Estimation of the concentration of hydroaromatic compounds in a hydrogenated anthracene oil

Roberto Rosal, Fernando V. Díez and Herminio Sastre
Department of Chemical Engineering, University of Oviedo, 33071 Oviedo, Spain
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^{1}H nuclear magnetic resonance spectroscopy and gas chromatography were used to study the changes in composition during hydrogenation of an anthracene oil. It is shown that the amount of hydroaromatic and naphthenic compounds determined by chromatography correlates well with the n.m.r. bands corresponding to protons in hydroaromatic and naphthenic rings. Most donor groups in the solvent correspond to substances identified and quantified by g.c.–m.s.

(Keywords: hydrogenation; anthracene; oil)

Transferable hydrogen plays an important role in reactions during coal liquefaction or coprocessing. Under the conditions used for the extraction of coal, reversible hydrogenation–dehydrogenation dominates the chemistry of polycyclic aromatic hydrocarbons. The complex organic structures encountered in coal undergo thermolysis which results in free radicals[1]. It has been shown that hydrogen from a donor solvent stabilizes the radicals thus generated. In addition, direct interaction between hydrogenated molecules in the solvent and coal or coal-derived fragments must be considered, in order to explain certain kinetic data from liquefaction experiments[2,3]. Anthracene oil contains a considerable amount of condensed aromatic hydrocarbons with molecular weights between those of naphthalene and chrysene. The corresponding hydrogenated fraction, even if prepared under relatively mild conditions, contains appreciable concentrations of hydrogen donor substances, mainly hydroaromatic compounds. In fact, hydrogenated anthracene oil has been employed as a start-up solvent in pilot plant studies of the LSE[4] and EDS[5] processes.

Several methods have been described for the evaluation of transferable hydrogen[6–8]. Of these, n.m.r. has been used extensively to assess the structure of coal liquids[9–13] and, less frequently, to study the changes in solvents during hydrotreating or digestion[14,15]. Gas chromatography is not suitable for the analysis of heavy mixtures from extraction processes, because they contain an appreciable concentration of non-volatile high-boiling compounds. However, it provides a reliable method of identification and quantification of individual components in a coal solvent fraction. In this work, the changes that occur during hydrogenation of an anthracene oil were determined by ^{1}H n.m.r. and capillary gas chromatography. The estimation of the amount of hydroaromatic and naphthenic compounds, which contain the most important donor groups, was performed by both techniques, and the results are compared. Interest was concentrated on relating chromatographic and ^{1}H n.m.r. analyses rather than on evaluating donatable hydrogen.

EXPERIMENTAL

Materials

A light fraction of anthracene oil (AO) was supplied by Industrial Química del Nalón (NalonChem), Spain. The composition of this material is given in *Table 1*.

Hydrogenation

Hydrogenation reactions were performed in a 500 cm^3 commercial batch reactor. Two different catalysts were used: nickel on silica–alumina (Süd-Chemie, G-134-ARS) and nickel–molybdenum on activated clay (BASF, M8-24). The reaction temperature was varied from 275 to 350°C and the hydrogen pressure from 10 to 13 MPa. The reaction time was 120 min for samples analysed by ^{1}H n.m.r. In runs performed with sulphided M8-24 catalyst, a variable amount of carbon disulphide was added to the feed. Details are given elsewhere[16].

Analyses

The concentrations of individual compounds in hydrogenated anthracene oil (HAO) were evaluated by capillary gas chromatography with flame ionization detection, a 50 m, 0.25 mm i.d. capillary column with OV-101 as stationary phase, and helium as carrier gas. Peak assignment was performed by g.c.–m.s. Calibration factors were determined experimentally, using pure compounds, whenever possible. In the case of hydroaromatic products, response factors were taken as unity, because no pure samples were available commercially except for 9,10-dihydroanthracene and 9,10-dihydrophenanthrene. The error introduced is neglible, as shown by the observed calibration factors relative to biphenyl

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of 9,10-dihydroanthracene (0.971) and 9,10-dihydrophenanthrene (0.983). The response factor was below 0.900 only for heteroatom compounds, but as they do not react under the experimental conditions used, no hydrogenated products derived from them were quantified.

^{1}H n.m.r. spectra of AO and HAO fractions were obtained with a 300 MHz instrument and chloroform-d as solvent. The deuterochloroform-insoluble material (<1 wt% in all cases) was removed by filtration with a 0.45 μm filter. Chemical shifts were assessed in ppm downfield to tetramethylsilane.

RESULTS AND DISCUSSION

Figure 1 and *Table 2* show the result of g.c.–m.s. analysis of a fraction of AO before hydrogenation. The fraction contains mainly condensed aromatic hydrocarbons and only a small amount of 9,10-dihydroanthracene. Under the reaction conditions used in this work, naphthalene, acenaphthene, anthracene, phenanthrene, fluoranthene and pyrene were hydrogenated to a certain degree. A slight decrease was observed in the amounts of some other compounds (chrysene, benzofluorenes, some methyl derivatives), but this could not be attributed to a specific hydrogenation or hydrogenolysis reaction, because no products from these compounds were identified. A chromatogram of an HAO is shown in *Figure 2*, where peak numbers again refer to *Table 2*. The peaks of some aromatic hydrocarbons have been omitted from *Figure 2* for simplicity. The hydrogenated compounds that were identified and measured in hydrogenated mixtures were: tetralin, 2*a*,3,4,5-tetrahydroacenaphthene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydroanthracene, 1,2,3,4-tetrahydrophenanthrene, 1,2,3,3*a*-tetrahydrofluoranthene, and 4,5-dihydropyrene.

The changes in proton distribution of AO during hydrogenation were followed by comparing the n.m.r. spectra before and after reaction. Both spectra are shown in *Figure 3*. The proton signals have been assigned as follows:

0.5–1.5 ppm CH_2 or CH further from β to an aromatic ring and aliphatic non-CH_3 β-groups ($H_{\beta+}$)
1.5–2.0 ppm β-CH_2 and CH in naphthenic rings (H_n)
2.0–3.5 ppm CH_3, CH_2, and CH α to an aromatic ring (H_α)
3.5–4.5 ppm ring-joining methylene ($H_{\alpha 2}$)
6.9–9.1 ppm aromatic protons (H_{ar}).

The signatures of some individual components of the samples can be observed in the n.m.r. spectra. At 3.80 ppm the signal corresponding to fluorene and, slightly downfield, that of 9,10-dihydroanthracene are clearly detected. The 3.30 ppm signal corresponds to the four aliphatic protons of acenaphthene.

The n.m.r. data shown in *Table 3* indicate that the main change during treatment was an increase in the H_α band due to the formation of hydrogenated rings. All the compounds listed in *Table 2* were used to calculate the relative concentration of protons corresponding to the individual components determined by g.c.

Table 1 Analysis of the light fraction of anthracene oil

	wt%	Std error
Naphthalene	3.23	0.10
2-Methylnaphthalene	1.32	0.15
1-Methylnaphthalene	0.95	0.17
Acenaphthene	5.52	0.16
Dibenzofuran	3.10	0.23
Fluorene	6.33	0.19
9,10-Dihydroanthracene	0.89	0.12
Dibenzothiophen	0.52	0.20
Phenanthrene	17.94	0.45
Anthracene	5.84	0.22
Carbazole	0.86	0.27
Methylphenanthrene	1.39	0.25
Cyclopenta[*def*]phenanthrene	1.42	0.31
Fluoranthene	11.41	0.38
Pyrene	9.06	0.25
Methylpyrene	1.34	0.32
Chrysene	0.68	0.36

Table 2 Products identified in fresh and hydrogenated fractions of anthracene oil

Peak no.[a]	Compound	Peak no.[a]	Compound
1	Indane	18	1,2,3,4-Tetrahydrophenanthrene
2	Tetralin	19	Dibenzothiophene
3	Naphthalene	20	Phenanthrene
4	2-Methylnaphthalene	21	Anthracene
5	1-Methylnaphthalene	22	5,6-Benzoquinoline
6	2*a*,3,4,5-Tetrahydroacenaphthene	23	Carbazole
7	Biphenyl	24	Methylanthracene
8	2-Ethylnaphthalene	25	Methylphenanthrene
9	Acenaphthene	26	Cyclopenta[*def*]phenanthrene
10	Dibenzofuran	27	1,2,3,3*a*-Tetrahydrofluoranthene
11	Fluorene	28	4,5-Dihydropyrene
12	Methylbiphenyl	29	Fluoranthene
13	4-Methyldibenzofuran	30	Pyrene
14	9,10-Dihydroanthracene	31	1-Methylpyrene
15	9,10-Dihydrophenanthrene	32	Benzofluorene
16	Methylfluorene	33	Chrysene
17	1,2,3,4-Tetrahydroanthracene	34	Triphenylene

[a]See *Figures 1* and *2*

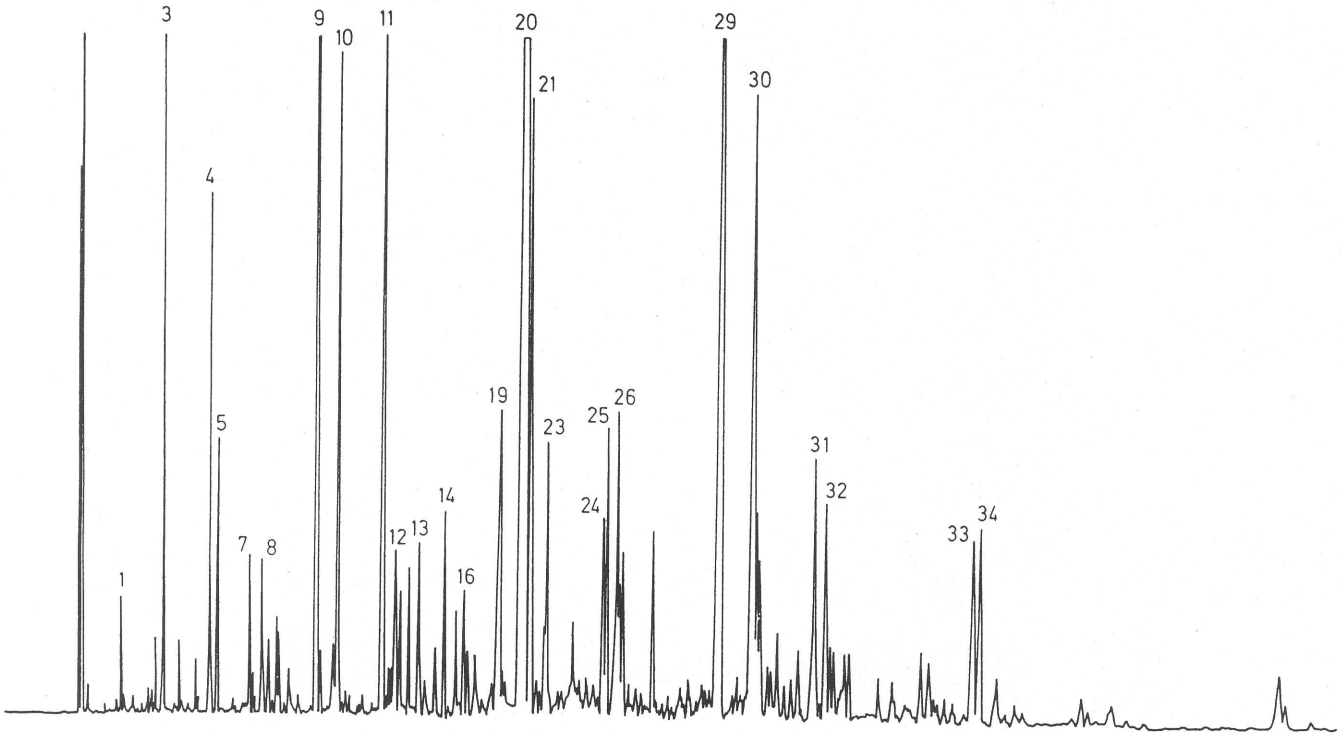


Figure 1 Gas chromatogram of fresh anthracene oil (see *Table 2* for peak identities)

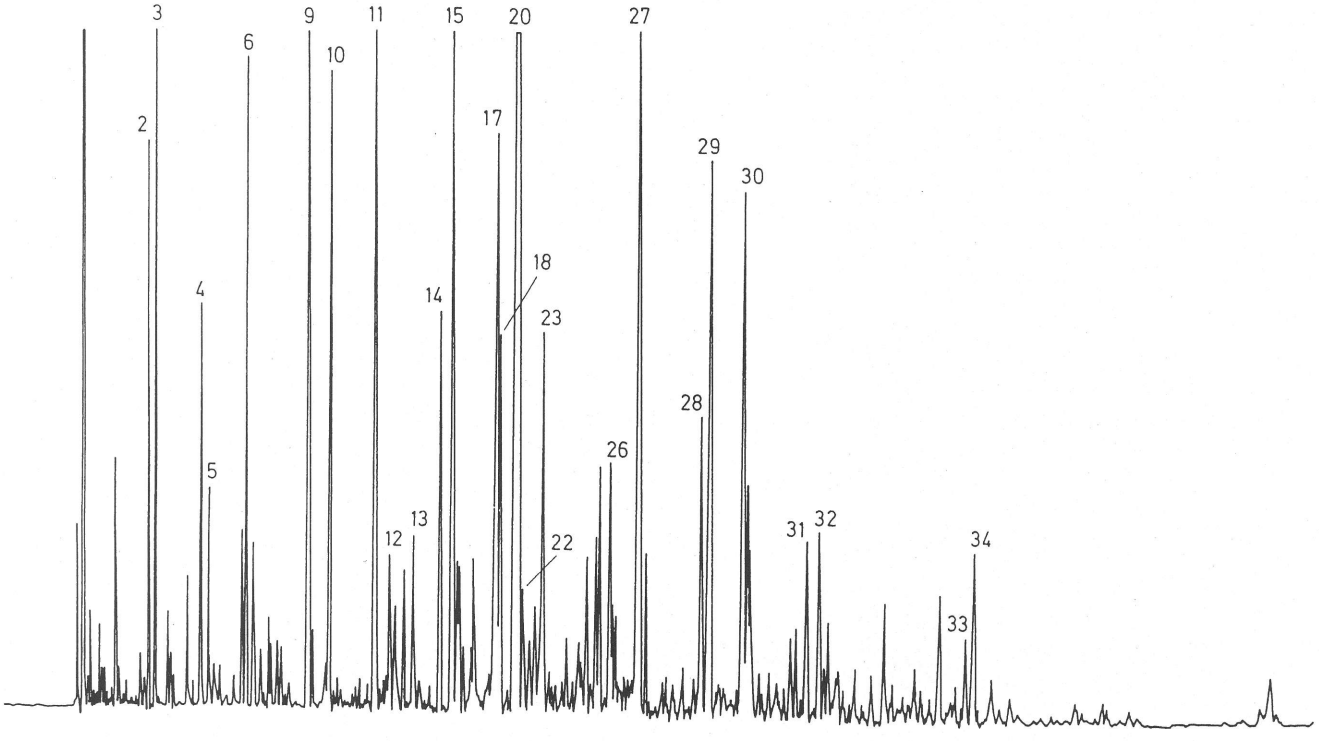
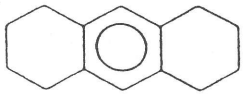


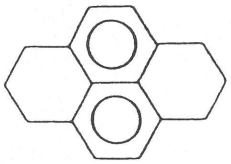
Figure 2 Gas chromatogram of hydrogenated anthracene oil (see *Table 2* for peak identities)

The comparison between the two sets of proton distributions indicates that after hydrogenation almost all the hydrogen in ring-joining methylene could be attributed to protons in 9,10-dihydroanthracene and fluorene.

Hydrogen corresponding to the H_α band in non-hydrogenated anthracene oil samples was due almost solely to methyl or ethyl groups attached to aromatic rings in compounds such as methylphenanthrene or methylpyrene. In HAO the compounds identified by g.c. and listed in *Table 2* accounted for 70–75% of the n.m.r. H_α band. In *Figure 4*, the g.c. calculated increase in H_α/H_{ar} after hydrogenation is plotted against the corresponding value from n.m.r. analysis. The difference from parity must correspond to minor reaction products that were not quantified by g.c. In fact some peaks such as those of chrysene, methylpyrene, benzofluorene, and cyclopenta[*def*]phenanthrene suffered a slight decrease

during the treatment, though their hydrogenation products were not detected. The total concentration of the compounds listed in *Table 2* amounted to almost 80% of the whole fraction. Thus most of the signal may be explained by assuming that the yield of α-protons for the uncharacterized 20% of the fraction is similar to that of the quantified compounds. To account for the balance, a certain degree of super-hydrogenation is assumed to occur yielding compounds such as *sym*-octahydroanthracene and hexahydropyrene:





The occurrence to a small degree of subsequent reaction steps leading to products with a content of hydrogen α to aromatic rings higher than that of hydroaromatic compounds could satisfactorily explain the differences observed in *Figure 4*. In support of this, mass balances for anthracene and its hydrogenation derivatives close at <97% in all cases, indicating the existence of unknown reaction products. A certain margin in the cases of phenanthrene, fluoranthene and pyrene also suggested the production of unidentified compounds.

In non-hydrogenated anthracene oil, the signal corresponding to the H_n band (*Figure 3a*) is very low, indicating a negligible concentration of naphthenic structures. The increase in this band during hydrogenation can be attributed 75–85% to the naphthenic compounds identified by g.c. This result is in good agreement with the comments regarding the H_α band, and the balance can be attributed to the 20% of the fraction whose components have not been quantified.

The increase in the $H_{\beta+}$ band can be attributed to highly hydrogenated derivatives or hydrogenolysis products. The occurrence of such reactions to a very limited extent, leading to non-donor compounds, is consistent with the preceding comments on H_α protons and reasonably explains the observed data. For example, the hydrogenation of naphthalene to tetralin involves the

Table 3 ^1H n.m.r. proton distribution in fresh and hydrogenated anthracene oil

Reaction temperature (K)	Hydrogen pressure (MPa)	$[H_2S]$ (mmol l^{-1})	$H_{\alpha 2}/H_{ar}$	H_α/H_{ar}	H_n/H_{ar}	$H_{\beta+}/H_{ar}$
Fresh oil						
–	–	–	0.058	0.176	0.008	0.083
–	–	–	0.067	0.186	0.009	0.090
Hydrogenated oil: Ni–Mo catalyst						
564	11.3	610	0.083	0.239	0.026	0.075
573	9.8	258	0.098	0.317	0.030	0.067
573	9.8	258	0.108	0.302	0.028	0.078
573	12.7	258	0.112	0.293	0.040	0.088
573	12.7	258	0.110	0.411	0.042	0.076
593	9.2	610	0.097	0.251	0.044	0.091
593	11.3	610	0.135	0.337	0.057	0.119
593	11.3	610	0.130	0.310	0.052	0.110
593	13.3	610	0.110	0.302	0.061	0.105
613	9.8	258	0.099	0.294	0.064	0.135
613	9.8	258	0.104	0.260	0.066	0.136
613	12.7	258	0.100	0.291	0.082	0.107
613	12.7	258	0.112	0.271	0.096	0.192
621	11.3	610	0.094	0.347	0.080	0.181
Hydrogenated oil: reduced Ni catalyst						
564	11.3	–	0.072	0.251	0.026	0.075
573	9.8	–	0.080	0.271	0.029	0.110
573	9.8	–	0.071	0.239	0.027	0.069
573	12.7	–	0.079	0.260	0.032	0.141
573	12.7	–	0.087	0.291	0.025	0.119
593	9.2	–	0.085	0.276	0.036	0.086
593	11.3	–	0.105	0.317	0.043	0.133
593	11.3	–	0.100	0.302	0.038	0.091
593	11.3	–	0.102	0.293	0.045	0.120
593	13.3	–	0.090	0.302	0.044	0.100
613	9.8	–	0.066	0.310	0.052	0.131
613	9.8	–	0.076	0.294	0.046	0.107
613	12.7	–	0.087	0.411	0.064	0.193
613	12.7	–	0.084	0.337	0.058	0.160
621	11.3	–	0.084	0.347	0.073	0.202

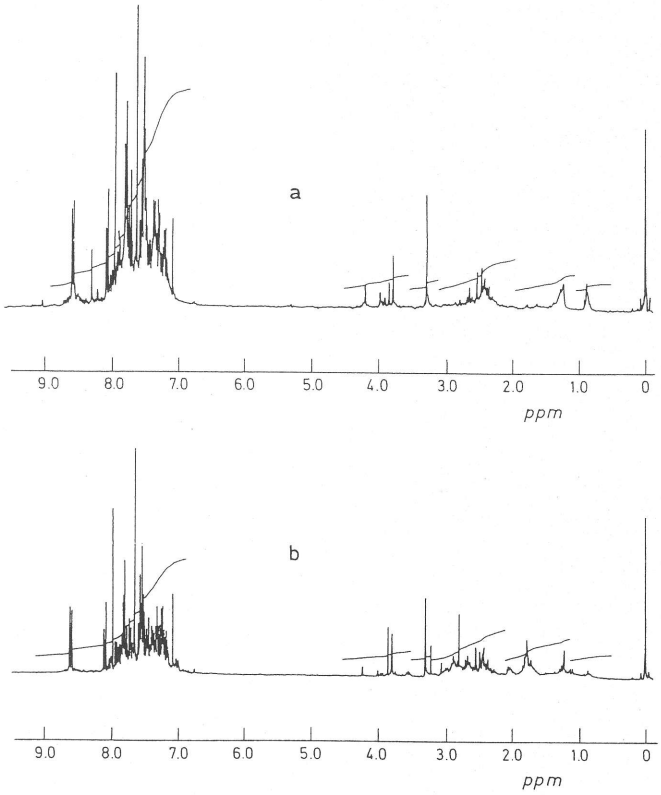


Figure 3 300 MHz ^{1}H n.m.r. spectra: a, fresh anthracene oil; b, hydrogenated anthracene oil

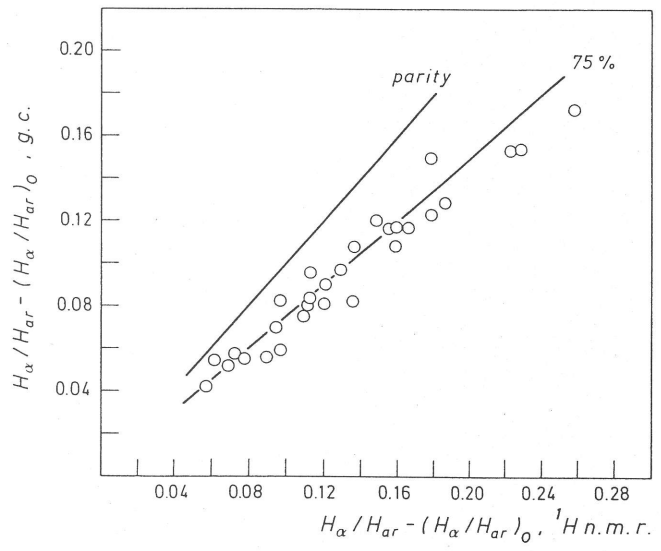


Figure 4 Increase in relative amount of α-hydrogen on hydrogenation of anthracene oil: g.c. versus ^{1}H n.m.r. data

formation of four β-protons, whereas reaction to decalin produces 16 aliphatic hydrogen atoms.

The data reported above show that the hydrogenation reactions proceeded essentially as far as the first hydrogenation derivatives. A total amount of $<5\%$ of hydrogenated products other than those listed in *Table 2* was enough to account for the n.m.r. data in the aliphatic zone. It has been previously established that the main hydrogen donor compounds in a solvent such as HAO are those containing hydroaromatic and naphthenic rings. Reaction parameters were selected to avoid super-hydrogenation and hydrogenolysis (ring-opening) reactions. It has been shown that, under these conditions, the amount of hydrogen in α-CH_3 and CH_2 groups produced during reaction is practically negligible. Whenever the foregoing assumption is not realistic, the evaluation from g.c. data of donatable hydrogen in a solvent will lead to important errors. In this case total concentrations of donatable hydrogen can be derived using ^{1}H and ^{13}C n.m.r.[15]. However, the availability of n.m.r. is often limited, and generally, reasonably accurate data on hydrogen distribution in a solvent can be obtained from g.c. analysis, provided that the fraction has been well characterized.

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