

CHEMICAL COMPOSITION OF RAW AND UPGRADED
ANTHRACENE OIL AND THE CHEMISTRY OF COAL
LIQUIDS UPGRADING(1)

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INTRODUCTION

Anthracene oil was hydrotreated using flow-through trickle-bed reactors containing Co-Mo-alumina catalysts (3). The conditions are specified in Table I. Samples of the feedstock and four reaction mixtures were separated using cation, anion, and complexation chromatography (4). The compound types and the weight percents of the individual homologs present in the acid, base, neutral nitrogen, and hydrocarbon + ether (neutral) fractions were determined from high- and low-resolutions FI/MS and high-resolution 70-eV EI/MS. The basic and neutral fractions were subjected to GC/MS analysis.

RESULTS AND DISCUSSION

The salient results are summarized. Hydrocarbons containing three aromatic rings account for ca. 40% of the feedstock. The parent member of the -18(H)Z series ($C_{14}H_{10}$) was preparatively isolated using GC and identified as $\geq 98\%$ phenanthrene. The dominance of phenanthrene over anthracene in both high- and low-temperature coal tars has been previously noted (5-10). Thus, phenanthrene and assumably its alkylated homologs comprise the -18(H)Z series and account for 15.6% of the feedstock.

The data in Table II demonstrate the occurrence of extensive phenol deoxygenation. The reactivity of -18(O) through -22(O) and -18(O₂) and -22(O₂) compounds is indicated to be independent of the experimental conditions. However, the weight percents for the lower -Z(O) and -Z(O₂) series reveal that the increased reaction time did not overcome the effect of a decrease in temperature upon reactivity. Comparison of the data in columns 6 and 7 with those in columns 3 and 4 indicates a very small net effect of decreases in both H₂ pressure and space time and catalyst change on deoxygenation.

The acid fraction contains significant amounts of -Z(N) compound types. These compounds and also the ones present in the neutral-nitrogen-containing fraction are indicated to contain the pyrrole nucleus based upon the chemistry associated with the separation and both the molecular weights and formulas for the first homolog observed

for each compound type. For example, as seen in Table III, the carbon number for the first homolog in the -9(N), -15(N), and -21(N) series are those expected for indoles, carbazoles, and benzocarbazoles, respectively. Comparison of the weight percents in columns 4 through 7 with the ones in column 3 of Table III reveal a net nonreactivity for compounds containing the pyrrole nucleus under the specified conditions.

The base fraction from the feed was found to contain -5(N) through -23(N) and -27(N) compound types. These specific -Z series are indicated to be principally composed of compounds possessing the pyridine nucleus based upon the chemistry associated with the separation, the formulas for the first homolog observed in each series, and GC/MS analysis. The -17(N) series ranging from $C_{13}H_9N$ to $C_{18}H_{19}N$ is the most abundant one, accounting for 28.8% of the base fraction. The principal components are assumably isomeric azaphenanthrenes and variously alkylated homologs possessing up to 5 alkyl carbons.

The -11(N) series ranging from C_9H_7N to $C_{16}H_{21}N$ is the second most abundant one, accounting for ca. 23.5% of the base fraction. The first members of this series, quinoline and isoquinoline by GC/MS, account for 0.9 percent of the feedstock. It is interesting to note that isoquinoline accounts for 1/2 to 2/3 of this total.

The feedstock base fraction also contains -11(NO), -19(NO), and -21(NO) compound types. The molecular formulas correspond to compounds containing both furan and pyridine nuclei. It is interesting to note that this fraction contains in excess of 40 heterocyclic compounds containing two nitrogen atoms (11). This appears to be the first report of numerous $C_N H_{2N+Z} (N_2)_2$ compounds in coal liquids and only the second instance (12) in which dinitrogen compounds have been observed in these materials.

The mass spectral and the GC/MS data demonstrate that the complexity of the base fractions is significantly increased under all conditions used (see Table I) in hydrotreating the anthracene oil. Table IV presents mole data for the reactant and product bases comprising the 129-139 molecular-weight series. The moles of quinoline (I) and isoquinoline (II) in the feed are ca. 2.2×10^{-3} and 4.4×10^{-3} , respectively, by GC/MS. In addition, GC/MS reveals the absence of II in the reactor bases. In regard to $C_9H_{11}N$, GC/MS indicates the presence of 1,2,3,4-tetrahydroquinoline (IIIa) and the absence of both 5,6,7,8-tetrahydroquinoline (IIIb) and tetrahydroisoquinolines (IV). Finally, the GC/MS analyses confirm the presence of minor and significant amounts of 2-propylaniline (V) in the feedstock and reactor-1 bases, respectively. These results are at least qualitatively consistent with those obtained from reaction of I with H_2 a) in a batch reactor

using MoS_2 as the catalyst (13) and b) in a high-pressure/high-temperature liquid-phase reactor using a variety of metal catalysts (14) and from the MoS_2 catalyzed reaction of II with H_2 (13).

As shown in Scheme 1 (14), rapid catalytic addition of H_2 to I produces IIIa and IIIb. The apparent presence of IIIa and the apparent absence of IIIb in the products is at least qualitatively consistent with the considerably greater reactivity of the latter compared to the former (14). Structure-reactivity relationships provide a preference for hydrogenolysis of the N-C(2) bond rather than the C(8a)-N bond in IIIa producing V rather than 3-phenylpropylamine. Both IIIa and IIIb are converted to decahydroquinoline (VI), mass 139; the rate constant for the latter conversion is significantly greater than the one for the former (14). The absence of significant amounts of VI in the products is consistent with its facile conversion to hydrocarbons and NH_3 (13,14).

The only nitrogen containing compounds observed from the MoS_2 catalyzed reaction of H_2 and II were IV and decahydroisoquinoline (VII) (14). VII is a minor product. As shown in Scheme 2, II reacts with H_2 producing either IVa or IVb. Hydrogenolysis of either the N-C(3) bond or the N-C(2) bond in IVa produces either 2-ethylbenzylamine (VIII) or 2-(2-methylphenyl)ethylamine (IX), respectively. Since VIII and IX contain a benzylic and aliphatic NH_2 group, respectively, their denitrogenation should be facile. In contrast, the NH_2 group in V, see Scheme 1, is aromatic and, hence, as observed would be expected to undergo hydrogenolysis less readily. Alternatively, hydrogenation of IVa and IVb produces VII which in turn suffers hydrogenolysis producing hydrocarbons plus NH_3 .

Table V lists the furan- and thiophene-compound types present in the neutral fractions from the feed and the products. Dibenzofurans and dibenzothiophenes were identified by GC/MS. Carbon-number distributions for these compound types in the feed and in selected reactor samples are also given in Table V. Table VI presents carbon-number distributions for the hydrocarbons in the feed and reactor sample 1.

The weight percents in Table V indicate that the furans were markedly resistant to both hydrogenation and hydrogenolysis under the experimental conditions. It should be noted that on a 100g basis the moles at C-16 and C-17 in the -22(0) series are 2.8×10^{-3} and 1.8×10^{-3} less in product 1 than in the feed. However, this decrease approximates the increase of 1.8×10^{-3} and 1×10^{-3} moles of C-16 and C-17 homologs in the -18(0) series in product 1. Similar results are observed for reactor-sample 3. This result suggests the hydrogenation of benzonaphthenofurans produces tetrahydroderivatives. The apparent unreactivity of the furans towards at least hydrogenation appears surprising.

The weight presents in Table V demonstrate that the thiophenes were very reactive toward sulfur removal under all experimental conditions. The absence of partially hydrogenated thiophenes in the products is consistent with the mechanism of dibenzothiophene desulfurization(15).

Comparison of the carbon-number distributions for the feedstock and reactor-sample 1 in Table VI reveals that the hydrotreating process significantly a) reduced the amount of aromatic and b) increased the quantity of hydroaromatic hydrocarbons. The occurrence of compound crossover in a number of these series, e.g., -14(H), -18(H), and -20(H), does not negate this conclusion although it complicates data interpretation. However, the following examples illustrate the qualitative information which can be deduced concerning the chemical processes occurring during hydrotreating. Dihydrophenanthrene ($C_{14}H_{12}$), tetrahydrophenanthrene ($C_{14}H_{14}$), and octahydrophenanthrene ($C_{14}H_{18}$) which are produced in chromia-alumina hydrotreating of phenanthrene(16) were identified in the product mixtures. Other C-14 compounds (16) involved in this process are 2-ethylbiphenyl, -14(H), 2-butylnaphthalene, -12(H), and 6-butyltetralin, -8(H). Reactor-sample 1 contains ca. 0.03 more moles of C-14 compounds in the -8(H) through -16(H) series than does the feed on a 100g basis. The former contains 0.018 fewer moles of phenanthrene than does the latter. This result suggests that the mechanism for hydrogenation of phenanthrene over chromia-alumina is at least qualitatively applicable to the conditions specified in Table I and that other compounds must contribute to the C-14 pool. In this regard, phenanthrene is a product in the hydrocracking of pyrene(17).

By GC/MS, acenaphthene and biphenyl account for 94% and 6% and 43% and 17% of the $C_{12}H_{10}$ hydrocarbons in the feed and reactor-sample 1, respectively. On a 100g basis, these values combined with the weight percents in Table VI result in a decrease of 14 millimoles in acenaphthene and an increase of 16 millimoles in tetrahydroacenaphthene between feed and products. This surprisingly good agreement suggests that the former is hydrogenated to the latter. Furthermore, the product mixture contains ca. 6 millimoles more biphenyl than does the feed. This result is not inconsistent with the expected formation of 4 millimoles from desulfurization(15) of dibenzothiophene.

Finally, the increase in the weight percent of the -8(H) Z-series from 0.4 in the feedstock to 7.0 in reactor-sample 1 and the distributions of weight percents across both the -8(H) and -12(H) series cannot be entirely explained by hydrogenation in the naphthalene family(17). Rather these results point to hydrogenation/hydrogenolysis of higher-molecular-weight hydrocarbons and/or heteroatom-containing compounds.

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TABLE I
CONDITIONS FOR HYDROTREATING ANTHRACENE OIL

	REACTOR-SAMPLE			
	1	2	3	4
Reactor Temperature (°F)	700	600	700	700
Reactor Pressure (psig)	1000	1000	1020	507
Space time (hrs)	1.48	2.50	0.75	0.75
Catalyst	Nalco Sphercat		Harshaw HT 400	
	474			

TABLE II
SUMMARY DATA FOR OXYGEN-CONTAINING ACIDS IN
FEEDSTOCK AND UPGRADED ANTHRACENE OIL

-Z	Parent Formula	Feedstock	Weight Percent in			
			Reactor-Samples			
			1	2	3	4
6(0)	C ₆ H ₆ O	4.0	0.1	0.9	0.3	0.8
8(0)	C ₉ H ₁₀	0.5	0.2	0.5	0.4	0.2
12(0)	C ₁₀ H ₈ O	1.0	< 0.0	< 0.1	0.0	0.0
14(0)	C ₁₂ H ₁₀ O	1.5	< 0.1	0.5	0.3	0.3
16(0)	C ₁₃ H ₁₀ O	1.2	0.1	0.5	0.3	0.3
18(0)	C ₁₄ H ₁₀ O	0.3	0.0	< 0.1	0.0	0.0
20(0)	C ₁₆ H ₁₂ O	0.4	0.0	0.2	0.1	0.2
22(0)	C ₁₆ H ₁₀ O	0.1	0.0	0.1	0.1	< 0.1
16(O ₂)	C ₁₂ H ₈ O ₂	2.8	0.0	0.4	0.0	< 0.1
18(O ₂)	C ₁₄ H ₁₀ O ₂	0.1	0.0	0.0	0.0	0.0
22(O ₂)	C ₁₆ H ₁₀ O ₂	0.1	0.0	0.0	0.0	0.0

TABLE III
 SUMMARY DATA FOR $C_N H_{2N+Z(N)} N$ COMPOUNDS
 IN THE ACID AND NEUTRAL-NITROGEN FRACTIONS FROM
 FEEDSTOCK AND HYDROTREATED ANTHRACENE OIL

-Z(N)	Parent Formula	Range In ^a N	Feedstock	Weight Percent			
				Reactor-Sample ^b			
				1	2	3	4
9	C_8H_7N	9-12	0.2	< 0.1	0.1	0.1	0.1
15	$C_{11}H_7N$	12-16	1.8	1.6	1.4	1.9	1.6
17	$C_{13}H_9N$	14-17	0.2	0.2	0.2	0.4	0.1
19	$C_{13}H_{11}N$	14-18	0.2	0.2	0.1	0.1	0.1
21	$C_{15}H_9N$	16-17	0.3	0.3	0.2	0.2	0.1

^aValues for feedstock. ^bConditions specified in Table I.

TABLE IV
 MOLES OF BASES AT MOLECULAR WEIGHTS 129-135
 IN FEED AND REACTOR-SAMPLE 1

Mass	Formula	Moles ^a $\times 10^3$ In	
		Feedstock	Reactor Sample 1 ^b
129	C_9H_7N	6.6	0.4
133	$C_9H_{11}N$	0.2	1.1
135	$C_9H_{13}N$	0.2	1.8
139	$C_9H_{17}N$	-	0.006
TOTAL		7.0	3.3

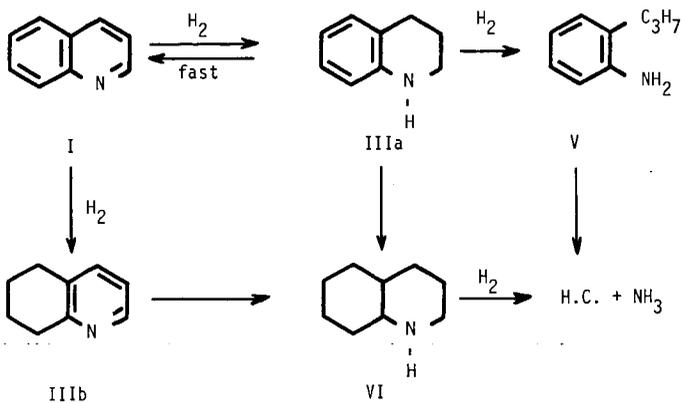
^aCalculated per 100g of feed. ^bConditions specified in Table I.

TABLE VI
CARBON-NUMBER DISTRIBUTIONS FOR THE HYDROCARBONS IN THE FEEDS AND IN REACTOR-SAMPLE 1

-Z(H)	Parent Formula	Sample ^a	Weight Percents at Carbon Number																	Total
			8	9	10	11	12	13	14	15	16	17	18	19	20					
6	C ₆ H ₆	F	0.1	0.04																0.1
		RI	0.2	0.2	0.1	0.1														0.6
8	C ₉ H ₁₀	F	0.2	0.1	0.1															0.4
		RI	0.5	3.2	1.4	1.1	0.6	0.2												7.0
10	C ₉ H ₈	F	-	-	-	-	-	-												0.0
		RI				3.0	1.0	1.5	0.5	0.2										6.2
12	C ₁₀ H ₈	F	4.8	2.3	1.3	0.6	0.2	0.03												9.2
		RI	3.9	2.2	1.4	0.7	0.3	0.2	1.2											9.9
14	C ₁₂ H ₁₀	F	5.3	1.8	1.4	0.4	0.4	0.3												9.3
		RI	3.5	1.4	3.3	0.9	0.6	0.3	0.1	0.05										10.1
16	C ₁₂ H ₈	F	2.6	1.8	0.7	0.3	0.1	0.05												5.6
		RI	2.7	3.7	1.2	1.6	0.5	0.3	0.1											10.1
18	C ₁₄ H ₁₀	F	10.4	3.2	1.3	0.4	0.1													15.4
		RI	7.2	2.4	3.9	1.2	0.7	0.2	0.1											15.7
20	C ₁₅ H ₁₀	F	1.4	2.4	0.9	0.3	0.3													5.3
		RI	0.9	2.7	0.8	1.0	0.2	0.2												5.8
22	C ₁₆ H ₁₀	F	12.1	2.7	1.6	0.3	0.2													16.9
		RI	6.1	1.3	0.9	0.3	0.3													8.9
24	C ₁₈ H ₁₂	F																		2.2
		RI																		2.2
26	C ₁₈ H ₁₀	F																		0.9
		RI																		0.4
28	C ₂₀ H ₁₂	F																		0.5
		RI																		0.1

^aF=Feedstock; RI=Reactor-Sample 1, Conditions specified in Table I.

SCHEME 1



SCHEME 2

