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CYCLIC HYDROCARBONS IN A LOW TEMPERATURE COAL-TAR

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Stepwise extractions with various strengths of H_2SO_4 of an aromatic hydrocarbon fraction from a low temperature coal-tar, and examination of the subfractions, confirmed the presence of alkylated monocyclics and bicyclics, and of olefinic structures, and pointed to the presence of alkylated cycloaromatic hydrocarbons of higher average molecular weight than the rest, and of benzenes having long alkyl side-chains.

Aromatic hydrocarbons containing one to six rings, mainly alkylated, are invariably found in low temperature tars from bituminous coals; alkylated benzenes and naphthalenes predominate.[1] A few more highly hydrogenated ring structures have been found, e.g. tetralins. Hydrogenated naphthalenes with unsaturated side-chains are also probably present.[2]

The main difficulty in systematic work on these hydroaromatics is the relatively small amounts of them occurring in the aromatic hydrocarbon fractions isolated, making identification difficult. A means of separating a concentrate of these compounds would be a great asset, enabling further detailed identification to be done. It seemed unlikely that column chromatography or solvent extraction could achieve this, because their properties, especially in the higher molecular weight range, would probably not be sufficiently different from the aromatic hydrocarbons occurring with them.

In the present work, a chromatographic fraction, known to consist mainly of alkylated mono and bicyclic aromatic hydrocarbons was reacted with sulphuric acid of various concentrations to see whether it was possible to effect a subdivision into materials of different degrees of aromaticity.

It was not to be expected that clear-cut separations of different types would occur under different conditions of sulphonation, for even the degree of alkylation of aromatic rings may affect the reaction. Thus, for example, tri-and higher-alkyl benzenes react with concentrated sulphuric acid at room temperature, but most mono-substituted derivatives do not.[3] However, it was hoped that, as a minimum, molecules containing olefinic side-chains and those compounds having more highly hydrogenated rings than the rest might be separated under appropriate conditions.

Experimental

1. *Preparation and Characterisation of Starting Material, Aromatic Fraction b*

Fraction *b* was prepared from 300 g of a low-temperature tar (made by the Rexco process[4]) by means of column chromatography on silica gel[5] of the light petroleum solubles in 500 ml of solvent (column, 100 cm × 94 mm).

The characteristics of fraction *b* (two separate samples) are given in Table 1.

2. *Sulphuric Acid Treatment*

(a) 85% H_2SO_4.—1 g of fraction *b* was dissolved in 50 ml light petroleum (40°–60°C) and extracted three times with 20 ml of the acid; the extracts were shaken with light petroleum (25 ml portions). The total light petroleum solution was reduced in volume to 10 ml by distilling off solvent, and rechromatographed on silica gel. In the two samples taken, only 1.0% and 0.6% reacted with the acid, the materials unreacted having $n_D^{20} =$ 1.5475 and 1.5480. Thus fraction *b* had virtually no reaction with 85% H_2SO_4.

(b) 98% H_2SO_4.—Similar experiments were done on two 2.7 g samples of fraction *b*, using four portions of acid, one of 40 ml, and three of 10 ml each. The characteristics of the unreacted portion, (mean of two determinations), fraction B1, are shown in Table 2.

(c) *Activated* H_2SO_4.—This was prepared by dissolving phosphorus pentoxide in 98% H_2SO_4 until some was left undissolved. 5–6 g portions of fraction *b* were dissolved in 80 ml light petroleum, immersed in ice, and shaken mechanically until cold. The acid (130 ml) was run in gradually, and shaking continued for 30 min. The separated acid sludge was washed several times with light petroleum, the combined solutions of petroleum then being washed with a saturated solution of sodium chloride, reduced in volume to 30 ml and chromatographed as before.

The unreacted materials from two experiments were colourless mobile liquids. The average characteristic of the samples, B4, are given in Table 2.

3. *Examination of Fractions*

The following determinations were carried out: refractive index, density, % carbon and hydrogen

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Table 1.—Characteristics of Fraction *b*.

	1	2
% by weight on dry tar	9·5	9·4
n_D^{20}	1.5490	1.5540
d_{20}^{20}	0.9611	0.9644
M	197	204
monoolefins (Wijs)%	33	34
C%	88.5	88.3
H%	9·9	9·8
O+%	1·6	1·9
C/H	0·75	0·75

Table 2.—Characteristics of Fractions from Treatment with Various Strengths of H_2SO_4

	Unreacted with 98% H_2SO_4,	Reacted with 98% H_2SO_4 (by calculation)	Unreacted with 98% H_2SO_4, but reacted with activated H_2SO_4 (by calculation).	Unreacted with activated H_2SO_4,
	B1	B2	B3	B4
% on fraction *b*	48	52	38.5	9.5
n_D^{20}	1.5065	1.5945	1.5141	1.4730
d_{20}^{20}	0.8860	1.0361	0.9056	0.8101
M	243	169	220	330
R_{obs} R_{calc}	7.0	9.3	6.2	10.7
% C_P	56.1	—	—	12.2
% C_N	9.9	—	—	61.3
% C_A	34.1	—	—	26.5
R_N	0.4	—	—	2.5
R_A	1.0	—	—	1.1
R_T	1.4	—	—	3.6
%C	88.1	88.7	88.1	86.9
H%	11.5	8.3	11.3	12.5
O+%	0.4	3.0	0.6	0.6
Molecular formula	$C_{18}H_{28}$	$C_{12}H_{14}$	$C_{16}H_{25}$	$C_{24}H_{41}$
C/H	0.64	0.9	0.65	0.58

by microanalysis, molecular weight in the Heitler ebulliometer,[6] and IR absorption in a double-beam Perkin-Elmer Infracord Spectrophotometer. Molecular refractions (R_{obs}) were derived from the Lorentz-Lorenz equation; R_{calc} values were obtained from the incremental constants of Vahrman *et al.*[7] from which the optical exaltations, R_{obs}–R_{calc} were obtained. These can be used to distinguish different classes of cyclic compounds. Structural group analysis by the n-d-M method was also used.[8] In this, C_A=% of total carbon in aromatic structures; C_N=% of total carbon in naphthenic structures; C_P=% of total carbon in paraffinic structures; R_A=ring-number per average molecule in aromatic structures; R_N=ring-number per average molecule in naphthenic structures; R_T=total ring-number per average molecule.

When the ratio C_A/C_N is greater than 1.5 (as was the case for B1) or the sum C_A+C_N is greater than 75 (as was the case for B4) the results by this method may be inaccurate.[10] However, although it would not be safe to rely on these results alone, they may be taken in conjunction with the other data.

Discussion

Fraction *b* (Table 1) had similar characteristics in all respects to such fractions previously made. In the infrared, it showed bands due to aromatic structure (at 1600 cm^{-1}, and at 1500 cm^{-1} corresponding to phenyl) and to alkyl groups, and the presence of isolated double bonds (band at 1630 cm^{-1}). Olefinic unsaturation was confirmed by the Wijs method, which gave 33–34% as monoolefins.

These olefins were not attacked by 85% H_2SO_4, unlike those in the aliphatic hydrocarbons from the same tar, which were mainly of the terminal variety.[9] The latter were found to be attacked even by 80% H_2SO_4.

The characteristics of the material reacting with 98% H_2SO_4 (52% of fraction *b*) were calculated from the detailed properties of the materials before and after this extraction (B2 in Table 2). This showed that all olefins had been extracted (no bands were shown in the unreacted material, as well as no action was shown by the Wijs reagent on B1), together with aromatic compounds, mainly having two rings; the latter were probably alkylated napthalenes and hydronaphthalenes.

The material unreacted (B1) probably contained mono and dialkylbenzenes, many of which do not react with concentrated H_2SO_4, but not trialkyl and higher benzenes, which are sulphonated under these conditions.[3] The data point to the predominance of monocyclic aromatics, some naphthenic structures, and much alkylation. This is consistent with a mixture of benzenes, monosubstituted by long-chain alkyl groups, together with some alkylated hydronaphthalenes.

The residue unreacted with activated H_2SO_4, B4 (9.5% of fraction *b*) had low refractive index and density, but its formula, and the absence of olefins, IR spectrum (bands at 1600,820 and 800 cm^{-1}), optical exaltation and n-d-M values, all point to the presence of aromatic rings. The value of R_{obs}–R_{calc}, in fact, corresponds to two aromatic rings.[7] The presence of alkylated cycloaromatic structures are indicated.

The data for the fraction reacting with activated but not with 98% acid, B3, obtained by calculation, correspond well with those of a benzene ring having about $C_{10}H_{20}$ in alkyl side-chains. These have not been recorded before in coal-tar, although long-chain alkyl benzenes have been found in petroleum.[9]

References

1. M. Vahrman, Fuel, Land., **49,** 5(1970).
2. M. Vahrman, J. appl. Chem. (London), **8,** 759 (1958), Chapter III.
3. C.M. Suter, *The Organic Chemistry of Sulfur* (John Wiley, 1944).
4. A non., Cocke and Gas, **16,** 383 (1954).
5. G.V. Blunt and M. Vahrman, J. Inst. Fuel, **33,** 522 (1960).
6. C. Heitler, Analyst, **83,** 223 (1958).
7. W.R. Dyson, J.A. Spence and M. Vahrman, J. Inst. Petrol., **51,** 285 (1965).
8. K. Van Nes and H.A. van Westen, *Aspects of the Constitution of Mineral Oils* (Elsevier, Amsterdam, 1951), p. 340
9. B. J. Mair, A.S.T.M. Special Technical Publication No. 389 (1965), p. 214.
10. B.T. Brooks, C.E. Boord, S.S. Kurtz Jr. and L. Schmerling, *The Chemistry of Petroleum Hydrocarbons* (Reinhold, New York, 1955), vols. 1 and 3.