

The Nitrogen Bases in Tasmanite Shale Oil

By

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INTRODUCTION AND HISTORICAL

The type of nitrogen compounds produced during the retorting of oil shale, although essentially of a heterocyclic nature, depends on several factors, the chief of which are :—

- (i) The rate of heating:
- (ii) The retorting method:
- (iii) The absence or presence of air.

Although these 'tar bases' are mainly derivatives of pyridine and/or quinoline, other compounds of a pyrrole nature have been reported to occur, for instance Petrie (1905) recorded the presence of pyrrole compounds in the oil obtained from the torbanites of New South Wales, and accounts of the shale oil from Colorado giving the same reaction have been reported by McKee (1925).

The first systematic work on the nitrogen compounds in shale oil was that of Williams (1854) on Dorsetshire shale. Williams wrote that they burnt with a smoky flame, possessed a very bad smell, were soluble in alcohol and gave a blue precipitate with cupric nitrate. He isolated pyridine and some of its lower homologues. Garret and Smythe (1902) working on Scottish shale oil succeeded in isolating and identifying seven members of the pyridine series by oxidation to the corresponding acids with potassium permanganate and by the preparation of the aurichlorides of the bases.

Robinson (1879) recorded the presence of nitrogen compounds in Scottish shale oil bases, occurring in the fractions boiling between 270° C. and 390° C. He proved that they were dicyclic compounds of the iso-quinoline series. In reference to the formation of salts, Robinson writes 'attempts were made to get crystalline salts from the mixed bases; the double chlorides of platinum, gold, cadmium, mercury, lead and zinc were tried but without success, only resinous sticky masses being obtained. The same failure in getting crystalline salts was experienced when the bases were treated with sulphuric, hydrochloric, nitric and oxalic acids'.

Kogerman (1931) gives a detailed description of the methods used to obtain the purified bases from Estonian shale oil, and makes the statement that 'The pure bases, separated from the shale oil, formed a reddish liquid with a quinoline-like odour, specific gravity—0.9731 at 15° and n_D —1.539/19°'. He also states that

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some of the higher bases failed to give crystalline salts, (cp. Robinson's remarks above), and, although he remarks that they belong to the pyridine and quinoline series, their presence was not confirmed. Eguchi (1927) has reported the presence of pyridine compounds in Fushun shale oil and identified methyl, dimethyl, and trimethylpyridines.

From the above brief summary it can be seen that aliphatic nitrogen compounds do not play an important role in the tar bases present in shale oil. These bases are, practically without exception, heterocyclic in structure and consist of alkylated pyridines and quinolines. The bases found in Tasmanite shale oil were typical of the above, members of the monocyclic and dicyclic series having been identified. However, a second type of base was found to be present, apparently belonging to the 'naphthenic base' group already discovered in Californian petroleum.

EXPERIMENTAL

The material used in this investigation was not a representative crude oil in the true sense of the word, because very gentle pyrolysis was used in its production, the temperature being kept at all times below 420° C., a description of the properties of this oil has been given elsewhere by Cane (1941). The amount of tar bases present in the oil as determined by a modification of the Universal Oil Products Laboratory method No. C-78-40 was 3.2 per cent, while an examination of 10° C. cuts showed zero per cent in the lower fractions, with increasing amounts to nearly six per cent in the higher ones. The oil was extracted with successive batches of 10 per cent sulphuric acid, the acid washings removed, bulked, and then made alkaline with caustic soda, the supernatant oily layer allowed to settle on the top and then removed. The united bases were extracted with anhydrous petroleum ether and the etherial layer concentrated. The bases were again converted into their sulphates and the aqueous layer washed with petroleum ether to remove traces of hydrocarbons, and finally the purified bases liberated with dilute caustic soda solution. The isolated bases were orange in colour with a distinct greenish fluorescence, and possessed the following properties:—

Specific Gravity @ 20° C.	0.9717
Refractive Index @ 20° C.	1.5242
Nitrogen	8.41%
Sulphur	0.27%

Their smell was characteristic of the shale bases; i.e., a mixture of pyridine and quinoline together with a faint peppermint smell. The smell of the bases lingered on the hands, even after several washings, and the physiological action was quite pronounced, the vapour producing the most acute headaches across the eyes and at the nape of the neck.

GENERAL REACTIONS OF THE BASES

- (I.) No carbylamine reaction.
- (II.) No crystalline quaternary ammonium salts with methyl iodide, but after standing for six months in a sealed tube a dark red tarry solid was formed.
- (III.) When diazotised and subsequently coupled with beta-naphol a dark green material was precipitated, and, when this was washed with sodium carbonate solution, a portion of the precipitate dissolved to form a deep red solution which dyed filter-paper orange. The residue from the sodium carbonate treatment was a green powder.
- (IV.) No Rimini's reaction and a very faint and doubtful Liebermann reaction.

- (v.) A deep blue precipitate was formed with cupric nitrate.
 (vi.) When the bases were reduced with sodium amalgam and alcohol for about 150 hours, a white water-soluble crystalline substance was precipitated.

Distillation of the Bases. The purified and dehydrated bases were distilled several times in all glass apparatus of special design, the column was silvered and vacuum jacketed, and the packing consisted of single turn wire helices. The following were the distillation results:—

Fraction No.	Boiling Range ° C.	Density @ 20° C.	Refractive Index @ 20° C.	Average Mol. Wt. (1).	Nitrogen. %	Vol. %
B1	165-213	0.9270	1.5070	128.3	10.89	5.7
B2	213-238	0.9518	1.5128	158.1	10.07	32.5
B3	238-250	0.9778	1.5299	169.9	9.39	22.0
B4	250-270	0.9803	1.5200	174.9	9.10	13.0
B5	270-290	0.9891	1.5349	171.8	8.89	13.7
B6	Residues and loss	13.1

The first fractions were colourless, but developed a light yellow colour on standing, while the higher fractions varied progressively from light yellow to a deep orange shade. All fractions deepened on standing, and it is interesting to note here the observations of Delaby and Hiron (1930) 'The alkyl quinolines are liquids of strong odour, light yellow in colour, and the colour becomes deeper, according to increasing molecular weight. Ethyl quinoline is nearly colourless when freshly distilled and under the same conditions butyl quinoline is straw yellow, but finally it assumes a brown red colour which deepens according to the time of preservation'.

Fraction B1.—When closely fractionated on a semi-micro scale, the following results were obtained. In this work the criterion for the acceptance of any one substance from the point of view of boiling point was that all of this fraction must distill between the boiling limits of 1° C.

Fraction No.	Boiling Point.	Specific Gravity @ 18° C.	Refractive Index @ 20° C.	M.P. of Picrate.	Nitrogen. %
B1 (i)	173.2	0.9181	1.4984	154	11.33
B1 (ii)	198.4	0.9390	1.5004	N.O. (2)	10.91
B1 (iii)	206.4	0.9503	1.5054	N.O.	10.24

The above picrate and all others in this paper was obtained in the following manner:—The base was dissolved in 35 ml. of acetic acid, and to it was added two grams of picric acid contained in 5 ml. of 50 per cent acetic acid. When the crystals were deposited they were centrifuged from the mother liquor and crystallised from alcohol, washed, dried, and the melting point found.

(1) The molecular weight was determined by the cryoscopic method, using cyclohexane as the solvent, Muscarelli and Benati (1909).

(2) Not obtainable.

Analysis of the results of Fraction B1 (i) agree closely with reported ones for γ -collidine (2, 4, 6, trimethylpyridine), but it must be kept in mind that different authorities give very divergent values for these constants, and it has been noticed that they even differ by as much as 6° C. in the case of the boiling points of uncommon derivatives.

Portion of this fraction was oxidised with potassium permanganate in a normal laboratory manner, and among the oxidation products the presence of trimesitic acid was confirmed.

Trimethyl pyridine has already been found in Fushun shale oil by Eguchi (1927) and also has been isolated from lignite tar by Krey (1895). No success was obtained in the analysis of the Fraction B1 (ii). The preparation of crystalline precipitates was rendered impossible on account of the formation of thick orange tarry masses when the bases were treated in accordance with the technique described above. Every case resulted in the formation of this resinous mass, no matter how the formation of crystals was promoted, and it is interesting to note that Robinson made the same observation. He tried many inorganic salts, but the only result was 'resinous, sticky masses being obtained'. From later researches it seems probable that Robinson's, and the present, results were due, in part, to insufficient purification, but even Baily (1930), in the last few years, has had the same difficulty in the elucidation of the structure of the tar bases occurring in Californian petroleum. The last fraction, together with Fraction B2, seemed to be a transition stage between, or a mixture of, the mono-cyclic and di-cyclic bases. That the next fraction was of quinolinic nature is indicated by the sudden drop in nitrogen content and rise in molecular weight. An analysis of the boiling points and refractive indices might indicate the presence of hydrogenated quinolines, for as far as could be ascertained from the available literature none of the simpler alkyl pyridines have boiling points approaching any of the above. Even assuming that this fraction was composed of a complex mixture of highly alkylated pyridines, the refractive index is much too high to allow this consideration, e.g., propyl pyridine (b.p. 178° C.) has a refractive index of only 1.4934. Similar statements could be made with regard to the presence of hydro-quinolines. No less than nine alkyl deca- and tetra-hydro quinolines have boiling points approaching the above. It may be assumed that, if these fractions contain hydro-quinolines at all, the refractive index would surely rise as the fraction was reduced, and with this end in view a representative sample was dehydrogenated according to the procedure of Diels and Karstens (1927):—Five gms. of the base and 7 gms. of powdered selenium were heated for 38 hours at a temperature of $185 \pm 1.5^\circ$ C. and the change in refractive index noted.

Refractive index before treatment	1.5126
Refractive index after treatment	1.5128

From a consideration of the hydro-quinolines, it can be calculated that the removal of four hydrogen atoms would cause an increase in the refractive index by an amount varying between 0.038 and 0.032, an increase which could be easily determined by refractometric methods.

Fraction B3.—From this fraction onward it can be seen that there is a drop in nitrogen content, while the refractive index and molecular weight still rise. The per cent of nitrogen in trimethyl quinolines is 8.9 and molecular weight 171.1, which are in the range of the above fraction, but there are two important properties which require explanation, i.e., the low refractive index and density.

From the preliminary work on a bulk sample, the presence of quinolines was confirmed, but members of the series boiling in this range have refractive indices

greater than 1.58. It was shown, by treatment with selenium as before, that hydro-quinolines were not causing this discrepancy.

The work of Baily and his collaborators on the nitrogen-containing bases in Californian petroleum, has shown that another important type of tar base (naphthenic base) may occur, and it seems probable that similar compounds occur in Tasmanite shale oil. They are apparently tri-cyclic in structure and contain a piperidine nucleus. Baily's process of a cumulative extraction was applied to a representative fraction boiling between 240° C. and 290° C. It was dissolved in 1 : 1 aqueous hydrochloric acid and treated with chloroform according to the procedure developed by Baily. The aqueous layer containing the hydrochlorides of the quinolinic bases was washed with decreasing amounts of chloroform; the chloroform layer containing the naphthenic bases with decreasing amounts of water. Under this treatment the refractive index of the 'aromatic section' rose from 1.5321 to 1.5845, and the specific gravity increased to nearly unity after five stages of extraction.

From this it can be seen that we are dealing with exactly the same set of conditions experienced by Baily. Furthermore, the values of the refractive index and density are now within the range of the tri-methyl quinolines.

The extracted bases consisted of a sticky, semi-crystalline mass of light yellow colour with a greenish yellow fluorescence. The chloroform washings of the 'non-aromatic' bases were treated so as to isolate the free bases and their general properties found. They were brownish red in colour, with a blue fluorescence and refractive index of 1.4985. They gave the normal reactions characteristic of pyrrole compounds. It is believed that the structure of these bases is very complex, and no attempt was made to elucidate their structure. The quinolinic bases were converted into their picrates in solution buffered with sodium acetate, purified, and then heated with ammonia, from which the bases separated out as nearly solid masses. The bases were further purified by treatment with acetone, and then very carefully distilled in vacuo.

Fraction No.	Temperature Range.	Refractive Index @ 20° C.	Density @ 15° C.	Molecular Weight.	Nitrogen. %
C1	244-245	1.5983	1.0641	142.0	9.39
C2	271-273	1.5903	0.9953	163.8	8.77
C3	277-279	1.5832	0.9307	177.4	8.01
C4	284-285	1.5742	0.9502	179.7	7.49

Analysing these results it can be seen that the first two fractions appear to contain methyl and di-methyl quinolines respectively, although their presence could not be confirmed. Tri-methyl quinoline was isolated from Fraction C3. This will be discussed later.

Great uncertainty exists with regard to the characteristics of these bases, and widely divergent values have been reported with regard to the higher alkyl quinolines; for example, four different values for the boiling point have been reported recently of 2-3-dimethyl quinoline varying between 261° and 273° C., so that in these analyses it has been attempted to class the quinolines according to the number of alkyl groups rather than to isolate individual compounds.

THE PRESENCE OF THE QUINOLINE RING IN THE HIGHER BASES

A small quantity of the 'non-extracted' bases corresponding to Fraction C2 (no more of the purified substance being available) was oxidised very carefully with 2 per cent aqueous alkaline potassium permanganate solution for 15 hours. Quite an amount of trouble was caused by the bumping of the solution on account of the precipitated manganese dioxide. A small air leak introduced into the solution helped to minimise this difficulty and also served to inject sufficient permanganate solution during the operation. The resulting solution of pale stone colour was filtered and rendered acid. This was slowly distilled and the vapours condensed into aqueous ammonia solution, and the volatile organic acids examined (I.), the non-volatile matter was extracted with benzene in a Soxhlet extraction apparatus (II.), and the residue recrystallised from hot water (III.).

THE VOLATILE ORGANIC ACIDS

The ammonium salts of the volatile organic acids were analysed, only the presence of acetic acid being confirmed in this solution, although a slight reducing action was observed, perhaps indicating the presence of formates, although they could not be confirmed.

THE BENZENE SOLUBLES

The yellowish non-volatile mass was placed in a Soxhlet thimble and extracted with benzene for 38 hours, the residue being left in the thimble and extracted with water (III.). The benzene solution was evaporated in vacuo. All attempts to elucidate the structure of this portion were unsuccessful, but results tended to prove that this was due to the presence of the naphthenic bases, which, according to other investigators, are extremely stable, both to neutral or alkaline permanganate oxidation.

THE WATER SOLUBLES

The water soluble material was concentrated and silver nitrate added; this caused an immediate dirty white precipitate, which was filtered off and purified. The amount of silver in the silver salt amounted to 58.6. Another portion of the silver salt was treated so as to liberate the free acid, no attempt being made to concentrate this on account of the difficulties encountered by Hantzsch (1882). The reaction with ferrous sulphate indicated a carboxylic acid in the *a* position. When this acid was distilled to dryness with lime, the odour of pyridine was observed.

It has been shown that the nitrogenous base present in the 271°-273° boiling range leads, on oxidation, to the production of pyridine carboxylic acids and, from the percentage of silver in the silver salt and basicity measurements, gives a molecular weight of 231.6 for the acid: this approximates fairly closely with methyl pyridine tri-carboxylic acid. Two of these carboxylic groups can be accounted for by the disintegration of the 'benzene' half of the molecule. This shows that there are two side chains in the 'pyridine' half of the molecule, one of which is obviously a methyl group.

From a study of the molecular weights of the base, it can be seen that we are dealing with either an ethylmethyl or trimethyl quinoline with perhaps a small percentage of higher homologues. However, assuming that trimethylquinoline is the major component, then there must be only one methyl group in the benzene half of the molecule. When the acid was heated and then coupled with resorcinol, a deep red substance was formed which had a distinct colour change from acid to alkaline solution; this compound, assumedly of the phthalein type, could only arise from an acid anhydride, necessitating two carboxyl groups in the ortho position to one another. Further proof of this orientation lies in the fact that it

was found, by using formaldehyde, that two and not three hydrogen atoms were replaced by carbinol, which, according to the results of Königs (1899), will only occur when the ortho position to the methyl radicle is substituted, that is, if the benzene ring is not acting as the ortho substituent.

Phthalone formation, requires a methyl or methylene group in the α or γ position. A small amount of the base was heated with phthalic anhydride and zinc chloride for five hours at 165°; the resulting compound was a fine deep-red solid, which dissolved in boiling alcohol to give a crimson-orange solution.

The lack of formation of quarternary ammonium salts by methyl iodine may well be explained by reference to the results of Decker (1905), who found that ortho substituted quinolines exhibit steric hindrance, in that they do not form quarternary ammonium compounds with iodides. Oxidation of the base with chromic acid gave brownish needles, soluble in hot water, which sintered about 245°. The distillation of the barium salt gave a liquid (n_D^{20} , 1.6053), which on oxidation with potassium permanganate, and distillation of the acid thus produced, gave quinoline itself.

SUMMARY OF THE BASIC BODIES

The only base isolated in the lower fraction was trimethylpyridine, the presence of which was confirmed by oxidation to the corresponding acid.

The compounds in the higher fractions consist, in the main part, of tertiary bases of the quinoline series, but results have shown that a second type of basic substance occurs, which possesses a low refractive index and probably contains a pyrrol nucleus in its structure.

The presence of hydrogenated quinolines was shown to be impossible from a study of the refractive indices before and after dehydrogenation experiment with selenium.

The presence of the quinoline ring was confirmed by oxidation, and from this it was shown that the alkyl radicles attached to the nucleus were nearly all methyl radicles.

The orientation of the methyl radicles in one fraction was elucidated, and it was found that one of them was in the 1; position, the other in the 2; position. The remaining radicle was in either the 5; or 8; position.

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