

CCCXXXV.—*The Chemistry of Petroleum. Part III.*
The Acid Sludge from the Refining of Persian
Kerosene. Part I. The Aromatic Hydrocarbons.

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IN order to isolate the neutral sulphur compounds from the light distillate (36% by volume) from crude Persian petroleum (J., 1925, 127, 898) by means of the reaction with alcoholic mercuric chloride, it is first necessary to eliminate hydrogen sulphide and the mercaptans. The former is completely removed by the use of aqueous sodium hydroxide, but the mercaptans are only partly extracted (*loc. cit.*). The oil may be freed from the last traces of mercaptans by repeated agitation with aqueous silver nitrate. A dirty white sludge* is produced, which is very difficult to filter. The small quantities of neutral sulphur compounds present in the petroleum necessitate dealing with a large volume; the process, besides being expensive, is therefore extremely tedious and inconvenient.† Consequently it was decided to make use of the known solubility of the neutral sulphur compounds in concentrated or fuming sulphuric acid. This method offers the advantage that in refinery practice the soda-washed distillate is redistilled, the greater part of the sulphur compounds remaining in the residue (kerosene), which is treated with fuming sulphuric acid; an unlimited supply of acid sludge, from which the required sulphur derivatives could be isolated, was therefore available.

In Part I of this series (*loc. cit.*) it was shown that during the soda-washing of the light distillate a part of the mercaptans is entirely removed, part is converted into disulphides which are left in the oil, and part remains unattacked. The unextracted mercaptans would consist chiefly of the higher (and less acidic) members of

* This may be purified to a white, crystalline powder by recrystallisation from a mixture of acetone and pyridine.

† Both mercaptans and sulphides may be precipitated together by means of mercuric chloride, and a separation attempted later; but neither this procedure nor that outlined above would serve to isolate disulphides, the presence of which was suspected (*vide infra*).

the series, which would remain in the residue on redistillation of the oil. It was therefore to be expected that during a subsequent treatment with sulphuric acid the remaining mercaptans would become oxidised to disulphides, which with those already present would eventually appear in the acid tar; this expectation has been verified in preliminary experiments, since sodium mercaptides are formed by the action of sodium on the oil recovered from acid tar. Since Thierry (J., 1925, **127**, 2756), who isolated a series of sulphides from an acid sludge from the refining of a Persian petroleum, had made no mention of disulphides, the investigation of our acid tar was continued, although Thierry's paper had appeared in the meanwhile.

It was soon found that the oil obtained by diluting the tar from the washing of kerosene with fuming sulphuric acid (20% SO_3) contained, besides sulphur compounds, large quantities of aromatic hydrocarbons, which were investigated.*

Owing to the difficulty of operation on a large scale, on diluting the original black, viscous sludge with water, a certain quantity of kerosene was also admitted. The agitation with acid was therefore repeated, but using 98% acid (dilution of this second tar giving a black oil, rich in the desired sulphur compounds); it was remarkable that the part which remained undissolved, and must have consisted largely of the original kerosene, had a much higher specific gravity than the latter (0.816 compared with 0.793), and still contained 0.5% of sulphur, which was not present in the elementary state. In an endeavour to locate the cause of the high specific gravity and sulphur content, about 87.5% of the material was taken off in a current of steam. The sulphur remained in the residue, but although the distillate now contained only 0.06% of sulphur, it still had d 0.803, which could only be due to the presence of a considerable quantity of aromatic hydrocarbons.

Further concentration of the aromatic constituents was effected by the method of Edeleanu (Brit. Pat., 11140), which consists in dissolving the benzene hydrocarbons in liquid sulphur dioxide; the reagent was used at its boiling point under atmospheric pressure. The extract, after removal of the sulphur dioxide, was fractionally distilled. It commenced to boil at about 60° and fractionation was continued to 220°. Each 5° fraction was separately treated with sulphuric acid (100% H_2SO_4) and the aromatic hydrocarbons were recovered by steam-distilling the acid layer (compare Armstrong

* M. Normand (private communication) suggests that the presence of aromatic hydrocarbons in the acid tar is due to the solvent action of sulphur dioxide, produced by the oxidising action of the acid on the kerosene, dissolved in the acid tar.

and Miller, J., 1884, **45**, 148). Each fraction of recovered hydrocarbon was investigated separately.

The methods recorded in the literature for isolating and identifying the higher aromatic hydrocarbons are surprisingly few and of limited applicability. The use of sulphonic acids has the advantage that the hydrocarbons can be regenerated by hydrolysing the purified acid, but the mixtures of sulphonic acids often fail to crystallise, and criteria of purity for their salts are usually somewhat indirect. The use of nitro-derivatives is unsatisfactory, partly on account of the tarry products formed, partly because they cannot be distilled (thus the methods of separation are limited to crystallisation), and partly because of the difficulty of bringing about complete substitution without the risk of attacking the side chains. If complete substitution is not effected, the formation of isomeric nitro-compounds from the same hydrocarbons introduces a further complication. This difficulty is overcome by replacing every nuclear hydrogen atom by bromine, the resulting bromo-compounds being stable and crystallisable substances, some of which have quite commonly been used for the identification of individual hydrocarbons isolated by other means. Moreover, the use of the brominated compounds provides a valuable, and, so far as we are aware, novel means of accomplishing an actual separation of unknown constituents, since even those bromo-derivatives of highest melting point can be distilled under reduced pressure with but little decomposition. Thus, if a series of hydrocarbon fractions has been isolated, they are exhaustively brominated in the nucleus and the product from each fraction is examined separately. Should a common constituent be found, the proportions in which it occurs in the bromides derived from the different hydrocarbon fractions provide a clue to the boiling point of the original hydrocarbon. This method has proved satisfactory, and is to be recommended for such systematic investigations.

Toluene, *m*-xylene, *p*-xylene, *p*-ethyltoluene, mesitylene, ψ -cumene, hemimellitene, a diethylbenzene, an ethylxylene, and naphthalene were identified; evidence was obtained of the presence of methylnaphthalene.

Careful but unsuccessful search was made for *o*-xylene, which has never, so far as we are aware, been detected in a petroleum, although *m*- and *p*-xylene are quite usual constituents. The presence in Persian oil of mesitylene and ψ -cumene is scarcely surprising, since these hydrocarbons are probably the commonest constituents of liquid petroleums, usually occurring together. Indeed, of all the different petroleums so far investigated, there appear to be only three in which neither mesitylene nor ψ -cumene has been detected—

an oil from Gemsah (Egypt) which gives only 4% of distillate between 160° and 200°, an oil from Kuba in the Caucasus, and a heavy petroleum from Oregon, U.S.A.; in the last two, aromatic constituents have not been found. Neither hemimellitene nor ethylxylene has previously been isolated from a petroleum. Ethyltoluene was suspected, but not identified, by Mabery and Hudson (*Proc. Amer. Acad. Arts Sci.*, 1901, **36**, 259) in the fraction of b. p. 159—163° of an oil from Fresno County, California. Markownikoff (*Annalen*, 1886, **234**, 89) thought that diethylbenzene was probably present in Baku petroleum. Naphthalene and its homologues are quite common constituents of petroleums; we have isolated naphthalene, and β -methyl-, dimethyl-, and trimethyl-naphthalenes (the last two in the form of their picrates) from Persian kerosene by direct extraction with liquid sulphur dioxide, omitting the previous treatment with sulphuric acid.

EXPERIMENTAL.

The starting material was the crude kerosene, left as a residue (12%) when the soda-washed primary distillate from the crude petroleum is redistilled. It is a faintly yellow liquid having d^{15} 0.793, a sulphur content of 0.19%, and a peculiar odour.

Five thousand gallons of this material were agitated for 45 minutes with 0.75% (by vol.) of fuming sulphuric acid (20% SO_3), and the mixture was allowed to settle during 30 minutes. The viscous, black tar was then allowed to run into water (*ca.* 100 gals.), a certain volume, estimated at 10 gallons, of kerosene being also admitted; the total separated oil, approximately 55 gallons, was then collected and twice extracted with half its volume of concentrated sulphuric acid; the acid gave on dilution a black oil, very rich in sulphur compounds, which was purified by steam distillation. The investigation of this material, which has been shown to contain disulphides by the formation of sodium mercaptides on treatment with sodium, will form the subject of a further communication. The oil which did not dissolve in the sulphuric acid had d^{15} 0.816 and contained 0.5% of sulphur; it was distilled in steam. The distillate (about 87.5%; d^{15} 0.803), which contained 0.06% of sulphur, was treated with its own volume of liquid sulphur dioxide in an open separating-funnel, the temperature being allowed to adjust itself automatically by the unchecked ebullition of the reagent (Edeleanu, *loc. cit.*). The heavier sulphur dioxide layer was separated and the solvent removed. The extracted oil, after being washed with aqueous alkali and then with water, was dried over calcium chloride; it had d^{15} 0.840. This oil was now fractionally distilled, using a 48-inch column packed with iron borings. A few drops of distillate

were collected up to 70°; fractions were then taken at 5° intervals up to 220°.

The extraction with sulphur dioxide, whilst serving to concentrate the aromatic hydrocarbons in the soluble portion, only gives a partial separation; this was therefore completed by treating each of the 5° fractions of the extract with its own volume of concentrated sulphuric acid, the aromatic hydrocarbons being recovered from the acid layer by distillation in steam (compare Armstrong and Miller, *loc. cit.*).

The residue (12.5%) from the large-scale steam distillation was subjected to a separate distillation using superheated steam, which left only a small residue. This second distillate was also treated with liquid sulphur dioxide, the extracted portion distilled, and the fractions up to 220° were treated as before with sulphuric acid, the recovered aromatic hydrocarbons being added to the corresponding fractions from the 87.5% distillate. Fractions boiling above 200° were always distilled with the aid of a lagged, electrically-heated column.

Toluene.—The presence of toluene in the three fractions from 100° to 115° was demonstrated as follows: Nitration gave 2:4-dinitrotoluene, m. p. 70—71°. Sulphonation gave *p*-toluenesulphonic acid, m. p. 106°; from this were prepared pure specimens of toluene, b. p. 110.5°, and of *p*-toluenesulphonanilide, m. p. 104°.

m- and p-Xylene.—The fractions boiling between 130° and 150° were converted into the calcium xylenesulphonates, the solution of which was evaporated in stages, the meta-derivative separating from the hot solution and being collected. From the cold, concentrated solution, the para-salt separated in clusters of large, colourless prisms. These precipitates were then separately purified by fractional crystallisation. The meta-salt was dissolved in cold water and precipitated by heating the solution; the para-salt was dissolved hot and allowed to crystallise by cooling. The hydrocarbons were then regenerated from the calcium sulphonates by heating with sulphuric acid in a current of steam. *m-Xylene* was boiled for 4—5 hours with dilute nitric acid (1 acid : 2 water), washed with aqueous alkali and then with water, dried, and distilled. It had b. p. 141—142° and gave, on bromination,* tetrabromo-*m-xylene*, m. p. 251° (Auwers and Koeckritz, *Annalen*, 1907, **352**, 299, give m. p. 247° (Found : C, 22.8; H, 1.6. Calc. : C, 22.75; H, 1.45%). *p-Xylene*, b. p. 137.5—138°, solidified on cooling, and had m. p. 12—13°. Bromination gave tetrabromo-*p-xylene*, m. p. 252° (Jacobsen, *Ber.*,

* Bromination was always carried out in the dark in the presence of iodine, a large excess of bromine being used (compare Crafts, *Compt. rend.*, 1892, **114**, 110).

1885, **18**, 359, gives m. p. 253°) (Found : C, 22.9; H, 1.5. Calc. : C, 22.75; H, 1.45%).

According to Patterson (J., 1925, **125**, 2489), calcium *o*-xylenesulphonate, being extremely soluble in water, is the last of the isomerides to crystallise on evaporation. The most soluble portion of our calcium xylenesulphonate was carefully examined; eventually this fraction was converted into the sodium salt, which was also examined; from this, in turn, the xylenesulphonamide was prepared and fractionally crystallised, but no ortho-derivative could be detected.

The Trimethylbenzenes and Ethyltoluene.—The three fractions between 155° and 170° each gave on sulphonation a crystalline and an oily acid, which were separated by filtration through glass wool. On being heated with concentrated hydrochloric acid at 100° in a closed vessel (compare Crafts, *Amer. Chem. J.*, 1900, **83**, 248; Armstrong, *Ber.*, 1882, **15**, 1697), both the crystalline and the oily acid gave (a) a liquid hydrocarbon, mesitylene, (b) crystalline ψ -cumenesulphonic acid, and (c) an oily sulphonic acid, which contained a certain quantity of the ψ -cumene acid, and was obtained in greatest amount from the 160—165° fraction.

The oily acid (c) was hydrolysed by heating with concentrated sulphuric acid in a current of superheated steam; the hydrocarbon produced was washed, dried, and fractionally distilled. It boiled between 158—168°, with a distinct peak at 162—166°. This peak fraction, which had a peculiar lemon-like odour, was shaken for 6 hours with concentrated sulphuric acid (2 mols.) at the ordinary temperature. The portion which did not dissolve was then treated for 6 hours at 50° with a fresh portion of acid. The hydrocarbon which remained was then brominated; the resulting tetrabromo-*p*-ethyltoluene was washed and dried in light petroleum solution, removal of the solvent then giving a crystalline solid which separated from ethyl alcohol in needles, m. p. 111° (Found : C, 25.0; H, 1.9. Calc. : C, 24.8; H, 1.9%). The somewhat indefinite m. p. of this substance has not hitherto been recorded (compare Klages, *Ber.*, 1903, **36**, 1637), but the identity of our product was established by comparison with a genuine specimen of the synthetic material.

The hydrocarbon (a) was again sulphonated; the deliquescent mesitylenesulphonic acid crystallised from chloroform and melted at 77°. A portion of the acid was converted through the sodium salt into mesitylenesulphonamide, which had m. p. 142° after crystallisation from water. Hydrolysis of the acid by heating with sulphuric acid in a current of steam gave mesitylene, b. p. 164°. Bromination of the pure hydrocarbon gave tribromomesitylene, which separated from benzene in needles, m. p. 226° (Fittig and

Storrer, *Annalen*, 1868, **147**, 11, give m. p. 224° (Found : C, 30.35; H, 2.5. Calc. : C, 30.2; H, 2.55%); the identity of this bromide was confirmed by comparison with a genuine specimen prepared from coal-tar mesitylene.

The crystalline ψ -cumenesulphonic acid (*b*) was purified by repeated crystallisation from dilute sulphuric acid; finally, the material was extracted by means of chloroform in a Soxhlet apparatus, the dry acid, free from sulphuric acid, being obtained in this way. From the same solvent, the acid separated in small, granular crystals, m. p. 110—112°, which were identical with a specimen prepared from genuine coal-tar ψ -cumene. ψ -Cumene was isolated from the acid by distillation with sulphuric acid in a current of steam; it had b. p. 168—169°. Bromination of the pure hydrocarbon gave tribromo- ψ -cumene, m. p. 232° (Jacobsen, *Ber.*, 1886, **19**, 1222, gives m. p. 233°), which was identical with a genuine specimen (Found : C, 30.3; H, 2.6. Calc. : C, 30.2; H, 2.2%).

Fractions 170—175° and 175—180° were refractionated. The portion of b. p. 175—178° was sulphonated and the sulphonic acid converted through the calcium salt into the sodium sulphonate. The aqueous solution of the sodium salt was then treated with less than the theoretical quantity of barium chloride; the precipitated barium sulphonate was reconverted into the sodium salt, and the incomplete precipitation repeated. The process of isolating and collecting the less soluble barium salt was continued until a specimen gave, through the sodium salt and the acid chloride, hemimellitene-sulphonamide, m. p. 195° (softening at 192°). Hemimellitene is apparently an important constituent of the aromatic portion of Persian kerosene; it has been isolated in considerable quantity from all the fractions boiling between 175° and 188° as tribromo-hemimellitene, which is comparatively insoluble in light petroleum or cold ethyl alcohol, but soluble in hot benzene, from which it separates in long needles, m. p. 245° (Jacobsen, *loc. cit.*) (Found : C, 30.6; H, 2.6. Calc. : C, 30.2; H, 2.65%).

Hydrocarbons C_9H_{12} and $C_{10}H_{14}$.—The fractions boiling above 175° were refractionated into 2° fractions, which were then brominated. Each fraction up to 188° gave a quantity of tribromohemimellitene (*vide supra*) from which the other products were separated by dissolving them in light petroleum. The soluble portion from fraction 186—188° solidified, and the soluble bromides from the other fractions deposited more of the same solid (A), which was collected. The mother-liquor from each fraction was then fractionally distilled under reduced pressure. From fractions 178—180° and 180—182° there was obtained a fraction of bromo-compound, b. p. 220—230°/9 mm., which solidified (B); the same hydrocarbon

fractions also gave a fraction of bromo-derivative, b. p. 200—220°/9 mm., which deposited a further crop of the solid (A). More of this was also obtained by fractionally distilling the soluble, liquid bromides from the other hydrocarbon fractions.

The solid (A) gave, on crystallisation from ethyl acetate, some tribromohemimellithene and a portion of m. p. 85—95°. From this, tribromoethylxylene was isolated in needles, m. p. 93°, by repeated crystallisation from ethyl acetate, which was occasionally replaced by acetone (Found : C, 32.35; H, 3.0. Calc. : C, 32.35; H, 3.0%). The fact that the soluble bromide (consisting almost entirely of the compound of m. p. 93°) from hydrocarbon fraction 186—188° solidified, seems to indicate that the b. p. of the parent hydrocarbon is very close to that temperature. It is not possible, however, to draw any inference from this, since the b. p.'s of all the known ethylxylenes lie within a very narrow range (185—191°). The m. p. of the tribromo-derivative of 1:2-dimethyl-4-ethylbenzene is given as 93° in the literature, whilst for that of 1:5-dimethyl-2-ethylbenzene Stahl gives m. p. 94—95°, and Anschütz m. p. 90—91°. Our bromide, m. p. 93°, may, therefore, be derived from either of these ethylxylenes. A sample of bromo-derivative having m. p. *ca.* 106° was also obtained (in very small quantity), and was evidently an isomeric tribromoethylxylene (Found : C, 32.6; H, 3.1%).

Great difficulty was experienced in the purification of the solid (B), the m. p. of which (originally about 48°) was only slightly raised by each crystallisation. After many crystallisations from ethyl acetate or acetone diluted with ethyl alcohol, hard prisms were isolated which still had a rather indefinite m. p., 60—64°. The quantity remaining at this stage was too small to permit of further purification. Nevertheless, the properties of this compound and its composition (Found : C, 26.9; H, 2.4. Calc. : C, 26.7; H, 2.2%) agree with the description of tetrabromo-*o*-diethylbenzene (Voswinckel, *Ber.*, 1888, **21**, 3501), m. p. 64.5°. Since our material was not crystallised "to constant melting point," it is possible, although scarcely probable, that we may have been dealing with an impure specimen of tetrabromo-*m*-diethylbenzene (prisms, m. p. 74°).

Naphthalene.—Treatment of the fraction of b. p. 200—225° with picric acid gave a quantity of picrate, which was freed from the oil as far as possible by pressing on porous porcelain; on heating the picrate with aqueous sodium hydroxide in a current of steam, naphthalene was recovered in the solid form. After crystallisation from ethyl alcohol, it had m. p. 80°, and was identified by means of its picrate, m. p. 151.5° (Found : C, 53.55; H, 3.4. Calc. : C, 53.8; H, 3.1%).

Naphthalene Hydrocarbons in the Sulphur Dioxide Extract.—The fractions boiling above 225° each gave picrates, but the quantities were too small for detailed examination. The deepening of the colour with increase in b. p. of the fractions indicated the presence of homologues of naphthalene (thus, a deep orange picrate, m. p. ca. 112°, was obtained from the 250—255° fraction); this was confirmed by a brief investigation of the relevant fractions of the oil extracted from kerosene by means of liquid sulphur dioxide.

The extract, obtained in the normal course of refining kerosene,* was washed with sodium hydroxide solution and the portion boiling up to 200° removed. The brown residue was distilled in steam and the distillate dried and exhaustively treated with picric acid. The collected picrates were freed as far as possible from oil and the hydrocarbons recovered by distillation with steam in the presence of aqueous sodium hydroxide. The heavy, oily distillate was dried and fractionally distilled, 5° fractions being collected.

The fraction of b. p. 215—220° solidified, and, together with the solid deposited on cooling from fractions 220—225° and 225—230°, was collected and identified as naphthalene.

The mother-liquor from these fractions, and the higher fractions (up to 270°), were treated with fuming sulphuric acid (10% SO₃) and the hydrocarbons recovered by steam-distilling the viscous acid layer. The recovered hydrocarbons were washed with sodium hydroxide solution, and dried over calcium chloride. The material was then refractionated.

β -Methylnaphthalene separated from the fraction of b. p. 237—245° on cooling to -21°, and was identified by its m. p. (33°; from alcohol) and its picrate, m. p. 115° (Found: C, 55.0; H, 3.7. Calc.: C, 55.0; H, 3.5%). An attempt was made to separate the mother-liquid (from the β -methylnaphthalene) by fractional crystallisation of the barium sulphonate (Wendt, *J. pr. Chem.*, 1902, **46**, 317). The picrates, prepared from the hydrocarbons recovered from the more soluble and the less soluble portions of the barium salt, were both found to have m. p. ca. 120—125°. Attempts to isolate the picrate of α -methylnaphthalene (m. p. 143°) were not successful.

The orange picrate from the dimethylnaphthalene fraction, b. p. 260—265°, was crystallised from ethyl alcohol; it had m. p. 114° (Found: C, 56.0; H, 4.1. Calc.: C, 56.1; H, 3.9%).

A deep orange-red *picrate*, m. p. 119—120°, was obtained from the portion boiling above 270°. Apparently owing to the passage through the combustion apparatus of unburnt hydrocarbon, difficulty was experienced in the analysis of this substance. It is

* In the refinery process, kerosene is agitated at 16° with its own volume of liquid sulphur dioxide; 10% of the oil is dissolved.

evidently the picrate of a trimethylnaphthalene, since it contains too great a proportion of both carbon and hydrogen for the dimethyl derivative (Found : C, 56.6; H, 4.3. Calc. for $C_{18}H_{15}O_7N_3$: C, 56.1; H, 3.9. Calc. for $C_{19}H_{17}O_7N_3$: C, 57.1; H, 4.3%).

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