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Catalytic Hydrogenation of Model Nitrogen, Sulfur, and Oxygen Compounds

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The relative rates of heteroatom removal from model N–, S–, and O– compounds and of hydrogenation of polynuclear aromatics have been measured in competitive experiments over sulfided CoMo catalysts (300–1500 psig, 300–450°C). Feed components and compositions were selected to approximate those of petroleum residua, shale oils, and coal oils and included fused ring thiophenes and furans, quinoline, indole and alkylphenols.

The NSO compounds could be grouped by chemical type, both with respect to relative rates and to the mechanisms of heteroatom removal. Experiments showed that, where nitrogen or oxygen were bonded to an aromatic ring, saturation of that ring was necessary before C–N or C–O scission could occur and was rate determining. This was not true of S species.

Based on experimentally determined product distributions from these model feeds, the hydrogen consumption associated with reaction of any given chemical type could be calculated. Comparison was made with the hydrogen consumed in the processing of atmospheric resids, shale oils, and coal oils.

INTRODUCTION

Accompanying the recent emphasis on new energy sources has been an increased interest in the upgrading of heavy charge stocks such as coal oils, shale oils, and petroleum residua. Upgrading is normally effected by hydrogenation over a cobalt–molybdenum (CoMo) or nickel–tungsten catalyst at 500–2500 psi pressure and at 350–450°C (*1*). Such processing, in addition to removal of ash (by its deposition on the catalyst), reduces the nitrogen, sulfur, and oxygen (NSO) content of the feed and effects a partial saturation of polynuclear aromatics.

The heteroatoms in resids, coal oils, and shale oils are mainly restricted to a small number of chemical types or classes. Some typical elemental analyses of heavy charge stocks are shown in Table 1. Sulfur, the major heteroatom in resids and in tar sands bitumen, is found primarily in the form of thiophenes and, to a lesser extent, of sulfides (*2–4*). Among the thiophenes, the benzo- and dibenzo-derivatives predominate.

Nitrogen is the major heteroatom in shale oils. As in petroleum, shale oil nitrogen occurs almost exclusively in 5- and in 6-ring heterocycles such as indoles, quinolines, and carbazoles (*5–8*). Phenolic oxygen is the primary heteroatom of coal oils (*9*), fused ring furans and carboxylic acids being also present in resids (*5*). Oxygen is not a significant component of petroleum, however.

Hydrogenation experiments over sulfide catalysts fall generally into two categories; those dealing with actual heavy charge stocks and those treating single components. As evidenced by the recent publication of Satterfield and co-workers

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TABLE 1

Heavy Carbonaceous Resources

	Arab light atmospheric resid	Athabasca bitumen	Shale oil, filtered NTU	Utah coal oil (COED)	Utah A coal
C	84.8	83.3	86.3	83.3	74.8
H	11.8	10.4	11.4	8.8	5.5
N	0.2	0.4	2.0	1.0	1.4
S	3.6	4.6	0.9	0.3	0.5
O	0.1	1.3	—[a]	6.6	6.1
H/C[b]	1.6	1.5	1.6	1.3	0.9
Ref.	—[c]	(*33*)	(*31*)	(*32*)	(*32*)

[a] Not given.
[b] Mole ratio.
[c] Present work.

(*34*), however, the behavior of the various components in a feed mixture can be interrelated, one affecting the other. Little information exists on the relative rates of reaction of heterocycles in a competitive conversion, as is typical of actual processing. Indeed, even the products of heterocycle hydrogenation under realistic, industrial conditions are often uncertain.

Desulfurization reactions have been widely studied but frequently at only atmospheric pressure (*1*, *10–15*). Benzo- and dibenzothiophenes, under these conditions, yield ethylbenzene and biphenyl, respectively, but ring saturation has been reported at elevated pressure (*15*). Elimination of nitrogen and of oxygen is substantially more complex. Hydrogenation of nitrogen heterocycles, for example, gives a multiplicity of hydrocarbon products as reaction severity is increased, products suggestive of significant secondary reactions competing with nitrogen removal (*1*, *16–22*). Phenol hydrogenates either to cyclohexane or to benzene, depending on reaction conditions (*1*, *23–24*), but it would be difficult to project the reported distribution to actual heavy feeds. Removal of oxygen from benzo- and dibenzofurans produces a mixture of hydrogenated and partially hydrogenated aromatics (*25*, *26*).

It has been the purpose of the present study to determine relative rates, products, and intermediates in the hydrogenation of model heterocycles under actual industrial process conditions, to determine where hydrogen is consumed in these processes, and to identify any distinctions in mechanism or behavior among catalysts.

EXPERIMENTAL METHODS

Two catalysts were used in these experiments, HDS-2 (CoMo) and HDS-1441 (SiO_2-stabilized CoMo). Both are commercial catalysts and were described in detail previously (*35*). Both were sized to 60/80 mesh and were presulfided prior to use.

Hydrogenation experiments were conducted in a down-flow, stainless steel reactor containing 20 cm^3 (13.9 g) of catalyst. The reactor measured 13.2 cm long, 1.5 cm diameter, with a 0.3 cm thermowell in the center, all preceded by a 20 cm preheater spiral. Provision was made at the preheater inlet for hydrogen, H_2S, and liquid hydrocarbon. Hydrocarbon was metered to the reactor system by a Milton-Roy piston pump; hydrogen, with a Matheson mass flow meter. Following the reactor was a Grove back-pressure valve to release the pressure, a waterjacketed liquid receiver, a liquid nitrogen trap, and a wet test meter. Reaction conditions were 290–430°C, 300–1500 psig, WHSV = 1–5, H_2/feed mole ratio = 7–10. Standard test conditions were 344°C, 700 psig, WHSV = 2, H_2/feed = 8 (~6500 SCF/bbl).

Prior to analysis, liquid products were contacted with Linde 3A molecular sieves to remove any water produced in the reactor. Both elemental and gas chromatographic analyses were obtained on all feed and product liquids. Elemental analyses (CHNSO) were performed by Microanalysis, Inc., Wilmington, Del., and totaled 100.0 ± 0.5%. Hydrogen consumption values were calculated from elemental analysis. In addition, liquids were analyzed for weight percent phenol, mercaptan sulfur, and basic nitrogen by caustic extraction, by silver titration, and by perchloric acid titration techniques, respectively.

Gas chromatographic results were obtained with a 150 ft polyphenyl ether (OS124, Applied Science Laboratories) 0.010 in. capillary column, programmed from 25 to 160°C, 4°min. Flame ionization response factors for all components were determined experimentally using pure compounds. Certain highly polar amines such as cyclohexylamine were not cleanly eluted from this column and a 10 ft column of 10% SE-30 on Gas Chrom Q was used to test for their presence. (They were absent.) Closure for any individual feed component was always over 90%.

RESULTS

A standard feed was selected comprising 9 components as detailed in Table 2. It contained both sulfide and thiophene sulfur and analyzed 3.61% S, 0.79% N, 0.90% O, 85.91% C, and 8.79% H. Two components, 1,2,4-trimethylbenzene and hexadecane, served as internal standards for analysis.

Each day, except during process variable studies, one component of the standard feed was changed but the mole fraction of all components was held constant. Dibenzothiophene (DIBT) was replaced by benzothiophene (BT) or thiophenol;

TABLE 2

Feed Compositions

Standard feed	Moles	Wt %
Dibenzothiophene	1.0	10.4
Dibutylsulfide	1.0	8.2
Quinoline	1.0	7.3
Dibenzofuran	1.0	9.5
Naphthalene	1.0	7.2
2-Methylnaphthalene	2.0	16.0
2,3-Dimethylnaphthalene	1.0	8.8
Hexadecane	1.5	19.1
1,2,4-Trimethylbenzene	2.0	13.5
Substitute components		
Benzothiophene		*p*-Cresol
Dioctylsulfide		4-Propylphenol
Thiophenol		2-Ethylphenol
		2,3-Benzofuran
Indole		2-Phenylphenol
o-Ethylaniline		*cis*-2-Phenyl-1-cyclohexanol
		1-Naphthol

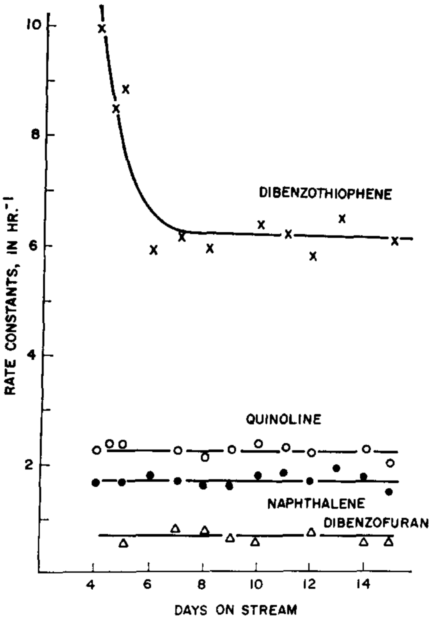


FIG. 1. Rate constants for hydrogenation. HDS-2, 700 psig, H_2/feed = 8, 344°C.

dibutylsulfide, by dioctysulfide; quinoline, by indole or *o*-ethylaniline; and dibenzofuran, by one of the oxygen species listed in Table 2. After a 15-day sequence of model feed experiments, an Arab light atmospheric resid was tested for comparison with the model feed behavior and for its effect on relative rates of reaction.

Rate Comparisons

Conversion data for the various feed components have been compared assuming a first-order rate expression (*14, 15, 18, 27*). The validity of this assumption, i.e., the validity of the relative rate relationships across a range of pressure, temperature, conversion, and catalyst age, are discussed below. Since the removal of NSO atoms is an essentially irreversible process, the following rate expression holds:

$$-\ln\,(\text{1-conversion}) = \frac{k_f\cdot f(\mathrm{H_2})}{(\mathrm{WHSV}\cdot\rho_c/\rho_l)} = \frac{k'}{\mathrm{WHSV}\cdot\rho_c/\rho_l}. \quad (1)$$

In this expression ρ_l and ρ_c are the densities of the liquid feed and of the catalyst particles, respectively. Conversion signifies the fraction of heteroatom removed from the respective charge component.

Naphthalene hydrogenation to tetralin approaches an equilibrium value less than 100% such that the appropriate equation for calculating its rate constant for conversion becomes the following:

$$\ln\frac{(\text{equilibrium conversion})}{(\text{Equil. conv.} - \text{observed conv.})} = \frac{k_f\cdot f(\mathrm{H_2}) + k_r}{(\mathrm{WHSV}\cdot\rho_c/\rho_l)}. \quad (2)$$

Little or no decalin was observed in the products of these runs. Based on the literature (*28*), equilibrium conversion of naphthalene to tetralin under present test conditions (700 psig, H_2/feed = 8) would be 96.9% at 344°C and 78% at 399°C. Tests at 399°C with fresh catalysts and at low LHSV gave conversion of 78–80% in good agreement.

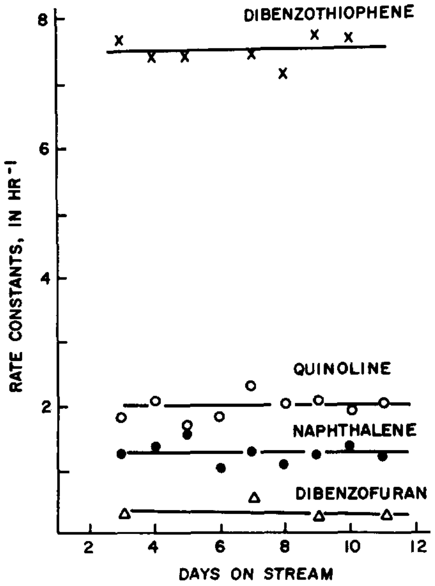


FIG. 2. Rate constants for hydrogenation. HDS-1441, 700 psig, H_2/feed = 8, 344°C.

TABLE 3

Relative Rate Constants for Conversion[a]

Rate constants[b]	HDS-2		HDS-1441	
	Stable	Aged	Stable	Aged
2-Methylnaphthalene[c]	1.0	1.0	1.1	1.0
2,3-Dimethylnaphthalene[c]	1.4	1.2	1.2	1.1
Dibenzothiophene	3.6	5.8	6.3	6.2
Benzothiophene	3.4	4.6	6.2	—
Thiophenol	≥10	—	—	—
Indole	0.9	—	0.9	1.1
o-Ethylaniline	1.1	—	—	—
Quinoline	1.3	1.5	1.7	1.7
2,3-Benzofuran	1.0	—	1.1	—
o-Ethylphenol	1.2	—	—	1.2
Dibenzofuran	0.4	—[d]	0.3	—[d]
2-Phenylphenol	1.4	—	1.4	—
cis-2-Phenyl-1-cyclohexanol	≥10	—	—	—
p-Cresol	5.2	6.5	7.2	—
4-Propylphenol	—	—	7.6	—
1-Naphthol	—	—	0.7	—

[a] 700 psig, H_2/feed = 8, 344°C; sulfided CoMo catalysts.

[b] Relative to naphthalene; reproducibility, ±20%.

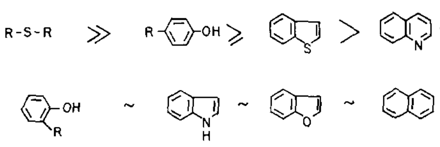
[c] Assumes equilibrium conversion is 97% at 344°C.

[d] Conversion too low for accurate comparison.

Rate constants are plotted for HDS-2 as a function of time on stream in Fig. 1. The reactor was conditioned for 2 days at 288°C and the temperature then was raised to that in Fig. 1. Relative rate constants for conversion reached a stable level after 5–6 days on stream. Data for the silica-promoted catalyst, HDS-1441, are plotted in Fig. 2 and show a stable performance almost immediately. Although the initial behavior of the two materials is different, most probably due to differing rates of coke deposition, both attain a stable activity from which rate data can be extracted. The performance of the two catalysts is compared in Table 3.

Under all conditions of space velocity, temperature and catalyst age, conversion of dibutylsulfide to butane and H_2S was 100%. The sulfide was nevertheless retained as a feed component in order (a) to prevent changes in catalyst composition with changing thiophene conversion and (b) to provide an approximately constant H_2S distribution across the reactor bed. This H_2S, present at about 1 mole%, would have reduced the apparent rate constant for thiophene conversion by about 10% (*14*).

With increasing time on stream, the relative rate constants for conversion over the two CoMo catalysts became almost identical. Although not all components were tested for both materials, the data in Table 3 indicate a decreasing reactivity, general to conventional CoMo catalysts, in the order:



In addition, the rate data in Table 3 led to conclusions regarding possible intermediates and rate determining steps in

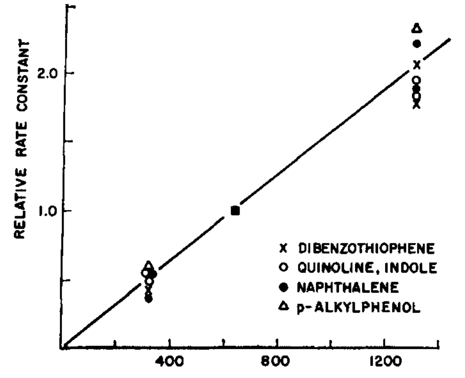


FIG. 3. Rate dependence on hydrogen pressure (relative to 640 psia H_2).

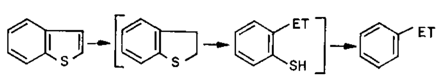
the conversion processes. One would not expect to observe cyclohexanols during phenol hydrogenation, for example. *o*-Ethylaniline on the other hand should be readily observed, if formed, during hydrogenation of indole.

Relative rate data are of limited use if they pertain to only a single set of reaction conditions, as in Table 3, and experiments were performed to show that these ratios are not strongly dependent on pressure or on temperature. The effect of hydrogen partial pressure over stable catalysts is shown in Fig. 3. To within the accuracy of the measurements, a first-order dependence on hydrogen for the components, dibenzothiophene, naphthalene, quinoline, indole, and *p*-cresol was found. Such a dependence has been reported by several investigators for naphthalene and for dibenzothiophene (*1*). The minimal effects of temperature are shown in Table 4. Activation energies were determined as follows (kcal/mole): Dibenzothiophene, 36; quinoline, 30; naphthalene, 31; indole, 28; and *p*-cresol, 26. Cecil *et al.* (*36*) reported a value of 38 kcal/mole for fuel oil desulfurization in the absence of diffusion problems.

Product Analysis

Sulfur. The desulfurization (deS) of benzo- and dibenzothiophenes at low temperature (344°C) was highly selective, producing ethylbenzene and biphenyl, respectively, as shown in Table 5. At higher severity (399°C), biphenyl selectivity was reduced (to about 75%) as increased phenylcyclohexane was observed. Ethylbenzene selectivity was also reduced but remained over 95%. Thiophenol yielded benzene.

In the studies of BT and DIBT, products were routinely analyzed for mercaptan sulfur and rarely contained even 100 ppm. This observation and the high reactivity of thiophenol would indicate that the rate determining step in deS is the initial ring opening of the S-heterocycle and not reaction of any mercaptan- or thiophenol-type intermediate, if indeed such intermediates exist as fluid phase species. (Brackets designate postulated but not observed intermediates in a conversion sequence.) This finding agrees with atmospheric pressure data of Givens and Venuto (*10*).



Observation of phenylcyclohexane in the product from DIBT suggests ring saturation may become a competing reaction to S-ring opening at higher temperature. It is not believed that phenylcyclohexane is a sequential hydrogenation product (of biphenyl). Biphenyl, as a component in test

TABLE 4

Temperature Dependence of Relative Rates[a]

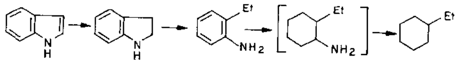
Compound	Relative rate constant[b]			
(°C):	288	316	344	399
Dibenzothiophene	5.3	6.0	6.2	5.2
Indole	—	1.1	0.9	0.7
Quinoline	1.0	1.7	1.5	—
p-Cresol	8.5	7.4	6.5	5.8

[a] 700 psig, H_2/feed = 8, CoMo catalysis.

[b] Relative to naphthalene hydrogenation.

feeds, was not hydrogenated, indicating a rate constant of ≤ 0.01 relative to naphthalene. Thus any ring hydrogenation which does occur must come prior to desorption from the catalyst. Dicyclohexyl was not formed from DIBT under the standard test conditions.

Nitrogen. As evident in Table 5, deN of indole, *o*-ethylaniline, and quinoline yielded cyclohexane derivatives in good selectivity. These data indicate a primary reaction sequence as follows:



In support of this sequence were the observations that (a) product distribution from *o*-ethylaniline was essentially identical to that from indole (Table 5), (b) at deN levels of over about 40% neither indole nor indoline, but only *o*-ethylaniline, was detected by gc analysis, (c) at all levels of conversion studied over 95% of the nitrogen in the liquid product was basic nitrogen (indole is nonbasic), and (d) the rate constant for deN of *o*-ethylaniline is equal to that of indole (Table 3). Similarly, *o*-propylaniline was the stable intermediate in the hydrogenation of quinoline (and propylcyclohexane the major product), indicating that the rate determining step in N removal from both quinolines and indoles is ring-saturation of an *o*-alkylaniline.

As shown in Table 5, selectivity to cycloparaffin decreases with increasing temperature, a trend common to both N– and O– removal. This decrease is attributed to a second, distinct reaction sequence, *o*-ethylaniline to ethylbenzene, and not to an equilibration of naphthene and aromatic. First, it was shown with aged catalyst that the reduced selectivity at 399°C was a temperature, not a conversion level, effect. Second 1,2,4-trimethylbenzene was a constituent of all present feed mixtures and was never hydrogenated.

TABLE 5

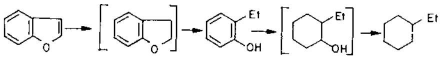
Alkylcyclohexane Selectivities over CoMo Catalysts[a]

Reactant	Selectivity (%) to alkylcyclohexane[b]	
	344°C	399°C
Benzothiophene	1	4
Indole	93	74
o-Ethylaniline	91	78
Quinoline	97	86
Benzofuran	95	92
o-Ethylphenol	95	88
4-Propylphenol	91	69

[a] 344–399°C, 700 psig, H_2/feed = 8.

[b] As opposed to alkylbenzene.

Oxygen. Considerable information exists on the hydrogenation of phenols but very little on O removal from heterocycles (*15, 23–26*). The data in Table 5 show that, under the standard reaction conditions, both benzofuran and substituted phenols give cyclohexane derivatives in high selectivity. The following reaction scheme is proposed analogous to that of N–removal:



As would be expected, benzofuran and *o*-ethylphenol show almost identical product distributions (Table 5). In addition, measurements of phenolic oxygen matched the elemental analysis, showing that phenol, not benzofuran was rate limiting in O– removal. The data in Table 3 show a close similarity between reactivities of the two oxygen species. The results of Landa *et al.* (*25*) would support these observations.

A further conclusion is suggested from Table 3, namely, that phenols can be divided into two groups, hindered (ortho-substituted) and nonhindered, the former showing the lower rate of reaction. The mechanism of O– removal remains the

TABLE 6

Summary of Relative Rates and Hydrogen Consumption[a]

Chemical species	Relative rate constant[b]	H_2/ hetero-atom	Hydrogen consumed[c]
Sulfides	>50	2	90 SCF
Benzothiophene	4–6	3	130
Dibenzothiophene	4–6	2	90
Indole	1.0	6	600
Quinoline	1.5	7	700
p-Alkylphenol	5–7	4	350
o-Alkylphenol	1.4	4	350
Benzofuran	1.1	6	530

[a] 344°C, 700 psig, H_2/feed = 8, CoMo catalysts.

[b] Relative to naphthalene, ±20%.

[c] Hydrogen consumed for each 1.0% heteroatom removed, assuming a charge stock density of 1.0 g/cm^3.

same, however, in both cases and cyclohexane derivatives are the major products.

DISCUSSION

The results in the previous section showed that NSO compounds could be ordered by chemical type, both with respect to the relative rates and to the mechanisms of heteroatom removal. Both rates and hydrogen consumption have been compared for the various model compounds in Table 6.

Sulfur compounds comprised the simplest group wherein elimination of heteroatom was facile and did not involve significant hydrogenation of any associated aromatic ring system. Thus only the stoichiometric 2–3 moles of H_2 are required to remove the sulfur atom, corresponding to about 110 SCF H_2/bbl to remove 1.0% sulfur from a resid of density 1.0 g/cm^3.

Two aspects of these results require special comment. First in high pressure experiments with BT and DIBT, some authors report only aromatic, others partially saturated hydrocarbon products (*3, 11, 37, 38*). Examination of these reports shows that, where aromatics hydrogenation occurred, high temperatures or fresh catalysts were employed. The present data suggest that, under conventional process conditions, these hydrogenation reactions are largely absent in desulfurization.

Second, deS rates of the two thiophene derivatives have been reported to be in the order BT > DIBT (*15, 27, 30*). This distinction in rate was not found in the present experiments. One possible explanation, that the similar rates were artifacts of competitive adsorption in these model mixtures, was excluded by replacing the thiophene component of the feed with 1:1 BT:DIBT. Both exhibited very similar reactivities. It is proposed instead that physical (diffusion) effects may have contributed to the differences reported earlier. The unusually low activation energy, 5 kcal/mole, in one of these reports (*15*) could well have resulted from diffusion restrictions.

Nitrogen removal from indole, *o*-ethylaniline and quinoline all yielded alkylcyclohexane as the major product, and it is proposed that this conversion is general to the nitrogen compounds found in our carbonaceous resources. Namely, whenever nitrogen is attached to an aromatic ring (as it almost invariably is), saturation of that ring is required prior to C–N bond cleavage. As a result, hydrogen consumption with CoMo catalysts is high, corresponding to a stoichiometry of 6–7 moles H_2/mole NH_3 produced or about 650 SCF/bbl to remove 1.0% nitrogen.

Distinction is again found between these results and those in the literature, and it regards ultimate products. Most authors agree that indoline and tetrahydroquinoline are the first products of hydrogenation and that there is little initial saturation of the carbocylic ring (*16–19*). Anilines follow, but there is often a multiplicity of subsequent reactions and eventual products. It is suggested that the present simple reaction sequence better represents actual process behavior and that the presence of H_2S is particularly important in modeling deN reactions. Wherever an extreme multiplicity of products has been found in the literature, the experiments have been conducted with fresh or unsulfided catalyst or in a closed autoclave system.

With oxygen compounds, the elimination reactions are analogous to those of nitrogen. It is proposed then that oxygen removal from a phenol (or from a benzofuran) over CoMo requires prior saturation of the attached aromatic and consumes 4–6 moles of H_2/mole of water produced. Regarding rates of deO of substituted phenols, it is suggested that the more facile conversion of the para-isomers is due to less steric hindrance. Supporting this suggestion was the generality of the relative rate behavior (*p*-CH_3 and *p*-propyl vs 2-ethyl and 2-phenylphenol). In the literature cresol reactivities decrease in the order $p > m > o$ (*1*).

Since it was an objective of this study to obtain conversion data under conditions approximating industrial practice, it is appropriate to check these results and conclusions with actual feed behavior. As shown in Table 7, despite significant differences in process conditions, over 70% of the hydrogen consumed in the three examples could be accounted for in terms of NSO– removal. Indeed, essentially all of the hydrogen consumed in the processing of the coal oil was associated with elimination of the phenolic oxygen. Thus no conflict exists between model and actual feed behavior.

TABLE 7

Hydroprocessing of Commercial Feeds

Feed	Arab light atm. resid	Shale oil, NTU-type (*31*)	Utah coal oil (*32*)
Pressure (psig)	700	3,000	2,500
H_2-circ. (SCF/bbl)	9,500	6,000	15,000
Temperature (°C)	399	375	397
LHSV	2.3	0.5	1.0
deS	80	89	99+
deN	36	65	67
deO	—	—	80
H_2-consumption (SCF/bbl)	520	1,000	2,240
Calcd H_2 consumed[a]	370	870	2,290

[a] Required for NSO– removal, based on the data in Table 7.

CONCLUSIONS

The present studies constitute an attempt to relate, semiquantitatively, the behavior of individual NSO– compounds and polynuclear aromatics to that of actual heavy charge stocks. Mixtures of model compounds representative of the chemical types predominant in petroleum residua, in shale oils and in coal oils were examined to determine the relative rates of hydrogenation of the individual feed components and the products of that hydrogenation.

Based on these comparisons, and on data obtained for postulated intermediates in the hydrogenation of NSO– compounds, an ordering of reactivity by chemical type was proposed as follows:

Sulfides ≫ *p*-alkylphenols > benzothiophenes > quinoline ~ *o*-alkylphenols ~ indoles ~ benzofurans ~ naphthalenes > dibenzofurans ≫ mononuclear aromatics.

Examination of the products of hydrogenation indicated that NSO–compounds fall into two categories in terms of the mechanisms of heteroatom removal. Sulfur compounds (sulfide, fused ring thiophenes) were readily cleaved to give H_2S and alkane or aromatic, respectively. With N– and O– species, saturation of any aromatic ring attached to the heteroatom was required prior to C–N or C–O bond scission.

Hydrogen consumption values were determined for NSO– removal from the model compounds, and these values were projected onto the observed behavior of atmospheric resids, coal oils, and shale oils.

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