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The Chemical Nature of Extracts from a Bituminous Coal

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The material studied in this paper was obtained from a Pittsburgh seam coal (Edenborn Mine) by extraction with benzene under pressure at a temperature of 260°, in the manner described by Asbury.[1] By solvent methods of fractionation similar to those used by a number of previous workers,[2] the material was divided into three fractions: I, that portion soluble in a large excess of cold petroleum ether; II, that portion insoluble in cold petroleum ether but soluble in ethyl ether on exhaustive extraction in a Soxhlet apparatus; and III, that portion insoluble in ethyl ether. The total yield of extract was 14.5% of the weight of the coal, and the percentages of the total constituted by the various fractions were 16.2, 50.4 and 33.4, respectively. The material in each of these groups could be divided further by treatment with various solvents, but the analyses and general properties of the fractions thus obtained were so similar that it did not seem advantageous to make these separations. The differences in solubility apparently were due more to differences in molecular size than to variation in chemical type.[3]

Fraction I consists almost entirely of hydrocarbons, and since it comprises only about 2.3% of the weight of the coal and since materials obtained in a similar way have been studied in detail by others,[4] it was not further examined in the present work. The substances contained in Fractions II and III have been studied only cursorily in most previous investigations, chiefly because their amorphous nature and the fact that they are non-distillable make the certain isolation of any component in pure form extremely difficult. They have been characterized vaguely as "resinous" or "resin-like." The object of the work described here was not the isolation of individual components, but the determination of the general type of structure characteristic of these substances.

The elementary microanalyses of the three fractions and of the original coal are shown in Table I. In the dry state Fractions II and III were reddish-brown powders, while their solutions were red in transmitted light and exhibited a strong green fluorescence. Fraction II softened at about 120°, and Fraction III softened, with pronounced decomposition, at about 300°. The molecular weights of both fractions as determined cryoscopically in catechol were about the same, approximately 285, but in diphenyl Fraction II gave a value of about 470 and Fraction III a value greater than 1000. The low molecular weights obtained in catechol were not compatible with the physical properties of the dry material, and could be explained only by assuming that the highly polar solvent exerted a dissociating or depolymerizing action.[5] The diphenyl values, on the other hand, probably represented the upper limit, since, with diphenyl, deviations from correct values are usually on the side of too large molecular weights. The fact that the catechol values were about the same for both fractions is evidence in favor of the viewpoint that the two materials differ more in the degree of association than in chemical type.

TABLE I

ANALYTICAL DATA ON FRACTIONS OF EXTRACT AND OF COAL (ASH FREE)

Fraction	C	H	N	S	O (by diff.)
I	87.42	8.83	0.44	0.65	2.66
II	86.98	6.44	1.37	.68	4.53
III	85.02	5.82	1.76	.74	6.66
Original coal	85.52	5.55	1.78	1.08	6.07

A series of group analyses and other experiments indicated that no carboxyl, ester, carbonyl or alkoxyl groups were present in either Fraction II or Fraction III.[6] The former, however, contained about 3.5%, and the latter about 2.5% of oxygen in the form of hydroxyl groups. These figures leave one-fourth of the oxygen of Fraction II and three-fifths of that of Fraction III unaccounted for. By process of elimination this oxygen must occur in ether linkages or in heterocycles.

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(1) R. S. Asbury, *Ind. Eng. Chem.*, **26**, 1301 (1934).

(2) W. A. Bone, A. R. Pearson and R. Quarendon, *Proc. Roy. Soc.* (London), **105A**, 608 (1924); F. Fischer, H. Broche and J. Strauch, *Brennstoff-Chem.*, **5**, 299 (1924); **6**, 33 (1925); E. Berl and H. Schildwächter, *ibid.*, **9**, 105 (1928).

(3) *Cf.* K. Peters and W. Cremer, *Z. angew. Chem.*, **47**, 576 (1934); *C. A.*, **28**, 6548 (1934).

(4) F. Hofmann and P. Damm, *Brennstoff-Chem.*, **3**, 73, 81 (1922); **4**, 65 (1923); A. Pictet, L. Ramseyer and O. Kaiser, *Compt. rend.*, **165**, 358 (1916).

(5) R. C. Smith and H. C. Howard, THIS JOURNAL, **57**, 512 (1935).

(6) Compare R. V. Wheeler and C. Cockram, *J. Chem. Soc.*, 706 (1927).

The general nature of the oxygen in the extracts having thus been determined, efforts were directed toward a study of the hydrocarbon skeleton. The work of Bone[7] on the permanganate oxidation of extracts similarly obtained had already gone far toward depicting the skeletal structure, in that remarkably high yields of benzene polycarboxylic acids were reported among the oxidation products. On the basis of this result Bone concluded that the extracts contain a foundation structure of aromatic rings. In the present work an attempt has been made to break the material down into stable units with as little change as possible in the original ring structure, for the purpose of determining the range of sizes of these units. The method used was that of catalytic hydrogenation under pressure. The lowest temperature at which complete removal of the oxygen, nitrogen and sulfur was obtained in a twenty-four hour treatment was found by experiment to be 425°. The products obtained, both from Fraction II and from Fraction III, were (1) gas, mainly methane and ethane, representing about 20% of the original carbon, (2) steam distillable oil, representing about 50% of the original carbon, and (3) a tarry residue of very low vapor pressure.

The presence of the gas was of little significance, since it is always obtained in hydrogenation at this temperature, and could have come from aliphatic compounds,[8] alkyl side chains, or from the decomposition of partially hydrogenated aromatic nuclei.[9]

The oils from the two fractions were examined separately but no differences were detected in the products. Fractional distillation showed them to be complex mixtures with a boiling point range of from about 70 to above 400° at atmospheric pressure. Distribution over the range was fairly uniform. The chemical properties and physical constants of the various fractions indicated that except for the low boiling materials, which contained small amounts of aliphatics, the oils were made up almost entirely of wholly or partially hydrogenated aromatics. To confirm this, samples of the oil were dehydrogenated over platinized charcoal. The products of dehydrogenation were almost exclusively aromatic, and contained representatives of monocyclic, bicyclic and higher ring systems. Hydrocarbons of the following formulas have been isolated in pure form through the picrates: $C_{10}H_8$ (naphthalene), $C_{11}H_{10}$ (β-methylnaphthalene), $C_{12}H_{12}$, $C_{16}H_{10}$, $C_{18}H_{18}$.

The material in the lower boiling fractions of the hydrogenated extract may have been derived from larger complexes,[10] and therefore affords little information as to the size of the original units. The higher boiling substances, however, even though they may be degradation products of still larger units, are large enough to be significant of the original structure of the extract. For example, the compound $C_{16}H_{10}$ must, on the basis of its composition, be a highly condensed molecule containing four rings.

The non-steam-distillable residue had an average molecular weight of about 250 in both catechol and diphenyl. The close agreement of the values obtained in the polar and non-polar solvents indicated that the tendency toward polymerization had been removed, and the fact that this fraction, which contained only the largest molecules in the hydrogenated material, now had about the same molecular weight in catechol that the whole extract had originally is evidence that the stable units in the original extract did not greatly exceed this size. The average formula was about $C_{19}H_{18}$, neglecting the small amount of oxygen which it still contained. After dehydrogenation of this material with selenium, one pure substance, having an empirical formula of $C_{20}H_{14}$, was isolated from it as a picrate.

On the basis of the above work it is concluded that the general type of structure characteristic of Fractions II and III of coal extracts is represented by a network of carbon rings, with occasionally an oxygen atom, or, much more rarely, a nitrogen or sulfur atom, occupying a position either in the ring, or linking two nuclei. The atomic ratio hydrogen–carbon of the original extract (about $^6/_7$) indicates that some of the rings may be hydroaromatic. The distribution of oxygen, nitrogen and sulfur is probably a random one, in some places leaving large sections of continuous hydrocarbon structure, and in others possibly separating a mono or bicyclic unit from the remaining structure. Variations can be, and probably are, almost unlimited.

Further support for this viewpoint devolves from the fact that the extract could be converted

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(7) W. A. Bone, L. Horton and A. Ward, *Proc. Roy. Soc.* (London), **127A**, 508 (1930).

(8) A. N. Sachaven and M. D. Tilicheyev, "Chemistry and Technology of Cracking," Trans. by A. A. Boehtlingk, D. F. Brown and K. I. Steik, Chemical Catalog Co., N. Y., 1932, p. 349.

(9) N. A. Orlov and N. D. Lichatschev, *Ber.*, **63**, 2179 (1930).

(10) N. A. Orlov, *ibid.*, **60**, 1950 (1927); F. Hofmann and K. Lang, *Brennstoff-Chem.*, **10**, 203 (1929).

by mild oxidation into so-called humic acids in yields of about 60%. While the complete structure of humic acids is still unknown, those who have suggested type formulas for such acids have depicted skeletal structures similar to those described above.[11]

The color and fluorescence of the extract can be accounted for by this type of structure. Polycyclic aromatic hydrocarbons of the type of 1,2-benzpyrene and naphthacene are known to have a yellow color[12] and to fluoresce in the violet and ultraviolet. It is to be expected then that with larger complexes, containing oxygen substituents, the color would be deepened and the fluorescence would be shifted toward longer wave lengths.

In regard to the periphery of the "exact molecules" little is known. No doubt alkyl side-chains and hydrogen are frequently occurring peripheral groups, and hydroxyls, as previously mentioned, are present to some extent, probably where oxygen linkages have been broken by the pyrolytic effect[1,13] of the extraction process. The tendency toward polymerization may be due to some unstable peripheral condition, such as the presence of double bonds,[14] but as yet no definite information on this point is available.

Experimental Part

Preparation of Extract.—The apparatus and method described by Asbury[1] were used. The extraction was carried out in ten stages, the first lasting for one hour at 220°, the second and third lasting for two hours each at 240°, and the others lasting three hours each at 260°. The charge of coal, 16–20 mesh, was 250 g. One liter of benzene was used in each stage. When the extraction was finished, the benzene solutions were combined and the benzene was distilled off from a steam-bath until the volume was reduced to about 200 cc. The resultant mush was poured into about 4 parts of petroleum ether (30–60°) and the flocculent precipitate was filtered on a fritted glass funnel, and thoroughly washed with petroleum ether. The filtrate was freed of solvent, the last traces being removed under vacuum on a water-bath, and the viscous red oil left was extracted with fresh petroleum ether by digestion in the cold, until the undissolved portion had lost its gumminess and no more color was imparted to fresh petroleum ether. Distillation of the solvent from the combined solutions left 5.8 g. of a red oil, which was designated Fraction I. The combined residues were extracted exhaustively (about fourteen days) in a Soxhlet apparatus with ethyl ether. The soluble material, referred to as Fraction II, weighed 18.3 g., and the residue, Fraction III, weighed 12.1 g. The total yield of 36.2 g. amounts to 14.5% of the coal used. Analytical data are shown in Table I.

Extraction of Fraction II with Other Solvents.—In an effort to determine whether or not the ether soluble fraction could be separated into two or more types of material, samples of it were extracted exhaustively in a Soxhlet apparatus with (1) petroleum ether (40–75°) and (2) ethyl alcohol. About 40% of the fraction was removed by the petroleum ether, and about 20% by the alcohol. The extracts obtained, however, showed no appreciable differences in properties from the original material, and elementary microanalyses indicated that their composition was not greatly different from that of the whole fraction (*cf.* Table I). Petroleum ether extract: C, 86.18; H, 6.70; N, 1.15; S, 0.90. Alcohol extract: C, 84.21; H, 6.27; N, 1.23; S, 0.78.

Determination of Oxygen Containing Groups.—(1) Methoxyl.—Absence was indicated by standard microanalysis. (2) Hydroxyl.—This group was determined by methylation followed by micromethoxyl determinations. The most satisfactory method of methylation was found to be that of Waliaschko.[15] The conventional method using dimethyl sulfate and aqueous alkali was found to give lower and inconsistent values. Fraction II contained 3.5% hydroxyl oxygen and Fraction III about 2.5%. (3) Carboxyl and Ester.—Prolonged treatment with boiling 10, 20 or 50% aqueous sodium hydroxide failed to dissolve any part of either fraction. Hydrolysis of Fraction III (the method was not applicable to Fraction II since it is appreciably soluble in alcohol) with standard alcoholic potash showed a loss in alkali equivalent only to the known hydroxyl groups, which would remove alkali as insoluble potassium salts. No methylation took place when either fraction was refluxed for two hours with methyl alcohol saturated with hydrogen chloride. (4) Carbonyl.—Absence was indicated by the fact that both the hydroxyl content and the total oxygen content were unchanged after reduction at 300° for twenty-four hours with 100 atmospheres of hydrogen over Adkins' copper–calcium–chromium oxide catalyst.[16]

Hydrogenation of the Extract.—The determination of the lowest temperature at which all the oxygen could be removed from the extract was made in the following way. Small samples (2.5 g.) of Fraction III, mixed with half their weight of Adkins catalyst, were treated with 100 atmospheres of hydrogen (initial pressure) in a one-liter stainless steel bomb at temperatures ranging from 300 up to 425° at 25° intervals. The duration of the reaction in each case was twenty-four hours. The products were recovered by transfer to a Soxhlet cup and extraction with benzene, and the progress of the reaction was followed by complete analysis. At 300° the oxygen content was not changed, nor was any gas formed, but reaction had begun at 325° as was evidenced by a decrease in the oxygen content and by the formation of gas containing about 3% of the original carbon. The extent of the reaction increased fairly regularly at the higher temperatures, until at 425° practically all the oxygen, nitrogen and sulfur

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(11) W. Fuchs, "Die Chemie der Kohle," Julius Springer, Berlin, 1931, p. 445.

(12) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 402 (1933).

(13) H. H. Lowry, *Ind. Eng. Chem.*, **26**, 321 (1934).

(14) J. F. Weiler, *Fuel*, **14**, 190 (1935).

(15) N. Waliaschko, *Arch. Pharm.*, **242**, 225 (1904).

(16) R. Connor, K. Folkers and H. Adkins, THIS JOURNAL, **54**, 1142 (1932).

had been removed, and about 20% of the original carbon appeared in the gas.

Larger samples (15 g.) of each fraction were treated at the latter temperature. The gas was analyzed and its volume determined. The 20% of carbon in the gaseous products was distributed as follows: carbon dioxide, 9.7%; methane, 16.9% and ethane, 73.4%. The volatile products (7.3 cc.) were recovered by steam distillation directly from the bomb, and the residue was recovered by extraction of the catalyst-residue mixture with benzene in a Soxhlet apparatus. The relative proportions of the classes of products from the two fractions were about the same.

Examination of the Steam-Distillable Oils.—The crude product obtained on steam distillation was fractionated roughly at atmospheric pressure to determine the boiling point range. Distillation began at about 70° and continued to about 400°. The initial boiling points and the refractive indices (Abbé) of fractions boiling at 79° and higher are shown in column (a) of Table II. Small percentages of aromatics were present, as shown by the fact that trinitro-*m*-xylene, m. p. 181° (not depressed by an authentic specimen), was obtained on nitration of the appropriate fraction, and by the formation of a picrate on the addition of picric acid to an alcoholic solution of the oils boiling above 200°. This picrate, as yet unidentified, crystallized from alcohol in dark red, glistening needles, m. p. 210°. *Anal.* Calcd. for $C_{18}H_{16}\cdot C_6H_3N_3O_7$: C, 62.47; H, 4.12; N, 9.11. Found: C, 62.28; H, 4.26; N, 9.05.

TABLE II

REFRACTIVE INDICES AND INITIAL BOILING POINTS OF FRACTIONS OF OIL (a) FROM HYDROGENATION OF EXTRACT AND (b) FROM HYDROGENATION FOLLOWED BY DEHYDROGENATION

(a)		(b)	
Initial b. p.	$n^{25}D$	Initial b. p.	$n^{25}D$
79	1.4412	80	1.4740
132	1.4577	117	1.4910
182	1.4887	143	1.4980
232	1.5262	173	1.5160
280	1.5540	207	1.5870
328	1.6050	218	1.5935
		242	1.5995

A new sample of the oil was washed repeatedly with 83% sulfuric acid to remove sulfur compounds, and was then dehydrogenated by Zelinsky's method using platinized charcoal prepared by the method of Kaffer.[17] The initial boiling points and the refractive indices of the various liquid fractions of the dehydrogenated oils are shown in Table II. The fact that the refractive indices were now about the same as those of pure aromatics of comparable boiling point was sufficient evidence of their aromatic nature. No attempt was made to isolate individual substances in the monocyclic range. The fractions boiling at 207, 218 and 242°, when treated with picric acid, yielded, respectively, naphthalene picrate, m. p. 151° (not depressed by an authentic specimen), β-methylnaphthalene picrate, m. p. 117° (not depressed by an authentic specimen), and two picrates of formula $C_{12}H_{12}$. The latter were obtained in such small amounts that they could not be separated sharply enough to give reliable melting points. They were probably dimethylnaphthalenes. *Anal.* Calcd. for $C_{12}H_{12}\cdot C_6H_3N_3O_7$: C, 56.1; H, 3.9. Found: (1) C, 56.36; H, 3.70. (2) C, 56.82; H, 3.67. The higher boiling substances were strongly adsorbed on the charcoal catalyst and could be recovered only by extraction with benzene in a Soxhlet apparatus. This material yielded two crystalline picrates, only one of which could be obtained in sufficient purity for microanalysis. It crystallized from alcohol or benzene in long red needles, m. p. 218°. *Anal.* Calcd. for $C_{16}H_{10}\cdot C_6H_3N_3O_7$: C, 61.25; H, 3.02. Found: C, 61.30; H, 3.10. This substance is isomeric with pyrene, but the melting point of the picrate is depressed by addition of pyrene picrate.

Examination of the Non-Steam Distillable Residue.—This residue could be distilled in vacuum without appreciable decomposition, and at atmospheric pressure with only slight losses. The distillate was a very viscous, greenish yellow oil, $n^{25}D$ 1.6470. It was heated with an equal weight of selenium at 320° for twenty-four hours, and was then distilled under vacuum. The distillate, on treatment with alcoholic picric acid, yielded a picrate which crystallized in red-brown needles, m. p. 183°. *Anal.* Calcd. for $C_{20}H_{14}\cdot C_6H_3N_3O_7$: C, 64.46; H, 3.53. Found: C, 64.14; H, 3.75.

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Summary

The physical properties of the amorphous portion of the benzene extract from a bituminous coal have been described. It has been shown that the oxygen content is distributed between hydroxyl groups and inert linkages, probably of the heterocyclic type, and that hydrogenation under suitable conditions converts the material largely into a mixture of hydroaromatic oils, some of which contain as many as four or possibly five rings. It is concluded that the skeletal structure of these "resinous" coal extracts consists of a network of carbon rings interspersed with oxygen rings or ether linkages, and that the difference between the more and less soluble portions of the extract is one of molecular size rather than of chemical type.

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[17] H. Kaffer, *Ber.*, **57**, 1261 (1924).