour; its sp. gr. at 14° is 0·9380 and it boils at 159—159·5°.

Its mercurichloride forms fine needles melting at 127°. On analysis:

0·4870 gave 0·3305 HgS. Hg = 58·49.
0·6390 „ 0·6662 AgCl. Cl = 25·77.
0·3622 „ 0·3796 AgCl. Cl = 25·90.

$C_7H_9N,HCl,2HgCl_2$ requires Hg = 58·41; Cl = 25·84.

View Article Online

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

The picrate was obtained by direct precipitation as a yellow precipitate melting at 178—180°.

With auric chloride, the base gave a yellow oil which rapidly crystallised and melted at 94° without decomposition. On analysis:

0·4454 gave 0·1958 Au. Au = 43·95.
$C_7H_9N,HCl,AuCl_3$ requires Au = 44·13 per cent.

The platinichloride crystallises extremely well in orange-red crystals, which become dim on exposure to air without losing weight; on slow heating, they melt at 216°, and on rapid heating at 223° with decomposition. On analysis:

0·3020 gave 0·0951 Pt and 0·4126 AgCl. Pt = 31·49; Cl = 33·78.
$(C_7H_9N)_2,H_2PtCl_6$ requires Pt = 31·24; Cl = 34·00 per cent.

On oxidation, an acid was obtained crystallising in white, silky needles containing water of crystallisation and melting at 235° with decomposition; with ferrous sulphate, it gives a deep red colour; with copper acetate, no precipitate even on boiling; with silver nitrate, a white, flocculent precipitate; and with lead acetate a white precipitate soluble in excess, the solution depositing crystals on standing.

When heated at 210° for two hours, the acid decomposed, giving a white sublimate and an infusible residue; both the sublimate and the residue sublimed without melting when heated at above 200°, and were proved to be *iso*nicotinic acid by this fact, and also by their behaviour with ferrous sulphate, silver nitrate, copper acetate, and lead acetate.

The acid is, therefore, lutidinic acid, and the base 2:4-dimethylpyridine.

2 : 5-*Dimethylpyridine.*

This base (which had not previously been described) was isolated from the fractions boiling at 150—165° by means of its mercurichloride; this salt forms small, heavy crystals melting at 163°, and contains 6 mols. of mercuric chloride. On analysis:

0·5260 gave 0·4120 HgS and 0·5472 AgCl. Hg = 67·51; Cl = 25·70.
0·5515 „ 0·4315 HgS „ 0·5746 AgCl. Hg = 67·42; Cl = 25·22.
0·9688 „ 1·0140 AgCl. Cl = 25·86.
$C_7H_9N,HCl,6HgCl_2$ requires Hg = 67·43; Cl = 25·86 per cent.

The base is a colourless liquid boiling at 154—155° and gives a picrate melting at 151—152°.

The *aurichloride* melts at 156—157° without decomposition. On analysis:

0·1681 gave 0·0738 Au. Au = 43·90.
$C_7H_9N,HCl,AuCl_3$ requires Au = 44·13 per cent.

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

The *platinichloride* is of an orange-red colour and crystallises well, but very diverse melting points were observed with the same samples on different days, the lowest being 195° and the highest 216°; the *anhydrous* salt melts at 238° with decomposition. On analysis:

0·8671 hydrated salt lost 0·0472 H_2O at 105°. $H_2O = 5·44$.
$(C_7H_9N)_2,H_2PtCl_6,2H_2O$ requires $H_2O = 5·46$ per cent.
0·3169 anhydrous salt gave 0·0970 Pt. Pt = 30·62.
0·2291 ,, 0·2290 CO_2 and 0·9654 H_2O. C = 27·14; H = 3·17.
0·2502 ,, 0·2457 CO_2 ,, 0·0740 H_2O. C = 26·79; H = 3·36.
$(C_7H_9N)_2,H_2PtCl_6$ requires C = 26·93; H = 3·21; Pt = 31·24 per cent.

On oxidation, an acid melting at 237—238°, with effervescence was obtained. With ferrous sulphate, it gave a fine yellow colour; with copper acetate, a bright blue precipitate on boiling; with silver nitrate, a white, gelatinous precipitate, and with lead acetate, a white precipitate insoluble in excess. On treatment with methyl alcohol and hydrochloric acid, it formed an ester crystallising in white needles melting at 160°.

When heated for 2 hours at 210°, it decomposed, and the residue sublimed completely; that this residue was nicotinic acid was proved by its melting at 229° and by its behaviour with copper acetate, ferrous sulphate, and silver nitrate.

The acid is therefore *iso*cinchomeronic acid, and the base 2 : 5-dimethylpyridine.

Since the above was completed, Errera (*Ber.*, 1901, **34**, 3699) has obtained this base synthetically, but in too small quantity for purification, and his description in no way agrees with ours, possibly because his compound had not been thoroughly purified.

2 : 6-*Dimethylpyridine.*

From the fraction boiling between 140° and 145°, a considerable quantity of the trimercuric salt of this base was obtained in colourless plates melting at 160—161°. On analysis:

0·6725 gave 0·4900 HgS. Hg = 62·80.
0·5395 ,, 0·3935 HgS. Hg = 62·86.
$C_7H_9N,HCl,3HgCl_2$ requires Hg = 62·77.

A second mercurichloride of this base was obtained from several of the fractions of low boiling point, and forms small, lustrous scales resembling cadmium iodide; it melts at 186°. On analysis:

0·5034 gave 0·2817 HgS. Hg = 48·32.
$C_7H_9N,HCl,HgCl_2$ requires Hg = 48·30 per cent.

The base itself was found to be a colourless liquid, fairly easily

View Article Online

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

soluble in water, having a characteristic odour resembling that of both pyridine and peppermint, and boiled at 142·5° under 760 mm. pressure.

The platinichloride crystallised well and melted at 210° with decomposition. On analysis:

0·422 gave 0·3175 Pt. Pt = 31·22.

$(C_7H_9N)_2,H_2PtCl_6$ requires Pt = 31·24 per cent.

The base was oxidised by potassium permanganate, and gave a good yield of *dipicolinic acid* (Ladenburg, *Ber.*, 1885, **18**, 53, and Epstein, *Annalen*, 1885, **231**, 1). After filtering off the precipitated oxide of manganese, the solution was reduced to a small bulk, acidified slightly with dilute sulphuric acid, and left to stand for some hours, when a crystalline precipitate (apparently a mixture of the free acid and an acid potassium salt) was obtained. This was warmed up with absolute alcohol and a little hydrochloric acid, and some potassium chloride filtered off; from the filtrate the acid separated in rosettes of needles melting at 232°, and these, on recrystallising from alcohol, formed very small prisms melting at 226° (darkening at 225°), whilst from water they gave long, hair-like crystals also darkening at 225° and melting at 226°. Further recrystallisation produced no change in the melting point, and on no occasion were we able to confirm Epstein's observation of 236° as the melting point of this acid.

2 : 4 : 6-*Trimethylpyridine* (s-*Collidine*).

From several fractions between 150° and 180°, considerable quantities of a mercuric compound were obtained which separated in large, fern-like or saw-like crystals built up apparently of many small plates, and melted at 154°. The mean of four determinations gave 57·16 per cent. of mercury (maximum 57·3, minimum 56·97 per cent.), the percentage calculated for $C_8H_{11}N,HCl,2HgCl_2$ being 57·22.

From 200 grams of this salt, 25 grams of base were recovered and again worked up with mercuric chloride; the salt formed after being fractionally crystallised yielded 93 grams of crystals melting sharply at 154° and yielding 13 grams of the base:

0·483 gave 0·3215 HgS. Hg = 57·38 per cent.

The base was a colourless liquid with a not unpleasant odour; its sp. gr. at 20° was 0·917, and it boiled at 170·5° under 763 mm. or at 169·5—170° under 746 mm. pressure. Its platinichloride was easily obtained in well defined, orange-red crystals melting at 223—224° with decomposition.

On oxidation, an acid crystallising in feathery needles, darkening at 225° and melting at 228°, was obtained; and this yielded, with abso-

View Article Online

Published on 01 January 1902. Downloaded by University of Illinois at Chicago on 28/10/2014 22:24:18.

lute alcohol, an ester melting at 127·5°. It is therefore trimesitic acid, and the base must be the 2 : 4 : 6-trimethylpyridine.

The authors have pleasure in stating that this work has been carried out by the aid of a grant from the Research Fund Committee of the Chemical Society.

THE DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.