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Hydrogen incorporation during the hydrogenation reaction of an anthracene oil

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Abstract

The kinetics of the production of a hydroaromatic-rich material from the light fraction of an anthracene oil has been studied. A nickel catalyst was employed and reactions were carried out at moderate temperatures to avoid overhydrogenation. Gas chromatography was employed to determine the concentration of the main constituents of the fraction. Concentration data were fitted to simple kinetic expressions. Chromatographic results showed that the use of ^1H nuclear magnetic resonance data for predicting the donor ability of a solvent is difficult because of the presence of methyl and ethyl groups.

1. Introduction

Hydrogen transfer plays an important role in the thermal chemistry of polycyclic aromatic hydrocarbons. Several processes under development, such as coal liquefaction [1] and coke production via cocarbonization of low rank coals with pitch-like materials [2], involve hydrogen transfer from hydroaromatic molecules to reactive radicals. It has been shown that the concentration of donor compounds in coal liquefaction must be carefully controlled. Donor compounds must provide enough hydrogen to avoid recondensation of thermally produced radicals, but an excess has a detrimental effect, increasing gas production and decreasing oil yield [3]. On the contrary, naphthenic and perhydroaromatic compounds exhibit low donor ability and their formation should be avoided. Furthermore, highly hydrogenated derivatives accumulate in recycled solvents, decreasing their quality.

Extensive work has been performed in hydrogen transferring reactions employing model compounds [4, 5] and in the hydroprocessing of pure polyaromatics [6]. However, much less attention has been paid to characterization, hydrogenation and reactivity of process-derived solvents or other high boiling point aromatic and hydroaromatic complex mixtures.

The goal of this work was to determine the amount of donatable hydrogen in an anthracene oil in order to obtain optimum conditions for it to be used as a coal liquefaction solvent after hydrogenation. Several methods have been reported for evaluation of transferable hydrogen [7, 8]. In this work gas chromatography and ^1H nuclear magnetic resonance (NMR) have been employed and compared.

Experimental details

2.1. Materials

The light fraction of the anthracene oil employed (90% recovered between 215 and 400 °C) was supplied by Industrial Química del Nalón (Asturias, Spain). Major components of this material are listed in Table 1.

A commercial nickel catalyst (G-134-ARS), kindly supplied by Süd-Chemie AG, was employed. It con-

TABLE 1. Composition of the anthracene oil fraction

Component	Amount (wt.%)	Standard error
Naphthalene (NAPH)	3.15	0.12
Acenaphthene (ACE)	5.49	0.19
Dibenzofuran	3.06	0.36
Fluorene	6.24	0.22
Dihydroanthracene	0.87	0.14
Phenanthrene (PHE)	17.69	0.55
Anthracene (ANT)	5.97	0.24
Carbazole	5.51	0.21
Fluoranthene	11.25	0.49
Pyrene (PYR)	8.96	0.24

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tains (by weight) 50%–52% nickel partially oxidized, 26% SiO_2 and 9.5% Al_2O_3. The surface area (Brunauer–Emmett–Teller) was 285 $m^2\ g^{-1}$ and the mean pore diameter 68 Å. The catalyst was crushed and sieved to an average particle size of 0.075–0.100 mm. To ensure constant activity it was preactivated in hydrogen for 2 h at 300 °C before each run.

2.2. Analysis

Fresh and hydrogenated anthracene oil were analysed by gas chromatography, in both a packed and a capillary column. A non-commercial 320 cm packed column was employed in a method described before [9] to obtain quantitative measurements of compositions of all major compounds in the fraction. A capillary column (50 m, 0.25 mm inside diameter, OV-101) was installed afterwards. It allowed, in combination with gas chromatography–mass spectroscopy (HP 5987A), the complete identification of all important compounds in hydrogenated and non hydrogenated samples.

^1H NMR analysis was performed in a Brucker AC 300 instrument (300 MHz). Deuterochloroform-insoluble materials were removed by filtration with a 0.45 μm Millipore filter. The deuterochloroform-insoluble content was found to be less than 1 wt.% in all cases. Tetramethylsilane was used as internal standard. Peak assignment included the peaks due to hydrogen attached to aromatic carbon atoms at 6.9–9.1 ppm, hydrogen in ring-joining methylene at 3.5–4.5 ppm, hydrogen in α carbon atoms at 2.0–3.5 ppm and hydrogen in β or further carbon atoms between 0.5 and 2.0 ppm. This is in good agreement with generally accepted values [10, 11].

2.3. Hydrogenation conditions

Hydrogenation reactions were performed in a commercial 500 cm^3 Magnedrive autoclave purchased from Autoclave Engineers. Anthracene oil (20 wt.%) was dissolved in toluene. The reason for this was to avoid the experimental error derived from handling the crude oil which at ambient temperature splits into two phases. No differences were detected in kinetic data obtained on varying the proportion of oil. The catalyst concentration was fixed at 1.5 wt.% and a stirring speed was chosen so that all the catalyst could be held in suspension. During the initial heating period, low hydrogen pressure and stirring speed were used to minimize both catalyst damage and reaction extent. After the desired temperature was reached, the stirring speed and hydrogen pressure were increased to their operation values. The reaction time was taken as zero and the first sample was drawn. Additional samples were taken during the run. The effect of the temperature was studied in the range 300–350 °C and the hydrogen pressure varied between 100 and 130 bar. Central composite designs were employed.

3. Results and discussion

The hydrogenation products of the main aromatic compounds in anthracene oil detected in measurable quantities were tetralin (1,2,3,4-tetrahydronaphthalene), 2a,3,4,5-tetrahydroacenaphthene, 9,10-dihydroanthracene (DHAN), 9,10-dihydrophenanthrene (DHPH), 1,2,3,4-tetrahydroanthracene (THAN), 1,2,3,4-tetrahydrophenanthrene (THPH), 1,2,3,3a-tetrahydrofluoranthene (THFL) and 4,5-dihydropyrene. No other hydrogenation or hydrogenolysis products were identified. The packed column chromatographic method employed in this work allowed accurate determinations of all major compounds and detection of all hydrogenation products mentioned, but it did not allow quantitative determination of compounds present in low concentrations, because of overlapping with small peaks. THAN and THPH peaks overlapped and individual concentrations could not be evaluated. THFL was not separated from cyclopenta[*d*,*e*,*f*]phenanthrene and its evolution could not be followed because the latter was a reactive compound, as capillary chromatography showed. Its reaction products were not detected and it was supposed that they were masked by major components. Mass balances suggested that no other hydrogenation products were present in significant amounts. PHE reaction was so slow that concentration of DHPH was measured with difficulty. ANT reacted so quickly that only DHAN determination was reliable.

A reaction scheme was assumed for the reactions taking place. It is represented in Fig. 1. Reaction kinetics was assumed to be first order with respect to the reactant hydrocarbon and first order with respect to hydrogen whenever it acted as a reactant. In the case of PHE, this equation is representative of its global rate of disappearance. The actual reaction path for PHE is more complex [12] but data did not allow discrimination between reaction via DHPH or THPH. DHAN concentration profiles could be explained only by a reaction scheme including reversibility between DHAN and THAN. This result is in agreement with reaction paths proposed in previous work on ANT hydrogenation [13]. The initial reaction of ANT to THAN was neglected. This is justified because hydrogenation of ANT to DHAN is very fast. THAN was not present in the initial reaction mixture. The analysis performed employing gas chromatography–mass spectroscopy did not

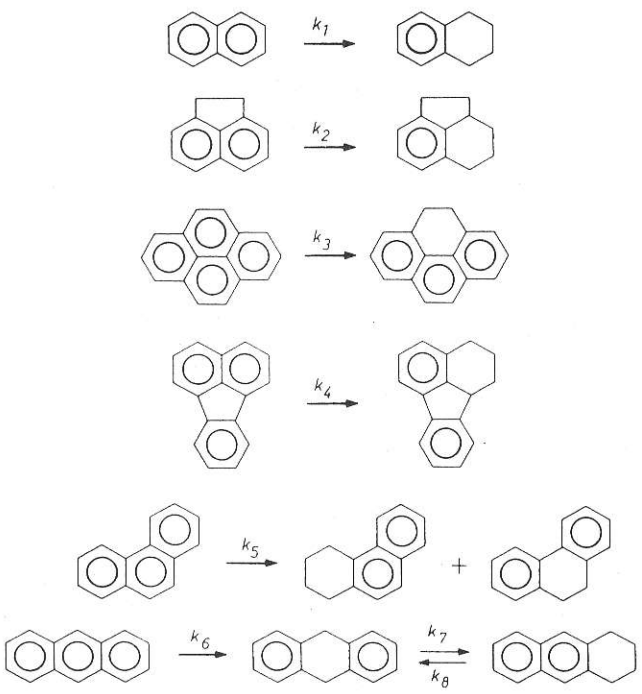

Fig. 1. Proposed reaction network.

detect hydrogenation products from ANT other than DHAN and THAN. For this reason THAN concentration, although not directly measured, was obtained by difference. Only DHAN and initial ANT concentration data were employed to obtain kinetic expressions, because ANT concentration decreases to values too low to be considered reliable in the early stages of the reaction.

Hydrogen solubility is proportional to hydrogen pressure by means of the Henry's law constant, but variation in this solubility with temperature was not taken into account. Reaction rate expressions employed to fit the data are given below (where FLU ≡ fluoranthene):

$$r_{NAPH} = k_1[H][NAPH] \quad (1)$$

$$r_{ACE} = k_2[H][ACE] \quad (2)$$

$$r_{FLU} = k_3[H][FLU] \quad (3)$$

$$r_{PYR} = k_4[H][PYR] \quad (4)$$

$$r_{PHE} = k_5[H][PHE] \quad (5)$$

$$r_{ANT} = k_6[H][ANT] \quad (6)$$

$$r_{DHAN} = k_6[H][ANT] + k_8[THAN] - k_7[H][DHAN] \quad (7)$$

The integration of eqns. (1)–(7) was performed employing the data at zero time as initial values. As the extent of the reactions during the heat-up period was low, the uncertainty in measuring initial concentrations was due almost solely to analytical error. This procedure allowed us to deal with data obtained employing different heating-up periods with accuracy.

Parameter estimation was based on the minimization of a non-linear sum of squares, performed by the Marquard–Levenberg algorithm. Kinetic constants were considered to vary with temperature following an Arrhenius-type expression. For estimation of parameters the following reparametrization was adopted [14]:

$$k_i = k'_i \exp[-(E_i/R)(1/T - 1/T_m)] \quad (8)$$

T_m is the average temperature of the experiments (593 K). The objective function involved the overall minimization with respect to two parameters in the case of eqns. (1)–(6) and six parameters for the reaction path corresponding to ANT hydrogenation. Specific reaction rates and activation energies were obtained in a simultaneous regression process. All parameter estimates are listed in Table 2 with their 95% confidence intervals. In the case of the ANT pathway, the parameters $k_{8'}$ and E_8 were a consequence of the fitting requirements for ANT and DHAN as no values were available for THAN concentration. This was the reason why their confidence intervals were relatively high.

Comparison of experimental and predicted concentrations can be observed in Figs. 2, 3 and 4 for different components and reaction conditions. Full lines represent calculated concentrations obtained solving eqns. (7), (3) and (4) for ANT, FLU and PYR respectively. It can be observed that the accord between experimental and calculated concentration profiles is quite good.

^{1}H NMR data provide a basis for the measurement of all protons, whether in compounds quantified by chromatography or not. Protons in ring-joining methylene groups ($H_{\alpha 2}$), in carbon atoms α to an aromatic nucleus (H_α) and in β or further positions ($H_{\beta+}$) are listed in Table 3 for all temperature and pressure conditions at a reaction time of 120 min. Hydrogen

TABLE 2. Parameter estimates for hydrogenation reactions

Reaction	$k_i \pm$t.s(k_i) (min^{-1} (g catalyst)$^{-1}$)	$E_i \pm$t.s(E_i) (K)
k_1	0.000426 ± 0.000024	3682 ± 1103
k_2	0.000449 ± 0.000269	10114 ± 1208
k_3	0.00142 ± 0.00006	6839 ± 913
k_4	0.000707 ± 0.000036	5004 ± 1011
k_5	0.000373 ± 0.000024	7051 ± 1373
k_6	0.0115 ± 0.0002	5655 ± 1373
k_7	0.00375 ± 0.00065	12250 ± 2645
k_8	0.00751 ± 0.00261	9328 ± 4648

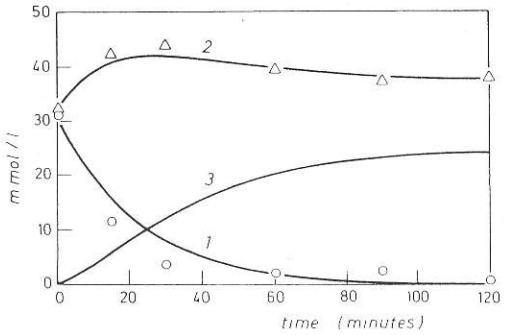

Fig. 2. Calculated concentration profiles and experimental concentrations of ANT derivatives (reaction conditions, 340 °C and 130 bar): curve 1, ANT; curve 2, dihydroanthracene; curve 3, tetrahydroanthracene.

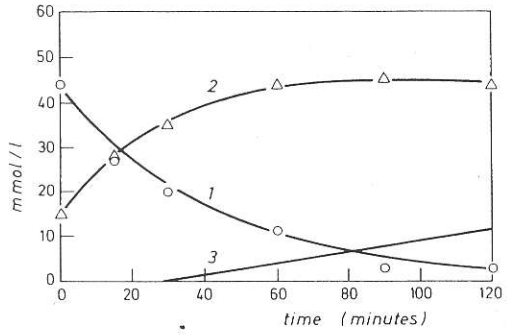

Fig. 3. Calculated concentration profiles and experimental concentrations of ANT derivatives (reaction conditions, 300 °C and 130 bar): curve 1, ANT; curve 2, dihydroanthracene; curve 3, tetrahydroanthracene.

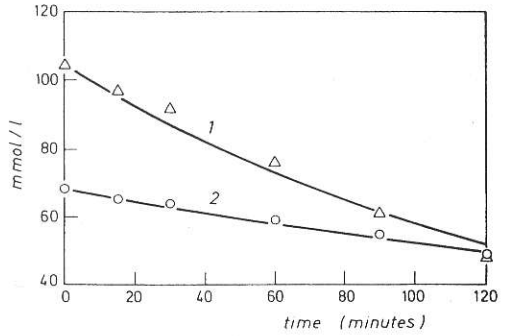

Fig. 4. Calculated concentration profiles and experimental concentrations of FLU (curve 1) and PYR (curve 2). Reaction conditions, 340 °C and 130 bar.

amounts are expressed in relation to the aromatic proton integral.

Compounds quantified by chromatography and their reaction products, whose concentrations can be found by solving eqns. (1)–(7), represented over 60 wt.% of the total fraction, as stated before. Proton distributions calculated by using these concentration profiles are shown in Table 4.

Comparison with observed ^{1}H NMR values presented in Table 3 shows that, after hydrogenation,

TABLE 3. ^{1}H nuclear magnetic resonance proton distribution in hydrogenated oils

T (°C)	P (bar)	$H_{\alpha 2}$:H_{ar}	H_{α}:H_{ar}	$H_{\beta+}$:H_{ar}
320	115	0.1045	0.3169	0.1758
320	115	0.0996	0.3015	0.1294
320	115	0.1021	0.2928	0.1652
340	130	0.0867	0.4105	0.2572
340	130	0.0844	0.3365	0.2184
340	100	0.0658	0.3102	0.1828
340	100	0.0761	0.2944	0.1534
300	130	0.0792	0.2598	0.1732
300	130	0.0874	0.2910	0.1441
300	100	0.0798	0.2713	0.1390
300	100	0.0708	0.2391	0.0956
348	115	0.0842	0.3473	0.2745
291	115	0.0715	0.2505	0.1011
320	136	0.0903	0.3023	0.1436
320	94	0.0849	0.2763	0.1123
Blank		0.0582	0.1763	0.0907
Analysis		0.0678	0.1860	0.0991

TABLE 4. Gas chromatography calculated proton distribution

T (°C)	P (bar)	$H_{\alpha 2}$:H_{ar}	H_{α}:H_{ar}	$H_{\beta+}$:H_{ar}
320	115	0.0636	0.0944	0.0540
340	130	0.0696	0.1181	0.0818
340	100	0.0648	0.1055	0.0680
300	130	0.0622	0.0841	0.0417
300	100	0.0585	0.0782	0.0358
348	115	0.0685	0.1178	0.0824
291	115	0.0590	0.0765	0.0336
320	136	0.0661	0.1010	0.0609
320	94	0.0608	0.0879	0.0472
–	–	0.0266	0.0432	0.0013

almost all the ring-joining methylene groups could be explained by those found in DHAN, DHPH and fluorene. Hydrogen in carbon atoms α to an aromatic group that can be attributed to known hydrogen donor molecules was in all cases between 20% and 30% of the total ^{1}H NMR α protons. The rest is explained by protons in methyl and ethyl groups that cannot be transferred in a re-aromatization process and by hydrogenated compounds other than those detected. In the case of β and further hydrogen atoms, similar figure were obtained. The proportion of α hydrogen (^{1}H NMR) that could be attributed to identified compounds was expected to increase with the extent of hydrogenation. The absence of such a tendency in the data in Table 3 indicates that hydrogenation reactions other than those listed in Fig. 1 occurred. A global conversion of the 40 wt.% of non-quantified compounds in the oil similar to that observed for substances listed in Table 1

would explain practically all the differences between values in Tables 3 and 4. In fact, capillary chromatography detected hydrogenation of chrysene, methylpyrene, benzo[*b*]fluorene and some other three ring compounds, such as cyclopenta[*d*,*e*,*f*]phenanthrene and various methyl derivatives. Employing a similar raw material, Del Bianco *et al.* [15] found that the evaluation of donatable hydrogen calculated by low voltage mass spectrometry led to values greater than those from ^{1}H and ^{13}C NMR data. The reason is the overlap between chromatographic peaks corresponding to compounds with similar molecular weights. This limitation can be avoided by employing calculated concentrations of minor hydrogenation products rather than their direct evaluation. Data on kinetic constants and reaction paths are then required but, once obtained, results are much more accurate.

4. Conclusions

Results show that the hydrogen content of a fraction of anthracene oil can be increased in mild hydrogenation conditions to give a considerable amount of compounds with a high donor ability for use in coal liquefaction processes. Measurement of this donatable hydrogen is a difficult task when dealing with fractions that consist of a high number of compounds, many of which are present in very low amounts. Gas chromatography was employed for measuring the evolution of the concentration of all major compounds, from which kinetic expressions for the hydrogenation reactions were developed. ^{1}H NMR gave actual proton distributions in the sample, but it has been shown that probably more than 50% of α protons could be attributed to non-donating groups. There is still the problem that not all the compounds that are supposed to be good donors have the same donating ability. Moreover, their particular contribution to radical stabilization depends on process conditions and must be checked in actual coal conversion reactions.

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Appendix A: Nomenclature

E_i	activation energy defined in eqn. (8)
k_i, k'_i	specific velocity constant defined in eqn. (8)
T_m	average temperature of all experiments