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Catalytic Hydrogenation of Multiring Aromatic Hydrocarbons in a Coal Tar Fraction

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The kinetics of the hydrogenation reaction of the main aromatic hydrocarbons found in a light fraction of an anthracene oil was studied employing two different commercial catalysts: reduced nickel and sulfided nickel-molybdenum. Kinetic expressions considering the effect of temperature and hydrogen pressure were obtained. The effect of sulfur concentration in the feed was also evaluated. Specific reaction rates and activation energies were calculated assuming first order with respect to all reagents including hydrogen in hydrogenation reactions. The concentrations of naphthalene, acenaphthene, phenanthrene, fluoranthene, and pyrene were fitted to a first-order decay. The reaction path for anthracene involves a reversible reaction between 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene.

Introduction

During liquefaction or coprocessing, coal undergoes a series of chemical and physical processes leading to a cleavage of bonds and a solubilization of the organic matter into liquid products. The upgrading of these fractions to remove heteroatoms is essential if they are employed as raw material in the manufacture of chemicals or synthetic fuels. Hydrodenitrogenation and hydrodesulfurization are required to prevent poisoning of the catalysts employed in subsequent reaction steps. On the other hand, liquids produced from coal must be upgraded in order to reduce their content in sulfur, nitrogen, and oxygen, which are recognized as a major source of environmental pollution and a cause of damage of equipment such as power plants and combustion engines. In these processes, a parallel hydrogenation of aromatic and polycyclic aromatic compounds takes place to some extent. The saturation of aromatic rings is a previous step before nitrogen removal in the hydrodenitrogenation of aromatic compounds such as carbazole and acridine (Katzer and Sivasubramanian, 1979).

The hydrogenation of aromatics is also important in the development of coal liquefaction technology itself (Davies, 1977; Chiba et al., 1987). The solvent behaves as a vehicle by means of which hydrogen from the gas phase is transferred to the liquefying coal. The donatable hydrogen depleted during extraction is then restored by catalytic hydrogenation. The partially hydrogenated hydrocarbons originating from two- to four-ring aromatics have been recognized as particularly good donor substances. Large quantities of such fused aromatics and methyl aromatics are found in the oils formed in coal liquefaction and in fractions from coal tar, like anthracene oil or creosote oil.

Almost all the available results have been obtained by employing a pure compound or a mixture of a reduced number of components rather than a real fraction (Chu

Table I. Properties of Catalysts

	G-134-ARS, Süd-Chemie	M8-24, BASF
composition, %	Ni 50–52% SiO ₂ 25% Al ₂ O ₃ 10%	NiO 4% MoO ₃ 16%
surf. area, m ² /g	285	207
mean pore diameter, Å	68	67
cumul desorption surf. area of pores between 10 and 300 Å, m ² /g	274	189
cumul desorption pore vol of pores between 10 and 300 Å, cm ³ /g	0.41	0.31

and Wang, 1982). The kinetics of the hydrogenation of naphthalene and phenylnaphthalene has been reported employing a sulfided CoO-MoO₃/γ-Al₂O₃ catalyst at 325 °C and 75-atm hydrogen pressure (Sapre and Gates, 1982). The reaction of 1-methylnaphthalene starts with hydro-dealkylation to yield naphthalene (Patzer et al., 1979). Several reaction paths have been proposed for the hydrogenation of anthracene (Wiser et al., 1970; Wiser, 1982) and phenanthrene (Shabtai et al., 1978; Girgis, 1988), but results are fragmentary due to the great complexity of the product. Quantitative networks for hydrogenation of fluoranthene and pyrene have been established in part (Lapinas et al., 1987; Girgis, 1988). Moreover, comparison between the data reported in the literature is difficult because each group of researchers employs different conditions and sometimes the reaction rates reported are not given in mutually consistent units. Most of the work has been performed at a fixed temperature, and, therefore, no information is available on the activation energies.

This paper aims at the study of the hydrogenation of the main constituents of an aromatic fraction from coal tar distillation. Reactions taking place are fitted to simplified rate expressions.

Experimental Section

Materials. Two commercial hydrogenation catalysts were employed: nickel on silica-alumina (G-134-ARS,

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Table II. Components Identified in the Anthracene Oil Fraction

component	wt, %	std error
naphthalene	3.15	0.12
acenaphthene	5.49	0.19
dibenzofuran	3.06	0.36
fluorene	6.24	0.22
9,10-dihydroanthracene	0.87	0.14
phenanthrene	17.69	0.55
anthracene	5.97	0.24
carbazole	5.51	0.21
fluoranthene	11.25	0.49
pyrene	8.96	0.24

Süd-Chemie) and nickel-molybdenum on activated clay (M8-24, BASF). Their composition and physical properties are given in Table I. Surface area and pore characteristics were obtained on a Micromeritics ASAP 2000 nitrogen adsorption instrument. The catalysts were dried, crushed, and sieved to an average particle size of 0.075–0.100 mm prior to use. Hydrogenation runs were carried out by employing a light fraction of anthracene oil supplied by Industrial Química del Nalón S. A. (NalonChem, Asturias, Spain). Major components identified in this material are listed in Table II.

Equipment and Experimental Procedure. The hydrogenation reactions were carried out in a 500-cm³ electrically-heated commercial batch reactor (Autoclave Engineers) equipped with a variable-speed magnetic stirrer. An initial charge of 170 mL containing 20 wt % of anthracene oil in toluene (purity 99+%) was employed. In reactions employing mixtures of pure compounds dissolved in toluene, it was proved that the rate of hydrogenation of toluene was much smaller than that of polyaromatic compounds from anthracene oil. The autoclave was also provided with a two-valve system which allowed sampling during the reaction. The volume of each sample was about 1 mL, and the influence of the volume removed on reaction rates was supposed negligible. Before each run, the nickel catalyst was activated in hydrogen for 2 h at 300 °C and the nickel-molybdenum one was sulfided at 350 °C with 10 vol % H₂S in H₂ for 24 h. The catalyst load was fixed at 1.5 wt %, and the stirring speed was selected so that the agitator was able to keep all the catalyst in effective suspension. Mass-transfer resistance was neglected and the effect of the stirring speed attributed only to the ability of the stirrer to keep a homogeneous suspension. During the heating period, both the stirring speed and hydrogen pressure were maintained at low levels in order to avoid catalyst damage and minimize the extent of reactions. Once the desired temperature was reached, the agitation speed was increased, an initial sample was taken, and the hydrogen pressure was increased to its reaction value. A limited but not negligible reaction takes place, however, during the heating period. For this reason initial samples do not provide actual conversion data but initial conditions for integrating kinetic expressions. Additional samples were taken at 15-, 30-, 60-, 90-, and 120-min reaction times. Hydrogen pressure was kept constant during each run by feeding hydrogen when required.

In order to keep the catalyst in the sulfided form, carbon disulfide was added to the reaction mixture whenever the nickel-molybdenum catalyst was employed. In a hydrogen atmosphere, the CS₂ is converted totally into H₂S at the reaction temperature. Reactions were studied under the following conditions: temperature, 291–348 °C; hydrogen pressure, 100–130 atm; carbon disulfide, 1.00–3.64 wt % (equivalent to 258–964 mmol of H₂S/(L of feed)). The variables were combined so that five temperatures were investigated: 291, 300, 320, 340, and 348 °C.

Analysis. Anthracene oil fractions were analyzed by gas chromatography in a Hewlett-Packard 5987A apparatus equipped with a flame ionization detector. Two columns were employed for separation of the products: a 320-cm × 0.31-cm (1/8-in.) stainless steel packed column with OV-101/BMBT on Chromosorb W-AW 100–120 and a capillary of 50 m × 0.25 mm i.d., OV-101. Peak assignment was performed by GC-MS (HP 5987A) following a standard procedure described elsewhere (Teo and Watkinson, 1987). Response factors for the main reactive components of fresh oil were determined experimentally with pure compounds (Aldrich, Merck). Response factors of hydrogenated compounds, for which no pure samples were available, were taken as the unit.

Results and Discussion

The aromatic compounds present in fresh anthracene oil that hydrogenated to a certain measurable degree were naphthalene (NAP), acenaphthene (ACE), anthracene (ANT), phenanthrene (PHE), fluoranthene (FLU), and pyrene (PYR). A slight decrease was observed in the amount of some other compounds (cyclopenta[def]-phenanthrene, chrysene, benzofluoranthenes) that could not be attributed to a given hydrogenation or hydrogenolysis reaction because no products were clearly identified. The hydrogenation products from the main aromatic hydrocarbons which were detected and (whenever possible) quantified were tetralin (TET), 2a,3,4,5-tetrahydroacenaphthene (THAC), 9,10-dihydroanthracene (DHA), 9,10-dihydrophenanthrene (DHP), 1,2,3,4-tetrahydroanthracene (THAN), 1,2,3,4-tetrahydrophenanthrene (THP), 1,2,3,10b-tetrahydrofluoranthene (THFL), and 4,5-dihydropyrene (DHPY). Hydrogenation reactions proceeded in a degree that was typically below 40%. This resulted in considerably higher relative errors in the determination of reaction products with regard to their aromatic parent hydrocarbons. Their chromatographic peaks partially overlap with those from other minor compounds in the mixture so that determination of all hydroaromatic compounds except DHA was difficult. On the other hand, anthracene hydrogenates so quickly that reliable concentrations could be obtained only for DHA. Mass balances, performed under the assumption that no other hydrogenation or hydrogenolysis compounds different from those listed above were produced, reached 93% or more in all cases.

A simplified scheme accounting for reactions taking place within the experimental region explored was developed in order to fit concentration data:



It was found that the reactions involved in the hydrogenation kinetics of phenanthrene could not be accurately represented in the model. The reason is that phenanthrene reacts so slowly that concentrations of DHP and THP are too low to be determined with precision. Moreover, the peak of THP partially overlaps with the one corresponding to THAN. Equation 3 is representative for the global rate of disappearance of phenanthrene.

Reaction kinetics was assumed to be first order with respect to the reactant hydrocarbons and first order with

respect to hydrogen whenever it acted as a reactant. Hydrogen concentration in solution was supposed to be proportional to hydrogen pressure. As the primary hydrogenation reactions are reversible, some deviations from irreversible first-order behavior could be expected. However, the extent of the reactions was low enough to allow the approximation except for anthracene hydrogenation. In this case, some reaction schemes according to tentative pathways proposed in the past were tested, but good results were obtained only by introducing a reversible reaction between DHA and THAN. Other possibilities like reversible reaction between anthracene and DHA with formation of THAN from anthracene led to a poorer fitting.

The concentrations of minor components were not employed to fit the expressions based on models 1–6. This includes TET, THAC, THP, DHP, THAN, THFL, DHP-Y, and in some cases anthracene, for which only concentrations above 2 mmol/L were considered. As for minor amounts the peak was not properly integrated. Catalyst deactivation that could have taken place was not considered. According to them, the following equations were adopted to fit kinetic data:

$$r_{NAP} = k_{NAP}(P/\langle P \rangle)[NAP] \quad (7)$$

$$r_{ACE} = k_{ACE}(P/\langle P \rangle)[ACE] \quad (8)$$

$$r_{PHE} = k_{PHE}(P/\langle P \rangle)[PHE] \quad (9)$$

$$r_{DHA} = k_{ANT}(P/\langle P \rangle)[ANT] + k_{THAN}[THAN] - k_{DHA}(P/\langle P \rangle)[DHA] \quad (10)$$

$$r_{FLU} = k_{FLU}(P/\langle P \rangle)[FLU] \quad (11)$$

$$r_{PYR} = k_{PYR}(P/\langle P \rangle)[PYR] \quad (12)$$

$\langle P \rangle$ is the average pressure of the experimental design (115 atm). Differential equations were integrated via a fourth-order Runge-Kutta algorithm for which the concentrations corresponding to the initial samples were considered initial conditions. The estimation of kinetic parameters was performed by minimization of a nonlinear sum of squares, using the Marquardt-Levenberg routine. Reaction time, hydrogen pressure, and temperature were dealt with simultaneously so that the whole set of experimental data was employed for each equation. The acceptance of a model was based upon the analysis of residuals and the *F*-test by comparing the residual sum of squares due to the lack of fit with the one associated with pure experimental error (Froment and Hosten, 1981). The latter was determined from repeated experiments distributed throughout the experimental space. Kinetic constants were considered to vary with the temperature following an Arrhenius type expression:

$$k_i = k'_i \exp\{-(E_i/R)[(1/T) - (1/\langle T \rangle)]\} \quad (13)$$

As stated before, hydrogenation runs performed by employing the nickel-molybdenum catalyst should take place in the presence of hydrogen sulfide. In order to explain kinetic data for hydrodesulfurization and hydrodenitrogenation on sulfided CoMo/Al₂O₃ or NiMo/Al₂O₃ catalysts, several researchers have found it necessary to postulate the existence of at least two different kinds of active sites (Desikan and Amberg, 1964; Shabtai et al., 1989). The active sites corresponding to sulfur vacancies exposing the molybdenum atom to bonding with aromatic rings are responsible for hydrogenation reactions (Kwart et al., 1980; Broderick and Gates, 1981). The amount of sulfur in the feed should then result in an inhibition of hydrogenation rates, and a Langmuir-Hinshelwood expression would be expected to fit the data favorably. The

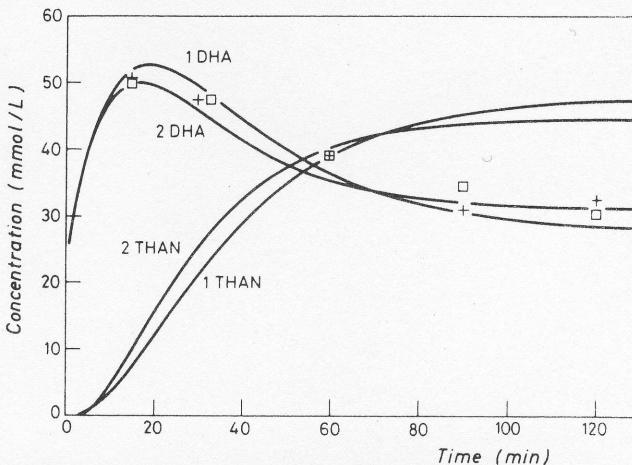


Figure 1. Comparison of model predictions with the experimental data for the reaction products from anthracene conversion in the presence of Ni-Mo/Al₂O₃ at 340 °C, 130 atm, and a concentration of H₂S in the feed of 258 (□) and 964 mmol/L (+). Curves 1 and 2 fit both sets of data, respectively. The profiles represent DHA and THAN.

dependence of pseudo-first-order rate constants with hydrogen sulfide concentration was fitted to the following equation:

$$k'_i = (k''_i / (1 + K_{i,S}[H_2S])) \quad (14)$$

All the estimated values of the adsorption parameters, $K_{i,S}$, were in the range of 10⁻⁴ L/mmol H₂S, low enough to justify considering the influence of sulfide concentration in the feed upon reaction rates negligible. Confidence intervals for adsorption parameters were large, including zero in most cases. This suggests that they may be redundant parameters, having practically no influence on rate constants. Figure 1 shows the calculated profiles (employing eq 14) and experimental concentrations of DHA and THAN for reactions with different concentrations of hydrogen sulfide in the feed. The effect of increasing the amount of sulfur compounds in the system should be a decrease in reaction rates according to eq 14. However, experimental results do not evidence inhibition by sulfur within the range studied, either in the case of anthracene or for the other quantified hydrogenation reactions.

According to the data available on the structure of sulfided catalysts, hydrogen sulfide should produce an inhibition of the hydrogenation and hydrodesulfurization reactions inasmuch as hydrogenation activity is associated with sulfur anion vacancies (Massoth et al., 1984). Sapre and Gates (1982) reported an inhibition effect of hydrogen sulfide upon the hydrogenation reaction of biphenyl. Their data were fitted to a modified Langmuir-Hinshelwood expression, and a slight inhibition effect was detected. In fact, the product of the adsorption parameter and the concentration was of the order of 1, comparable to the self-inhibition shown by biphenyl. The conditions employed by Sapre and Gates very much favored the detection of the inhibition effect as reactions were performed with a diluted solution of the reactant hydrocarbon (less than 30 mmol/L). At 300 °C for example, the adsorption parameter was 25.6 ± 4.0 L/mol whereas at 350 °C a value of 12.0 ± 3.2 L/mol was reported. In our work, a greater effect of the self-inhibition was expected as the concentration of polynuclear aromatic hydrocarbons was about 100 times greater than the one employed by Sapre and Gates. Moreover, the dispersion of the data obtained with a real fraction should be greater than the one corresponding to the data obtained by employing very dilute

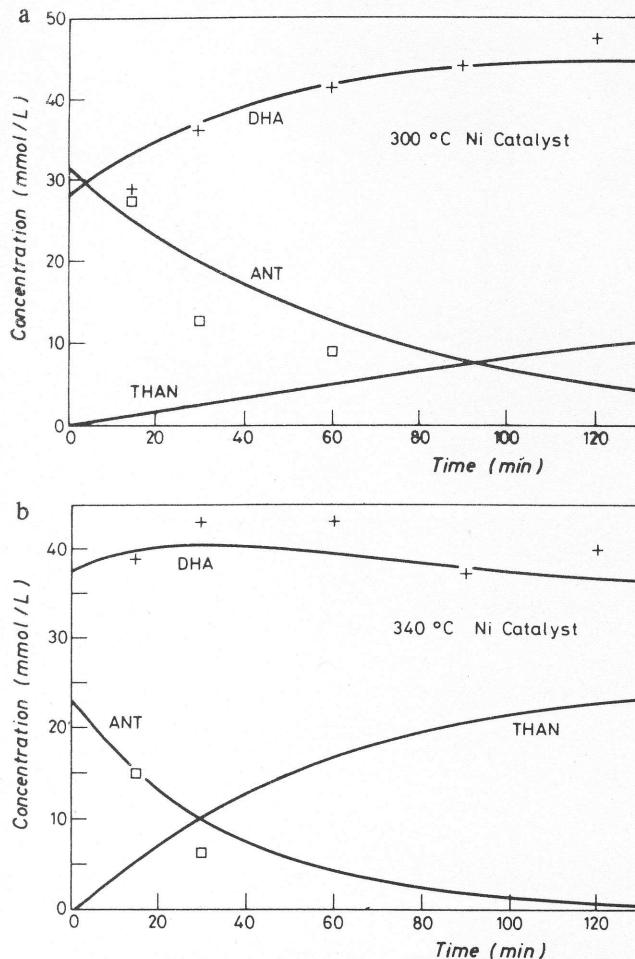


Figure 2. Experimental concentrations of ANT (□) and DHA (+) and calculated concentrations of ANT, DHA, and THA as a function of reaction time at 100 atm in the presence of a reduced nickel catalyst: reaction temperature, 300 (a) and 340 °C (b).

solutions of a single component because experimental uncertainty contributes to masking the inhibition effect by enlarging the confidence intervals.

It has also been shown that the inhibition effect of hydrogen sulfide is strong on the hydrogenolysis activity of sulfided catalysts, but it did not affect hydrogenation reactions (Broderick and Gates, 1981; Van Parijs et al., 1986). In neither work was the concentration of sulfur included in the rate expression for hydrogenation. Fitting results described in what follows have been calculated considering $k_i' \equiv k_i''$.

The residuals do not show anomalous behavior and there are no significant deviations between predicted and observed concentrations of the major component involved in each reaction for all pressures and temperatures and over the entire range of conversions. Table III presents the parameter estimates and their corresponding 95% confidence intervals for all models. Specific reaction rates at the average temperature of all the experiments (320 °C), k_i' , are nearly equal within the range of experimental error for the same reactions in both catalysts. The relatively low activity of the reduced nickel catalyst can be attributed to the effect of poisons. The fraction contains 0.52 wt % of dibenzothiophene that reacts in a certain range. The reaction kinetics could not be quantified, but H₂S was detected in the gas phase. Pyrene, acenaphthene, naphthalene, and phenanthrene exhibit similar reactivities, whereas the hydrogenation of anthracene is almost 100 times faster. The reaction rate for hydrogenation of fluoranthene is intermediate. The activation energies fall

Table III. Parameter Estimates for the Kinetic Model of Equations 7–13

equation	$k_i',^a$ L/(g of catalyst)·h	$E_i/R,^a$ K
(a) Reduced Nickel Catalyst (G-134-ARS, Süd-Chemie)		
7 (<i>i</i> = NAP)	$4.12 \times 10^{-3} \pm 2.2 \times 10^{-4}$	3720 ± 990
8 (<i>i</i> = ACE)	$4.15 \times 10^{-3} \pm 2.3 \times 10^{-4}$	9980 ± 1100
9 (<i>i</i> = PHE)	$3.66 \times 10^{-3} \pm 2.4 \times 10^{-4}$	6970 ± 1140
10 (<i>i</i> = ANT)	$1.408 \times 10^{-1} \pm 2.0 \times 10^{-3}$	5466 ± 1370
10 (<i>i</i> = THAN)	$5.9 \times 10^{-2} \pm 2.7 \times 10^{-3}$	9310 ± 4600
10 (<i>i</i> = DHA)	$3.15 \times 10^{-2} \pm 6.5 \times 10^{-3}$	12350 ± 2630
11 (<i>i</i> = FLU)	$1.376 \times 10^{-2} \pm 6.2 \times 10^{-4}$	6970 ± 910
12 (<i>i</i> = PYR)	$6.48 \times 10^{-3} \pm 3.1 \times 10^{-4}$	5010 ± 1020
(b) Sulfidized Nickel-Molybdenum Catalyst (M8-24, BASF)		
7 (<i>i</i> = NAP)	$6.07 \times 10^{-3} \pm 3.7 \times 10^{-4}$	4780 ± 590
8 (<i>i</i> = ACE)	$3.78 \times 10^{-3} \pm 2.8 \times 10^{-4}$	9760 ± 820
9 (<i>i</i> = PHE)	$5.02 \times 10^{-3} \pm 2.7 \times 10^{-4}$	6590 ± 490
10 (<i>i</i> = ANT)	$1.80 \times 10^{-1} \pm 2.3 \times 10^{-2}$	6920 ± 1090
10 (<i>i</i> = THAN)	$5.0 \times 10^{-2} \pm 1.7 \times 10^{-2}$	7130 ± 3110
10 (<i>i</i> = DHA)	$5.00 \times 10^{-2} \pm 8.2 \times 10^{-3}$	12380 ± 1160
11 (<i>i</i> = FLU)	$1.35 \times 10^{-2} \pm 1.1 \times 10^{-3}$	8190 ± 750
12 (<i>i</i> = PYR)	$1.64 \times 10^{-3} \pm 2.6 \times 10^{-4}$	4550 ± 500

^a Values are listed plus/minus the limits of 95% confidence intervals.

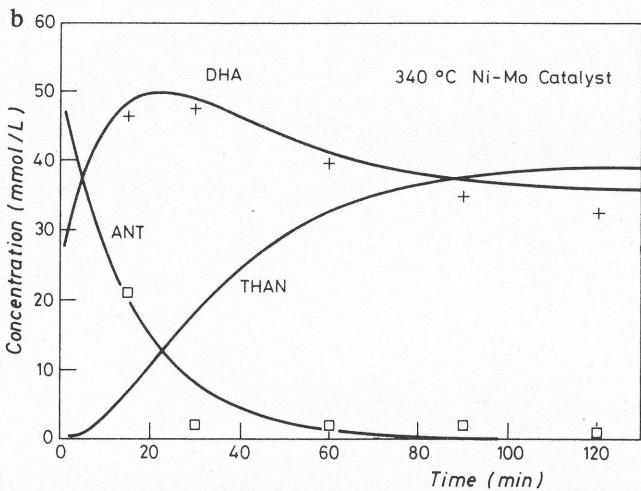
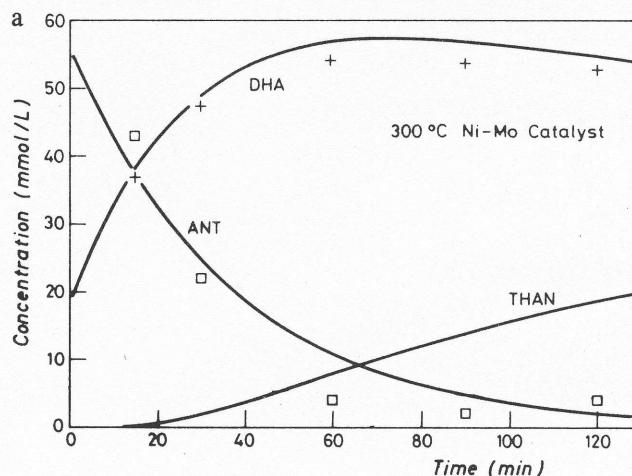


Figure 3. Experimental concentrations of ANT (□) and DHA (+) and calculated concentrations of ANT, DHA, and THA as a function of reaction time at 100 atm and 258 mmol of H₂S/(L of feed) in the presence of Ni-Mo/Al₂O₃ catalyst: reaction temperature, 300 (a) and 340 °C (b).

into the range 5000–10 000 K (about 10–20 kcal/mol) for all reactions, and differences between the two catalysts can be attributed to experimental uncertainty. Activation energy is particularly high for the reaction of DHA to yield THAN. A consequence of this is that DHA, a good hydrogen donor substance, is relatively favored at lower

temperatures with regard to THAN. Figures 2 and 3 show experimental data and concentration profiles for anthracene hydrogenation employing both catalysts and two temperatures. In all cases the dependence of the reaction rate on the temperature established by eq 13 fits experimental data suitably.

The comparison in reactivity of aromatic hydrocarbons that have between two and four fused rings has seldom been reported. Katti (1984) determined the relative conversions of several hydrocarbons in a mixture simulating a neutral fraction of a coal-derived oil. The data show that anthracene is much more reactive than naphthalene, acenaphthene, phenanthrene, fluoranthene, pyrene, and fluorene. At temperatures below 350 °C, the reactivity of fluoranthene is also considerably higher than that of the other compounds reported except anthracene. These results are in good agreement with kinetic data obtained in this work. Typically, the results from experiments performed with dilute solutions—and therefore in the absence of strong inhibition effects—were fitted considering reversibility in hydrogenation reactions. Katti et al. (1988) determined the hydrogenation rates at 355 °C of the major polycyclic aromatic hydrocarbons in a heavy distillate fraction from the SRC-II hydroliquefaction process. The individual hydrogenation reactions of most of the aromatic hydrocarbons were well represented by irreversible first-order kinetics. Only in the case of naphthalene and related two-ring compounds did equilibrium limitations have to be considered. In this work the kinetics of naphthalene hydrogenation fitted to an irreversible rate expression without evidence of lack of fit even at the highest temperature employed (348 °C). No hydrogenation products from tetralin were detected. The reason for the discrepancy seems to be the higher hydrogen pressure employed (100–130 atm) in comparison with that of Katti et al. (36 atm). In these conditions, the rate of hydrogenation reactions must be considerably higher with regard to those of dehydrogenation, and consequently the equilibrium conversion is higher. Moreover, the temperature employed in this work was lower than that reported by Katti et al., and the mean conversion is also shorter (25% for the central temperature versus over 50% in Katti's work). All reasons mentioned explain why, within the range of variables employed in this work, the kinetics of naphthalene hydrogenation fitted satisfactorily to an irreversible pseudo-first-order rate expression as they contribute to broadening the initial stage of the reaction for which the first-order assumption is correct. Similar results were reported also by Wilson et al. (1985). Grgis (1988) found that the kinetic data for the first step of fluoranthene hydrogenation employing the pure compound dissolved in an inert hydrocarbon required a reversible rate expression, the dehydrogenation rate constant being greater than the hydrogenation one. In this work, the conversion of fluoranthene reached 50% in most cases, yet concentration data fitted well to an irreversible expression in agreement with Katti et al. as stated before. A suitable explanation for this behavior is that inhibition due to competitive adsorption affects mainly hydrogenated products. The rate of reactions which give back aromatic hydrocarbons decreases, and the equilibrium conversion increases.

Conclusions

The rate of hydrogenation of the main constituents of an aromatic fraction of an anthracene oil has been established as a function of temperature by employing two different catalysts. The concentrations of the reacting aromatic compounds in the fraction were fitted to first-order kinetic expressions with regard to the reacting hy-

drocarbon and, in the case of hydrogenation reactions, to the relative hydrogen pressure. A reaction path for anthracene hydrogenation has been proposed that satisfies experimental data. Specific reaction rates indicate the following order of reactivities:



The activation energies ranged from 10 to 20 kcal/mol, and it is particularly high for the hydrogenation of DHA to THAN. These figures are compatible with chemical processes in the rate-controlling step. Differences in reactivity between the two catalysts are low and in most cases fall within the range of experimental error. Hydrogen sulfide concentration varied from 258 to 964 mmol of H₂S/L fed into the runs performed where the nickel-molybdenum M8-24 catalyst was employed. The effect of this variable was negligible and the corresponding adsorption parameters too low to be included in kinetic expressions.

A consequence of the kinetic data presented in this work is the limited importance of DHA as a hydrogen donor in liquefaction reactions. The effect of DHP is probably also low because in both cases the amount of tetrahydroderivatives increases quickly to the detriment of DHA and DHP, which are much better hydrogen donor molecules. The main donor compound is THFL and favorable conditions for its formation should be taken into account to yield a high content of hydrogen donor substances with low hydrogen consumption.

Acknowledgment

This work was supported by FICYT (Foundation for the Support of Research in Applied Science and Technology, Asturias, Spain).

Nomenclature

ACE	= acenaphthene
ANT	= anthracene
DHA	= 9,10-dihydroanthracene
DHP	= 9,10-dihydrophenanthrene
DHPY	= 4,5-dihydropyrene
E_i	= activation energy, cal/mol
FLU	= fluoranthene
$K_{i,S}$	= rate equation parameter, interpreted as adsorption equilibrium constant of species i , L/mmol of H ₂ S
k_i	= rate constant, L/((g of catalyst)·h)
k'_i	= rate constant at $\langle T \rangle$, L/((g of catalyst)·h)
k''_i	= rate constant defined by eq 14, L/((g of catalyst)·h)
NAP	= naphthalene
P	= hydrogen pressure, atm
$\langle P \rangle$	= average hydrogen pressure of the experiments, atm
PHE	= phenanthrene
PYR	= pyrene
r_i	= reaction rate, mmol/((g of catalyst)·h)
R	= gas constant = 1.987 cal/(mol K)
T	= absolute temperature, K
$\langle T \rangle$	= average absolute temperature of the experiments, K
TET	= tetralin
THAC	= 2a,3,4,5-tetrahydroacenaphthene
THAN	= 1,2,3,4-tetrahydroanthracene
THFL	= 1,2,3,10b-tetrahydrofluoranthene
THP	= 1,2,3,4-tetrahydronaphthalene

Registry No. NAP, 91-20-3; ACE, 83-32-9; ANT, 120-12-7; PHE, 85-01-8; FLU, 206-44-0; PYR, 129-00-0; TET, 119-64-2; THAC, 480-72-8; DHA, 613-31-0; DHP, 776-35-2; THAN, 2141-42-6; THP, 1013-08-7; THFL, 20279-21-4; DHPY, 6628-98-4; cyclopenta[def]phenanthrene, 203-64-5; chrysene, 218-01-9.

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The comparison in reactivity of aromatic hydrocarbons that have between two and four fused rings has seldom been reported. Katti (1984) determined the relative conversions of several hydrocarbons in a mixture simulating a neutral fraction of a coal-derived oil. The data show that anthracene is much more reactive than naphthalene, acenaphthene, phenanthrene, fluoranthene, pyrene, and fluorene. At temperatures below 350 °C, the reactivity of fluoranthene is also considerably higher than that of the other compounds reported except anthracene. These results are in good agreement with kinetic data obtained in this work. Typically, the results from experiments performed with dilute solutions—and therefore in the absence of strong inhibition effects—were fitted considering reversibility in hydrogenation reactions. Katti et al. (1988) determined the hydrogenation rates at 355 °C of the major polycyclic aromatic hydrocarbons in a heavy distillate fraction from the SRC-II hydroliquefaction process. The individual hydrogenation reactions of most of the aromatic hydrocarbons were well represented by irreversible first-order kinetics. Only in the case of naphthalene and related two-ring compounds did equilibrium limitations have to be considered. In this work the kinetics of naphthalene hydrogenation fitted to an irreversible rate expression without evidence of lack of fit even at the highest temperature employed (348 °C). No hydrogenation products from tetralin were detected. The reason for the discrepancy seems to be the higher hydrogen pressure employed (100–130 atm) in comparison with that of Katti et al. (36 atm). In these conditions, the rate of hydrogenation reactions must be considerably higher with regard to those of dehydrogenation, and consequently the equilibrium conversion is higher. Moreover, the temperature employed in this work was lower than that reported by Katti et al., and the mean conversion is also shorter (25% for the central temperature versus over 50% in Katti's work). All reasons mentioned explain why, within the range of variables employed in this work, the kinetics of naphthalene hydrogenation fitted satisfactorily to an irreversible pseudo-first-order rate expression as they contribute to broadening the initial stage of the reaction for which the first-order assumption is correct. Similar results were reported also by Wilson et al. (1985). Grgis (1988) found that the kinetic data for the first step of fluoranthene hydrogenation employing the pure compound dissolved in an inert hydrocarbon required a reversible rate expression, the dehydrogenation rate constant being greater than the hydrogenation one. In this work, the conversion of fluoranthene reached 50% in most cases, yet concentration data fitted well to an irreversible expression in agreement with Katti et al. as stated before. A suitable explanation for this behavior is that inhibition due to competitive adsorption affects mainly hydrogenated products. The rate of reactions which give back aromatic hydrocarbons decreases, and the equilibrium conversion increases.

Conclusions

The rate of hydrogenation of the main constituents of an aromatic fraction of an anthracene oil has been established as a function of temperature by employing two different catalysts. The concentrations of the reacting aromatic compounds in the fraction were fitted to first-order kinetic expressions with regard to the reacting hy-

drocarbon and, in the case of hydrogenation reactions, to the relative hydrogen pressure. A reaction path for anthracene hydrogenation has been proposed that satisfies experimental data. Specific reaction rates indicate the following order of reactivities:



The activation energies ranged from 10 to 20 kcal/mol, and it is particularly high for the hydrogenation of DHA to THAN. These figures are compatible with chemical processes in the rate-controlling step. Differences in reactivity between the two catalysts are low and in most cases fall within the range of experimental error. Hydrogen sulfide concentration varied from 258 to 964 mmol of H₂S/L fed into the runs performed where the nickel-molybdenum M8-24 catalyst was employed. The effect of this variable was negligible and the corresponding adsorption parameters too low to be included in kinetic expressions.

A consequence of the kinetic data presented in this work is the limited importance of DHA as a hydrogen donor in liquefaction reactions. The effect of DHP is probably also low because in both cases the amount of tetrahydroderivatives increases quickly to the detriment of DHA and DHP, which are much better hydrogen donor molecules. The main donor compound is THFL and favorable conditions for its formation should be taken into account to yield a high content of hydrogen donor substances with low hydrogen consumption.

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Nomenclature

ACE = acenaphthene

ANT = anthracene

DHA = 9,10-dihydroanthracene

DHP = 9,10-dihydrophenanthrene

DPHY = 4,5-dihydropyrene

E_i = activation energy, cal/mol

FLU = fluoranthene

K_{i,S} = rate equation parameter, interpreted as adsorption equilibrium constant of species *i*, L/mmol of H₂S

k_i = rate constant, L/((g of catalyst)·h)

k_{i'} = rate constant at *(T)*, L/((g of catalyst)·h)

k_{i''} = rate constant defined by eq 14, L/((g of catalyst)·h)

NAP = naphthalene

P = hydrogen pressure, atm

<P> = average hydrogen pressure of the experiments, atm

PHE = phenanthrene

PYR = pyrene

r_i = reaction rate, mmol/((g of catalyst)·h)

R = gas constant = 1.987 cal/(mol K)

T = absolute temperature, K

<T> = average absolute temperature of the experiments, K

TET = tetralin

THAC = 2a,3,4,5-tetrahydroacenaphthene

THAN = 1,2,3,4-tetrahydroanthracene

THFL = 1,2,3,10b-tetrahydrofluoranthene

THP = 1,2,3,4-tetrahydronaphthalene

Registry No. NAP, 91-20-3; ACE, 83-32-9; ANT, 120-12-7; PHE, 85-01-8; FLU, 206-44-0; PYR, 129-00-0; TET, 119-64-2; THAC, 480-72-8; DHA, 613-31-0; DHP, 776-35-2; THAN, 2141-42-6; THP, 1013-08-7; THFL, 20279-21-4; DPHY, 6628-98-4; cyclopenta[def]phenanthrene, 203-64-5; chrysene, 218-01-9.

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