NOTATION

a_1,a_2,a_3 = coefficients in Eq. 15
C = effective correction factor, Eq. 14
C_p = volumetric specific heat, ρc_p
c_1,c_2 = property correction factors, Eq. 12
c_p = specific heat
D = tube diameter
$\bar{d}_p$ = mean particle diameter
Fo_i = instantaneous Fourier number, $(k_D t)/[(\rho c_p)_D \bar{d}_p^2]$
Fo_m = time-mean Fourier modulus $(k_D \bar{\theta}_D)/(C_{pD} \bar{d}_p^2)$
h_{pi} = instantaneous heat transfer coefficient during transient conduction (numerical solution)
h_p = time-averaged heat transfer coefficient for disperse system residence time of $\bar{\theta}_D$ (numerical solution)
h_s = heat transfer coefficient due to surface renewal of a gas-solid medium with stagnant fluid (modified solution)
k = thermal conductivity
Nu_p = time-mean Nusselt number, $(h_p \bar{d}_p)/k_D$ (numerical solution)
T = temperature
T_1 = disperse system temperature in domain 1, Figure 1
T_2 = disperse system temperature in domain 2, Figure 1
t = time
w = natural log of conductivity ratio, $ln(k_D/k_g)$
x = distance from the wall, Figure 1
z = dimensionless distance from the wall, $x/\bar{d}_p$

Greek Letters

α = void fraction
η = excess temperature, $(T_2 - T_B)$
$\bar{\theta}_D$ = disperse system mean residence time
ρ = density
ϕ = excess temperature, $(T_1 - T_B)$

Subscripts

B = bed, (away from the wall)
D = disperse system
e = effective value
g = gas
s = solid/particle
w = immersed surface/wall

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Hydrodeoxygenation of 1-Naphthol Catalyzed by Sulfided Ni-Mo/γ-Al_2O_3: Reaction Network

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Liquids derived from coal and shale have high concentrations of organooxygen compounds that react with hydrogen under conditions of catalytic hydroprocessing to give hydrocarbons and water. These reactions are poorly characterized, and an understanding of the reaction networks and kinetics is expected to be of value in process design and modeling. Most of the few publications concerned with hydrodeoxygenation (HDO) reactions are concerned with (substituted) phenols and dibenzofuran. Hydrodeoxygenation of dibenzofuran in the presence of industrial hydro-

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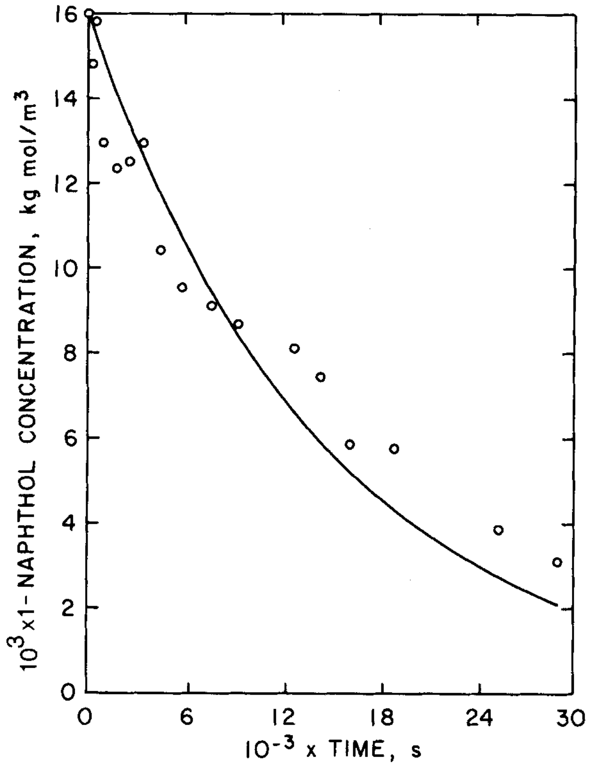


Figure 1. Conversion of 1-naphthol with hydrogen in the presence of sulfided $NiO-MoO_3/\gamma-Al_2O_3$ catalyst in a batch reactor at 473 K and 35 atm. The curve represents the prediction of the reaction network of Figure 3.

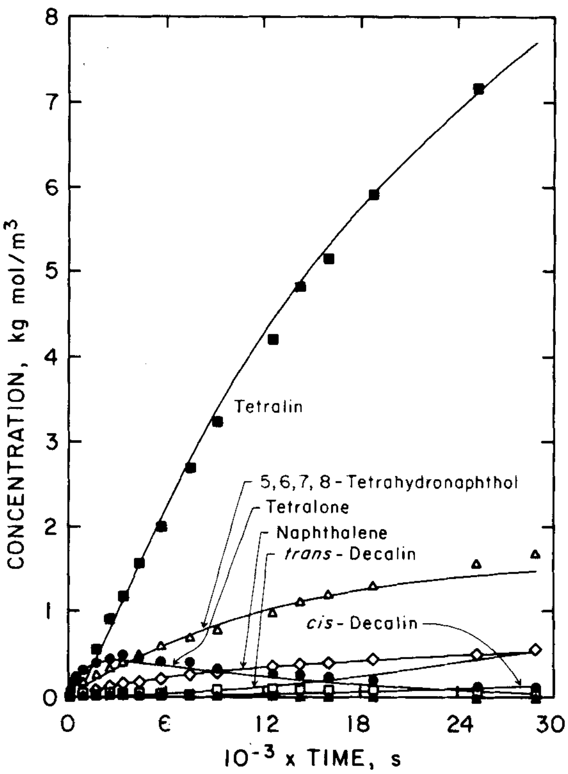


Figure 2. Conversion of 1-naphthol and hydrogen into hydrogenated and deoxygenated products the presence of sulfided $NiO-MoO_3/\gamma-Al_2O_3$ catalyst in a batch reactor at 473 K and 35 atm. The curves represent the predictions of the reaction network shown in Figure 3.

processing catalysts such as $Co-Mo/Al_2O_3$ takes place via simultaneous hydrogenation of the aromatic rings and C—O bond scission; a quantitative representation of the reaction network has been reported by Krishnamurthy et al. (1981).

Many of the oxygen-containing constituents of coal liquids are phenolic. Characterization of the acidic fractions of a SRC-II coal-derived liquid by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, infrared spectroscopy, and gas chromatography/mass spectrometry led to the conclusion that substituted (and partially hydrogenated) naphthols are the major organooxygen components (Petrakis et al., 1983; Li et al., 1984). The following compounds were identified as major components: 5,6,7,8-tetrahydro-1-naphthol, 2-hydroxyphenylbenzene, 4-cyclohexylphenylphenol, and an unidentified isomer of methylphenylphenol (Li et al., 1984). These phenolic compounds are much more reactive with hydrogen than dibenzofuran (Li et al., 1985).

The objective of the research reported here was to establish the reaction network for conversion of a simple compound representative of the organooxygen compounds in coal liquids, namely, 1-naphthol. The catalyst was a typical commercial, sulfided NiO $MoO_3/\gamma-Al_2O_3$, and the experiments were carried out with liquid-phase reactants under conditions approaching those of potential practical interest.

BATCH REACTOR EXPERIMENTS

The catalytic reaction experiments were carried out with a slurry in either a 1-L or a 0.3-L stirred batch reactor (Autoclave Engineers). 1-Naphthol (Aldrich, 99+%) was dissolved in a large excess of *n*-hexadecane (Humphrey Chemical Co., redistilled), and the solution was introduced into the reactor, saturated with hydrogen (Linde, 3500 psi grade), and brought to the reaction temperature (473 to 548 K). A loader (Shih et al., 1977) allowed charging of the catalyst (American Cyanamid HDS 9A, 4.0×10^{-4} kg) after the solution had been brought to the reaction temperature. The catalyst had been crushed and sieved to give a particle size range of 10 to 150 mesh. It was persulfided externally at 673 K and 1 atm with a flowing mixture of 10 vol. % H_2S in H_2 for 7.2×10^3 s. The physical properties and composition of the catalyst are given elsewhere (Houalla et al., 1978).

The reactant solution was saturated with hydrogen, providing a large stoichiometric excess of this reactant. Each reaction experiment was done at nearly constant pressure and temperature; the ranges of these variables were 22 to 34 atm and 473 to 623 K. The agitator speed was about 1,500 rev./min. Calculations by standard methods and comparisons with data obtained in similar experiments by Krishnamurthy et al. (1981) showed that the interphase and intraparticle mass transfer resistances were negligible.

At the beginning of each experiment, upon injection of the catalyst, the temperature dropped about 3 K from the set point and stabilized at the set point within about one minute. The reactor pressure was brought up to the desired value by addition of hydrogen and was maintained nearly constant by frequent addition of make-up hydrogen.

PRODUCT ANALYSIS

Liquid samples were drawn periodically from the autoclave and analyzed with a Perkin-Elmer 3120B gas chromatograph equipped with a flame ionization detector and a SE-54 capillary column, 30 m in length, programmed at a rate of 0.067 K/s from 323 to 493 K. The chromatograph was calibrated with the following authentic compounds: 1-naphthol; 5,6,7,8-tetrahydro-1-naphthol (Aldrich, 99%); 1-tetralone (Aldrich, 98%); 1,2,3,4-tetrahydronaphthalene (tetralin) (Aldrich, 99%); naphthalene (Supelco, No. 4-8765); *trans*-decahydronaphthalene (Aldrich, 99%); and decahydronaphthalene (a mixture of *cis* and *trans* isomers) (Aldrich, 98%). An external standard (2,6-dimethylnaphthalene) was weighed into each sample prior to the analysis. The products were identified by gas chromatography/mass spectrometry; each compound was identified by its cracking pattern.

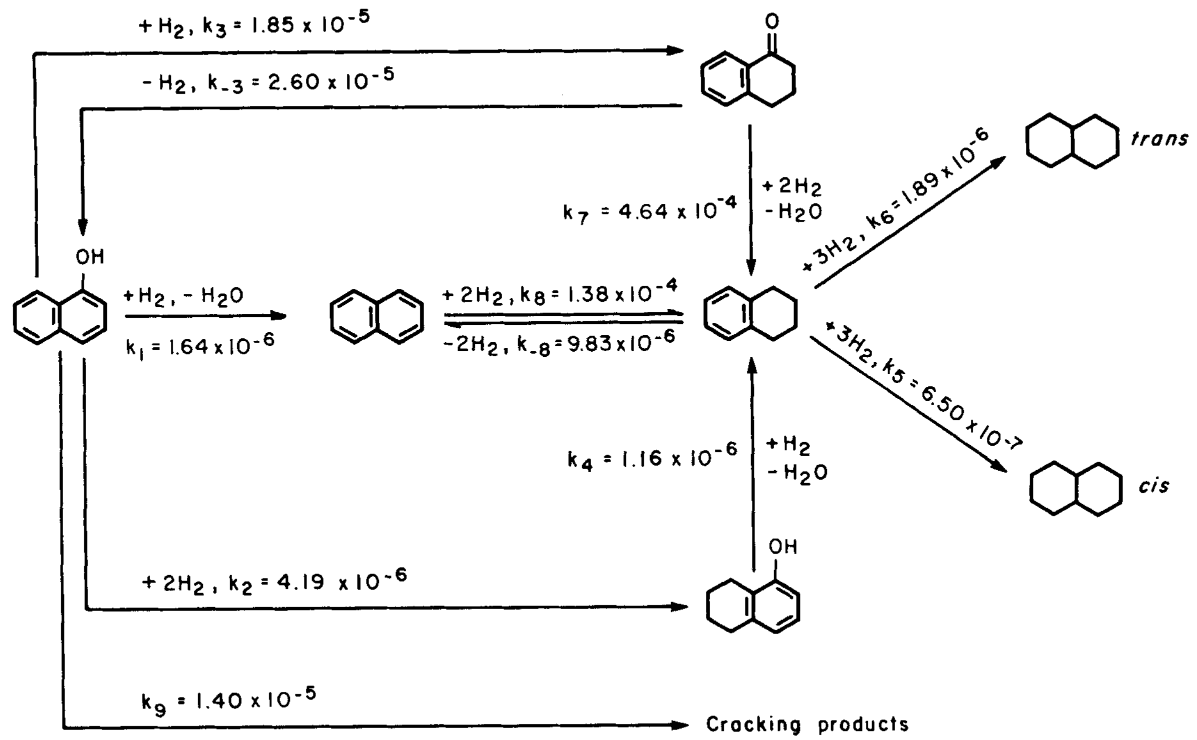


Figure 3. Conversion of 1-naphthol and hydrogen in the presence of sulfided NiO-MoO$_3$/γ-Al$_2$O$_3$ catalyst at 473 K and 35 atm: the reaction network. Each reaction is approximated as first order in the organic reactant; the numbers next to the arrows are pseudo-first-order rate constants in cubic meters per kilogram of catalyst per second.

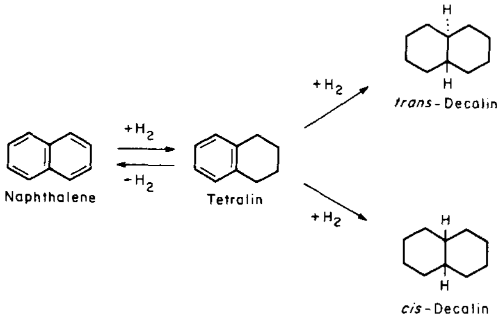
RESULTS

Typical conversion data are shown in Figures 1 and 2 for the reaction of 1-naphthol with hydrogen at 473 K and 35 atm. The results suggest that 1-tetralone, naphthalene, and 5,6,7,8-tetrahydro-1-naphthol are primary products, as inferred from the curves of Figure 2, which indicate that they were formed from the beginning of the experiment (the initial slopes of the curves were greater than zero).

The results indicate that tetralin and *trans*-decalin are not primary products, since the slopes of the curves at time zero appear to be zero. *cis*-Decalin was observed as a minor product after a long time (Figure 2); we infer that this is not a primary product either.

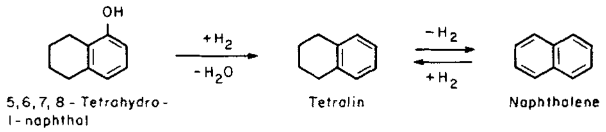
Trace amounts of low-molecular-weight compounds were also observed from the beginning of the experiment; these remain unidentified.

The curve representing 1-tetralone in Figure 2 passes through a maximum, which shows that this compound is an intermediate, being converted into one of the other compounds in the network. We also expect that naphthalene is an intermediate in the network (although the curve appears only to reach a plateau in Figure 2), since it has been shown in experiments carried out under similar conditions (Sapre and Gates, 1981) that naphthalene is sequentially hydrogenated:



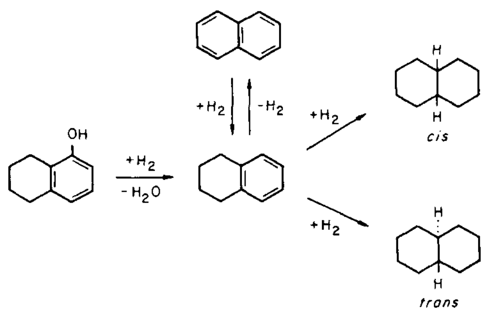
[The reversibility of the naphthalene hydrogenation is also demonstrated by these literature results (Sapre and Gates, 1981).] At longer times in the experiment, *cis*- and *trans*-decalin appeared in increasing concentrations in the products (Figure 2), consistent with the pathway shown above.

Since 1-naphthol reacts with hydrogen to give naphthalene as a primary product, we expect the corresponding HDO reaction of 5,6,7,8-tetrahydro-1-naphthol to give tetralin (which is dehydrogenated to give naphthalene):



As a test of this inference, a number of additional experiments were carried out at different temperatures and pressures and with hydrogen and 5,6,7,8-tetrahydro-1-naphthol (instead of 1-naphthol) as the reactants. These experiments were done at 35 atm and at 473 and 498 K. The conversion data (not shown) indicate that tetralin was formed initially (it was a primary product), and the initial rate of formation of naphthalene was approximately zero, although naphthalene formed later. These results confirm the occurrence of the pathway shown immediately above.

Putting these results together with those stated above, we infer the following network for hydrogen and 5,6,7,8-tetrahydro-1-naphthol:



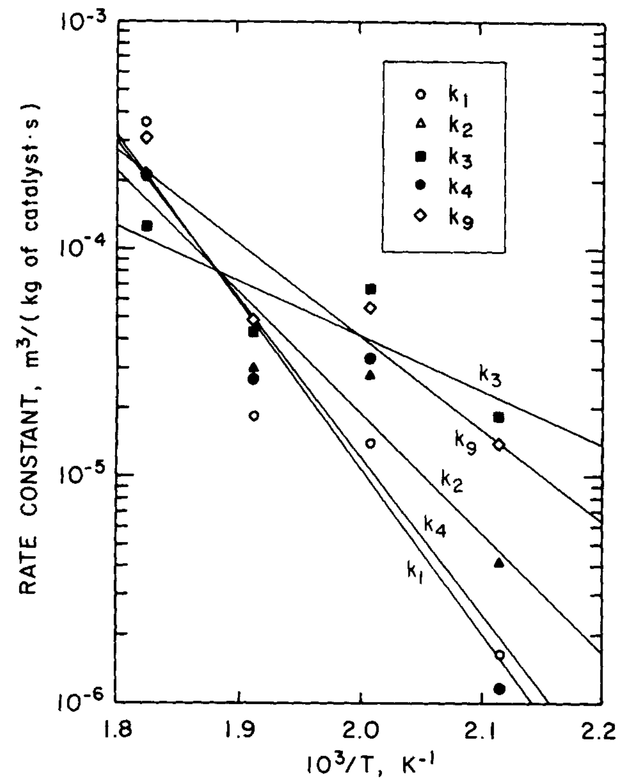
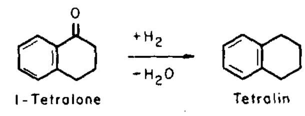


Figure 4. Arrhenius plot: rate constants in the 1-naphthol/hydrogen network of Figure 3.

In representing the hydrogenation of tetralin to give decalin we neglect the reverse reaction on the basis of literature data (Sapre and Gates, 1981).

When experiments were done with 1-naphthol and hydrogen as the reactants at higher temperatures (523 and 548 K) and otherwise the same conditions mentioned above, the same products were observed, and the conversion vs. time plot (not shown) for each of the following compounds passed through a maximum: naphthalene, tetralin, and 1-tetralone. These results indicate that each of these compounds was an intermediate in the network. The concentrations of *cis*- and *trans*-decalin increased throughout these experiments; no products were observed to have been formed from them. [Some experiments were also done with 1-naphthol and hydrogen in cyclohexane as the feed to a flow reactor packed with the same sulfided Ni-Mo/Al_2O_3 catalyst (Vogelzang et al., 1983). The results are consistent with those stated above; they also demonstrate that the catalyst underwent deactivation, losing about 80% of its initial activity in about 30-h operation at 498 K. A limitation of the data presented in this paper is that the catalyst deactivation is not represented in the model of the reaction network.]

It is clear from the foregoing results that 1-tetralone is an intermediate which reacts to give one of the other organic products already mentioned. From the chemistry, a likely reaction is inferred to be the following:



We postulate this reaction in the overall network. [We also infer that the following keto-enol equilibrium would be set up, not requiring a catalyst, and that the enol concentration was too low to detect (March, 1977):

We cannot determine from the available data which of these two compounds reacted with hydrogen to give tetralin.]

Table 1. Activation Energies of Reactions in Figure 3

Reaction	Activation Energy kJ/mol
1	139 ± 32
2	100 ± 23
3	44 ± 20
4	132 ± 38
9	77 ± 23

Taking all these results into account, we propose the reaction network shown in Figure 3. This network is consistent with all the qualitative observations; we develop a quantitative representation in the following paragraphs.

DISCUSSION

To determine a quantitative model of the reaction network shown in Figure 3, we made the following simplifying assumptions: 1) each reaction is first-order in the organic reactant [this assumption is consistent with data for conversion of a number of phenolic compounds with hydrogen under similar catalytic reaction conditions (Li et al., 1985)]; 2) the reverse reactions (except those shown) are kinetically insignificant; and 3) the trace products can be accounted for in the single reaction shown to give the lump referred to as "cracking products." (We emphasize that this term may not be entirely accurate and that other reactants may contribute to the formation of the trace products.)

The pseudofirst-order rate constants were estimated from the full set of conversion data from each experiment with 1-naphthol as the reactant, as follows: The data of Figures 1 and 2 [and, separately, the similar data collected at the other temperatures (498 and 548 K)] were used with equal weighing in the Carleton 2 program (Himmelblau et al., 1967) to determine best values of the rate constants. The best values of the rate constants shown in Figure 3 were used to predict the curves shown in Figures 1 and 2; it is evident that the model fits the data well. The rate constants determined at the other temperatures also fit the data well; some of the values are shown in the Arrhenius plot of Figure 4. (The data were not sufficient to determine statistically significant values for each rate constant at each temperature.) The activation energies calculated from the data for these reactions are summarized in Table 1.

Variations on the model of Figure 3 were also tested: for example, reactions of 1-naphthol with hydrogen other than reaction 3 were considered reversible; reaction 3 was considered irreversible; and some of the reactions shown in Figure 3 were omitted. In each case, the data were not as well represented as they are by the model of Figure 3 (the lack of a good fit being indicated by negative rate constants and/or by large deviations between predicted and observed value). We conclude that a better fit than that given by the network of Figure 3 would require a more complex network—and there is no experimental evidence to warrant greater complexity in the model.

In conclusion, the results summarized by the network of Figure 3 demonstrate that aromatic ring hydrogenation and direct oxygen extrusion (HDO) occur in parallel, as in the dibenzofuran/H_2 network (Krishnamurthy et al., 1981). The pattern is akin to that observed in catalytic hydroprocessing of organosulfur compounds such as dibenzothiophene (Houalla et al., 1978) and benzo[*b*]-naphtho-[2,3-*d*]thiophene (Sapre et al., 1980). The pattern is different from that observed in catalytic hydroprocessing of organonitrogen compounds such as quinoline—in which extensive aromatic ring hydrogenation precedes C—N bond breaking (Katzer and Sivasubramanian, 1979).

At 473 K, the rate of direct HDO of 1-naphthol is an order of magnitude lower than the rate of hydrogenation of the aromatic rings. At the higher temperatures (which are much more nearly representative of potential industrial practice), however, the rate of direct HDO exceeds the rate of hydrogenation, reflecting the relatively high activation energy of reaction 1 in Figure 3. These results suggest that HDO will proceed with high selectivity (and therefore low hydrogen consumption) under practical hydroprocessing conditions; we caution, however, that the effects on selectivity of reaction inhibitors such as basic organonitrogen compounds are unknown.

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