Hydrodeoxygenation of Dibenzofuran and Related Compounds

S. KRISHNAMURTHY
S. PANVELKER
and
Y. T. SHAH
Department of Chemical and Petroleum Engineering
University of Pittsburgh
Pittsburgh, PA 15261

The catalytic hydrodeoxygenation (HDO) of dibenzofuran was examined on a presulfided NiMo/γAl_2O_3 catalyst. Based on the reaction intermediates identified in the present study a reaction network for the removal of oxygen from dibenzofuran has been established. In view of the failure to detect certain key reaction intermediates an approximate network has been proposed for kinetic analysis. Using the approximate network the effects of temperature in the range 616-649K, hydrogen pressure in the range 6.89-13.78 MPa and initial concentration of dibenzofuran in the range $9.78 \times 10^{-5} - 21.39 \times 10^{-5}$ g mol/g oil were examined upon the individual steps.

The removal of oxygen from dibenzofuran under the above conditions proceeded via direct oxygen extrusion without hydrogenation of the adjacent benzene rings as well through the formation of hydrogenated intermediates, with the catalyst showing selectivity towards the latter mode of oxygen removal. Presulfiding the catalyst as well as addition of CS_2, to maintain a partial pressure of H_2S during the reaction, enhanced the activity of the catalyst. The effect of initial concentration of dibenzofuran indicated a retarding influence on its HDO, possibly due to the formation of refractory reaction intermediates.

The HDO of two key reaction intermediates in the network for dibenzofuran, namely, o-phenyl phenol and o-cyclohexyl phenol, was also examined on a presulfided NiMo/γAl_2O_3 catalyst to establish the reaction network for dibenzofuran. The primary mode of oxygen removal from both the phenols, in the temperature range of 561-644K and 10.34 MPa hydrogen pressure, was through the formation of highly reactive hydrogenated intermediates. All the primary reactions for o-phenyl phenol were catalytic in nature, whereas, o-cyclohexyl phenol was found to crack to phenol and cyclohexane even under purely thermal conditions. The rates of decomposition of the above phenols were fairly rapid and highly temperature sensitive, thereby explaining their absence in the reaction products of dibenzofuran.

SCOPE

The catalytic hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) of coal-derived liquids is carried out to provide a fuel that is low in nitrogen and sulfur content. The unusually high oxygen content of coal-derived liquids has recently caused a growing interest into the interactive effects between oxygen, sulfur and nitrogen compounds during their removal. Under conditions that favor HDN and HDS, HDO can also occur, with the formation of H_2O which is a known catalyst poison. The reactions involved in the removal of oxygen during hydroprocessing is poorly understood at the present time. The purpose of this paper is to clarify the reaction network for oxygen removal from dibenzofuran, which is known to exist significantly in coal liquids, using a presulfided NiMo/γ-Al_2O_3 catalyst. The effects of temperature, hydrogen pressure and initial concentration of dibenzofuran on the individual steps in the reaction network have been examined.

Two key reaction intermediates in the HDO of dibenzofuran, namely, o-phenyl phenol and o-cyclohexyl phenol were conspicuous by their absence in the reaction products. The effect of temperature on the removal of oxygen from the above phenols was therefore examined independently on a presulfided NiMo/γ-Al_2O_3 catalyst.

CONCLUSIONS AND SIGNIFICANCE

The HDO of dibenzofuran and two of its key reaction intermediates, namely, o-phenyl phenol and o-cyclohexyl phenol, have been examined on a presulfided NiMo/γ-Al_2O_3 catalyst. The removal of oxygen from dibenzofuran was found to proceed via direct removal of oxygen without the hydrogenation of the adjacent benzene rings, as well as through the formation of reactive hydrogenated intermediates, with the latter mode being dominant under conditions of the present study.

S. Krishnamurthy is presently with Mobil Research and Development Corp., Paulsboro, NJ 08066.

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The low reactivity of dibenzofuran, which has also been observed by earlier workers (Weisser and Landa, 1973) combined with the high yields of cyclohexane, cyclohexyl benzene, bicyclohexyl and cyclohexyl methyl cyclopentane observed in this study indicates the formation of 1,2,3,4 tetrahydrodibenzofuran to be the rate limiting step.

The effect of initial concentration of dibenzofuran on the various steps in its reaction network indicates strong adsorption of the reacting species on the active sites of the catalyst. Presulfiding the catalyst as well as addition of CS_2, to maintain a partial pressure of H_2S, appears to enhance the activity of the catalyst.

O-phenyl and o-cyclohexyl phenols react similarly to dibenzofuran, with the dominant mode of oxygen removal in both cases being through the formation of hydrogenated intermediates. The rates of decomposition of the above phenols were found to be rapid and highly temperature sensitive, thereby explaining their absence in the reaction products of dibenzofuran. O-cyclohexyl phenol, unlike o-phenyl phenol, was found to crack to phenol and cyclohexane under purely thermal conditions, indicating a decrease in the strength of the bond linking the aryl groups due to hydrogenation. It is evident from this study that oxygen compounds can consume extensive amounts of hydrogen during hydrodenitrogenation and hydrodesulfurization of coal liquids on commercial NiMo/γ-Al_2O_3 catalysts.

INTRODUCTION

In recent years there has been a growing interest in converting coal to liquid fuels for both stationary and transportation purposes. Several catalytic and noncatalytic processes are available for this purpose (Shah, 1981). The noncatalytic processes use a hydrogen donating solvent to liquefy coal. The resulting product has a high nitrogen, sulfur and oxygen content. Due to the undesirable nature of sulfur and nitrogen, they are removed by catalytic hydroprocessing at pressures in the range 6-15 MPa of hydrogen, temperatures in the range 600-650K and a catalyst which is usually a combination of metals such as CoMo, NiMo and NiW supported on SiO_2 and/or Al_2O_3. Under the above conditions the following reactions are expected to occur concurrently. Nitrogen containing compound + H_2 → Nitrogen free hydrocarbon + NH_3 Sulfur containing compound + H_2 → Sulfur free hydrocarbon + H_2S O_2 containing compound + H_2 → Oxygen free hydrocarbon + H_2O Aromatic hydrocarbons + H_2 → Hydrogen enriched compounds.

The deactivating effect of water on hydroprocessing catalysts has been mentioned in the literature (Lipsch and Schuit, 1969; Weisser and Landa, 1973). The retarding effect of oxygen containing compounds on the removal of nitrogen and sulfur may, therefore, be considered to be two fold: (1) due to competitive adsorption on catalyst sites; and (2) due to deactivation of catalyst sites by the ultimate product of oxygen removal, i.e., water.

Model compound studies on nitrogen removal from pyrrole and indole (Stern, 1979), pyridine (McIlvried, 1979), quinoline and acridine (Shih et al., 1977), have been reported in the literature. Studies on sulfur removal include those on benzothiophene (Givens and Venuto, 1970) and dibenzothiophene (Houalla et al., 1978). Fewer studies on mixtures of model compounds have been reported in the literature (Badilla Ohlbaum et al., 1979; Rollmann, 1976; Satterfield et al., 1976; and Bhinde, 1979). There is, however, a dearth of literature on the removal of oxygen during hydroprocessing and its effect upon the removal of nitrogen and sulfur. Hall and Cawley (1939) reported the hydrodeoxygenation of dibenzofuran over several MoS_2 catalysts. They found the removal of oxygen to proceed through ring hydrogenation prior to C-O bond scission as well as by direct oxygen extrusion without any hydrogenation, the latter mechanism gaining prominence at temperatures above 623K. Landa et al. (1969) have also reported the formation of a host of hydrogenated as well as unhydrogenated intermediates during the removal of oxygen from dibenzofuran. The above two studies were mainly qualitative and the relative importance of the various steps were not quantitatively evaluated. Very little information is available on the behavior of phenols under conditions that favor the HDO of dibenzofuran. The HDO of phenol is very sensitive to temperature, with the preferred mode of dehydroxylation being through the formation of cyclohexane at elevated temperatures.

It is the purpose of this paper to examine in depth the reaction network for the removal of oxygen from dibenzofuran, a compound frequently found in coal liquids (Shah, 1981) to a significant extent. In addition, the removal of oxygen from o-phenyl and o-cyclohexyl phenol was investigated independently in order to clarify the network for dibenzofuran, as well as to examine the mode of oxygen removal from such phenols.

Experimental Details

Equipment. All experiments were performed in a 1 liter batch reactor (Autoclave Engineers, PA). A schematic of the experimental apparatus is shown in Figure 1. A rapid injection system was used to facilitate injection of the reactant into the reactor after the latter had attained a predetermined temperature. This allowed the precise definition of zero reaction time and avoided complications which are consequences of long heat up periods. Samples were collected periodically from the re-

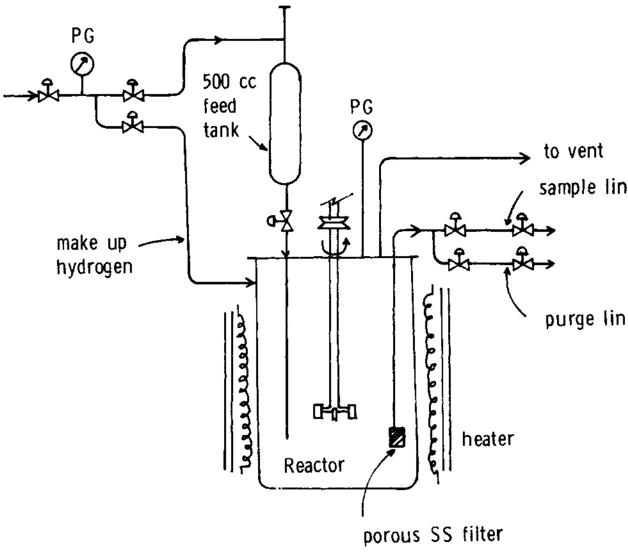

Figure 1. Experimental setup.

TABLE 1. CATALYST PROPERTIES

Type	$NiMo/\gamma Al_2O_3$ (Nalco NM-504)
NiO	5.5%
MoO_3	19 %
Surface Area	170 m/g
Pore Volume	0.41 cc/g
Average Pore Diameter	97 Å

actor through a sampling line provided with a porous stainless steel filter. The liquid in the sampling line was always rejected prior to sampling to enable the collection of authentic samples from the reactor. The reactor temperature was controlled by a PI controller (Autoclave Engineers, PA) to within ±1K. A stirrer speed of 1250 RPM was maintained in the present study as earlier experiments had shown external mass transfer resistances to be insignificant at this speed (Krishnamurthy, 1980).

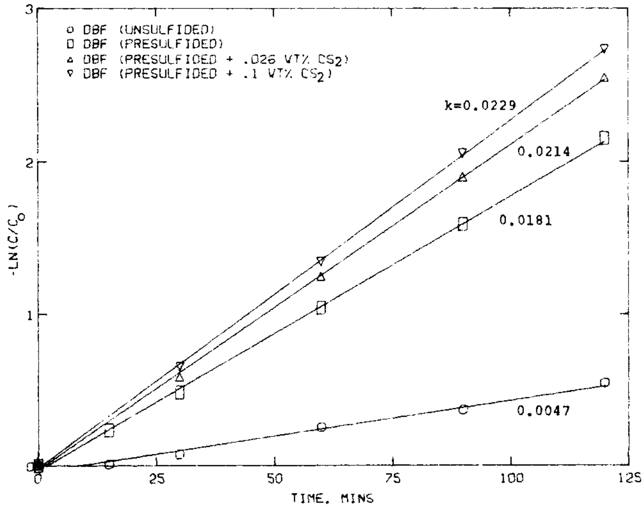

Figure 2. First order kinetic plot for the decomposition of dibenzofuran. The rate constants are given in g oil/g mol, min.

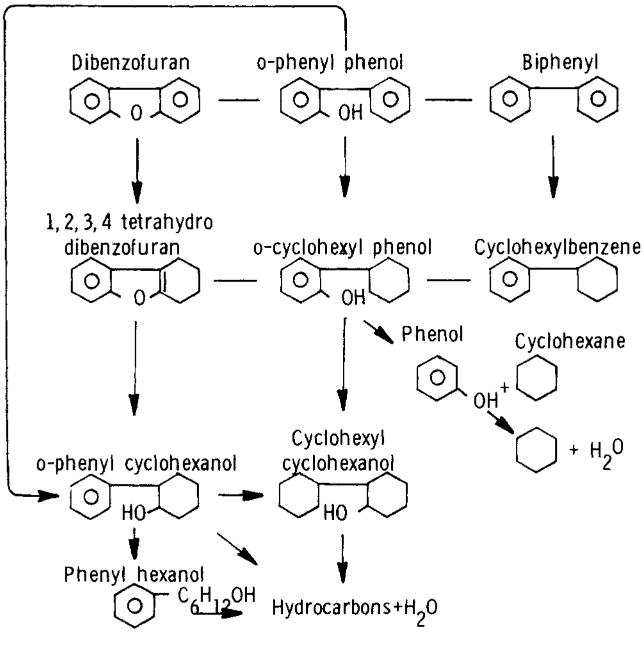

Figure 3. Reaction network for the HDO dibenzofuran.

TABLE 2. SUMMARY OF OPERATING CONDITIONS

Solvent	250 cc n-dodecane
Pressure, MPa	6.89-13.8 (dibenzofuran) 10.34 (o-phenyl and o-cyclohexyl phenols)
Temperature, K	616-649 (dibenzofuran) 598-644 (o-phenyl phenol) 560-624 (o-cyclohexyl phenol)
Reactant Loading, wt %	1.67-3.5 (dibenzofuran) 2.5 (o-phenyl phenol) 2 (o-cyclohexyl phenol)
Catalyst Loading, wt %	1.75-2.5 (dibenzofuran) 0.5 (o-phenyl and o-cyclohexyl phenol)
CS_2 Loading, wt %	0.053

Catalyst. A $NiMo/\gamma$-Al_2O_3 catalyst (NM-504) was crushed and sieved to particles sizes in the range of −150# to +200# and sulfided prior to use. Details of the catalyst are provided in Table 1. Effectiveness factor calculations indicated negligible intraphase resistance in the present system. The catalyst sulfiding procedure consisted of contacting a stoichiometric excess of a 10% H_2S/H_2 mixture with the catalyst at a temperature of 623K for two hours. In order to maintain the catalyst in a sulfided form a sufficient quantity of CS_2 was added to the reactor which, under experimental conditions, was rapidly converted to H_2S and CH_4. The beneficial effect of H_2S on the activity of the catalyst for oxygen removal from dibenzofuran is discussed in a later section.

Chemicals. High purity hydrogen (99.999%) supplied by Matheson was used in all the experiments. Dibenzofuran (98% purity), and n-dodecane (99% purity) supplied by Aldrich Chemical Co., o-phenyl phenol (99% purity, Eastman Kodak Co.) and o-cyclohexyl phenol (95% purity, ICN Pharmaceuticals) were used as received.

Procedure. The experimental procedure consisted in loading the reactor with 180 cc n-dodecane, and weighed amounts of catalyst and CS_2. Details of the operating conditions are provided in Table 2. The reactor was then purged, pressurized to 4 MPa with hydrogen and heated to about 15K higher than the reaction temperature. Once the reactor attained the set temperature, the reactant, dissolved in 70 cc of n-dodecane, was loaded into the feed tank and injected into the reactor using positive hydrogen pressure. Upon injection of the reactant the temperature dropped by 20K, however, it stabilized to the set point within one minute. Subsequently, the reactor was brought up to and maintained at operating pressure by adding make up hydrogen 3 cc liquid samples were collected from the reactor at suitable intervals through the sampling system described earlier.

Analysis. Liquid samples were analyzed on a HP5750B gas chromatograph equipped with a 15′ long 2 mm i.d. glass column packed with Carbowax 20M on Supelcoport using a flame ionization detector. The injector and detector were held at 583K. The oven was operated isothermally at 373K for 4 minutes after injection and subsequently programmed at a rate of 4K/min up to 537K at which temperature it was held for 5 minutes. Selected samples were analyzed using combined GC/MS for identification of reaction intermediates and products.

RESULTS

Effect of H_2S on Catalytic Activity

The effect of presulfiding the catalyst and addition of CS_2, in order to maintain a partial pressure of H_2S in the gas phase during the reaction, upon the decomposition of dibenzofuran, is shown in Figure 2 in the form of a first order kinetic plot. It is seen that while presulfiding the catalyst has a remarkable effect

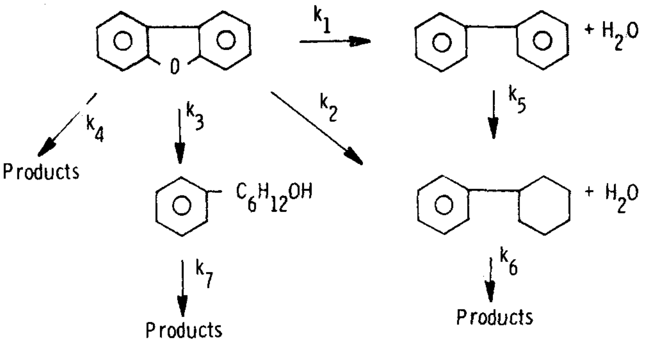

Figure 4. Approximate reaction network for the HDO of dibenzofuran.

on its activity, the addition of CS_2 shows only a marginal improvement. The greater activity of the sulfided catalyst is speculated to be due to the relative ease with which the -S-H- bond on a sulfided catalyst cleaves when compared with the O-H bond which exists with the catalyst in the oxidic state (Schuit and Gates, 1973). All the experiments in this study were made using a presulfided catalyst and with 0.053 wt % CS_2 added to the system in order to maintain the activity of the catalyst.

Reaction Network for the HDO of Dibenzofuran

The reaction intermediates detected in the HDO of dibenzofuran were 1,2,3,4 tetrahydrodibenzofuran, biphenyl, cyclohexylbenzene, phenyl hexanol, bicyclohexyl, cyclohexylmethyl cyclopentane and cyclohexane. O-phenyl phenol, o-cyclohexyl phenol, cyclohexyl cyclohexanol, phenol and benzene were not detected either due to their low concentrations or high reactivities. The presence of biphenyl indicated that the direct extrusion of oxygen occurred prior to hydrogenation of the adjacent benzene ring, similar to sulfur removal from dibenzothiophene (Houlla et al., 1978). This is in contrast to nitrogen removal from carbazole wherein hydrogenation of the heterocyclic ring is a necessary prerequisite (Weisser and Landa, 1973). The formation of phenyl hexanol indicates that 1,2,3,4 tetrahydrodibenzofuran can undergo scission of C-O bond adjacent to the benzene ring. Combining the above results with those obtained from HDO of o-phenyl and o-cyclohexyl phenol (discussed later), we propose the reaction network shown in Figure 3 for the HDO of dibenzofuran.

1,2,3,4 tetrahydrodibenzofuran was detected only in trace quantities and therefore its concentration could not be measured accurately. Furthermore, due to the failure to detect other reaction intermediates such as o-phenyl and o-cyclohexyl phenols, the reaction network was simplified, as shown in Figure 4, for detailed kinetic analysis.

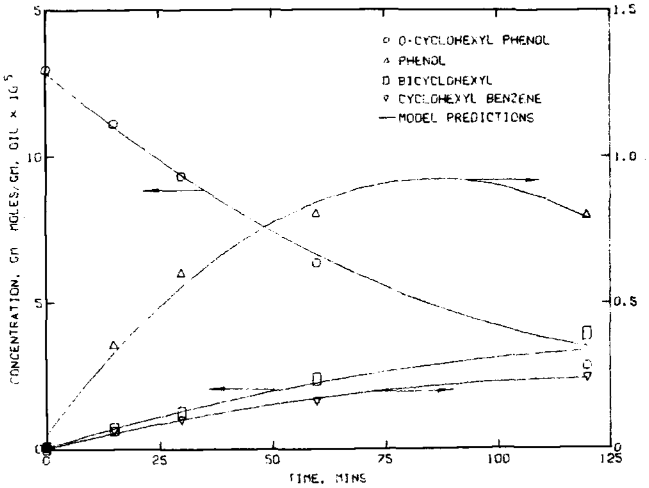

Figure 5. Comparison of experimental and predicted concentration profiles for the various reacting species in the approximate reaction network for dibenzofuran at 616K and 10.34 MPa with a reactant to catalyst ratio of 1:0.5.

The above network, though not in detail, is useful for evaluating the relative rates of the primary steps in the HDO of dibenzofuran. In this network the reaction dibenzofuran $\xrightarrow{k_4}$ products, represents the reaction sequence forming cyclohexyl cyclohexanol, phenol and cyclohexane through the formation of o-cyclohexyl phenol.

Determination of Rate Constants

The rate constants for the various steps in the approximate network were estimated, assuming all the reactions to be first order in the reactant, in the manner described below. The rate equation for the i^{th} specie in the j^{th} reaction step can be written as

$$r_i = k_j C_i$$

where k_j is a pseudo first order rate constant in g oil/g cat, min, and C_i the concentration of reactant in g mol/g oil.

The individual concentration vs. time data was spline fitted using the method of cubic splines. Next, the defining differential equations for an isothermal batch reactor, assuming hydrogen to be in excess, were integrated with respect to time for various time intervals—beginning with time zero. Finally, the optimum rate constants were determined by minimizing the sum of the squares of a weighted error defined using the integrated solution, subject to the constraint that the rate constants are non negative. The hill climbing technique of Hooke and Jeeves (1962) was used for this purpose. The optimum rate constants were subsequently used in a fourth order Runge

TABLE 3. EFFECT OF TEMPERATURE ON THE RATE CONSTANTS IN THE APPROXIMATE REACTION NETWORK FOR DIBENZOFURAN AT 10.34 MPA AND A REACTANT TO CATALYST RATIO OF 1:0.5

Temperature, K	616	638	649	E kJ/mol
Rate Constant, g-oil/g-cat, min				
Dibenzofuran $\xrightarrow{k_1}$ Biphenyl	0.017	0.028	0.036	68.4
Dibenzofuran $\xrightarrow{k_2}$ Cyclohexyl Benzene	0.043	0.077	0.090	76.2
Dibenzofuran $\xrightarrow{k_3}$ Phenyl Hexanol	0.013	0.026	0.033	97.3
Dibenzofuran $\xrightarrow{k_4}$ Products	0.626	0.710	0.770	20.5
Biphenyl $\xrightarrow{k_5}$ Cyclohexyl Benzene	1.442	1.633	1.711	19.4
Cyclohexyl Benzene $\xrightarrow{k_6}$ Products	0.286	0.377	0.420	38.9
Phenyl Hexanol $\xrightarrow{k_7}$ Products	0.0147	0.235	0.230	49.0

TABLE 4. EFFECT OF HYDROGEN PRESSURE ON THE RATE CONSTANTS IN THE APPROXIMATE NETWORK FOR DIBENZOFURAN AT 638K AND A REACTANT TO CATALYST RATIO OF 1:0.5

Pressure, MPa	6.89	10.34	13.78	n_j
Rate Constant, g oil/g cat, min				
Dibenzofuran $\xrightarrow{k_1}$ Biphenyl	0.020	0.028	0.029	1.07
Dibenzofuran $\xrightarrow{k_2}$ Cyclohexyl Benzene	0.055	0.077	0.093	1.53
Dibenzofuran $\xrightarrow{k_3}$ Phenyl Hexanol	0.019	0.026	0.026	0.92
Dibenzofuran $\xrightarrow{k_4}$ Products	0.467	0.710	1.116	2.47
Biphenyl $\xrightarrow{k_5}$ Cyclohexyl Benzene	0.710	1.633	1.505	2.28
Cyclohexyl Benzene $\xrightarrow{k_6}$ Products	0.197	0.377	0.524	2.83
Phenyl Hexanol $\xrightarrow{k_7}$ Products	0.089	0.235	0.205	2.55

Kutta scheme to predict the concentration profiles of the various reacting species. Details of this technique are available elsewhere (Krishnamurthy, 1980).

Effect of Temperature

The effect of temperature was evaluated at 616, 638 and 648K. The rate constants were determined by the technique described earlier and are given in Table 3 along with the activation energies for the various steps in the reaction network. The experimental and predicted concentration profiles for the various reacting species at 616K are shown in Figure 5. The agreement between the experimental results and model predictions appear to be reasonably good for this case. The agreement for the other cases was equally good and the results are available elsewhere (Krishnamurthy, 1980). It is seen that the rate constant for the step dibenzofuran $\xrightarrow{k_1}$ biphenyl, which involves the direct extrusion of oxygen, is lower than that of the steps involving ring hydrogenation, i.e., dibenzofuran $\xrightarrow{k_4}$ cyclohexyl benzene and dibenzofuran $\xrightarrow{k_4}$ products. It is, however, comparable to the rate constant for the step dibenzofuran $\xrightarrow{k_3}$ phenol hexanol which could be formed through either hydrogenation of o-phenyl phenol or C-O bond scission in 1,2,3,4 tetrahydrodibenzofuran. Thus, the catalyst selectivity is more towards the formation of hydrogenated intermediates. The steps dibenzofuran $\xrightarrow{k_4}$ products and biphenyl $\xrightarrow{k_5}$ cyclohexyl benzene have low activation energies. A similar result was observed for the latter reaction step in the HDO of o-phenyl phenol.

Effect of Hydrogen Pressure

The effect of hydrogen pressure was evaluated at 6.89, 10.34 and 13.78 MPa H_2 at 638K. The rate constants are given in Table 4. A comparison of rate constants in this table shows that the reactions involving the direct extrusion of oxygen through the formation of o-phenyl phenol and the formation of phenyl hexanol are insensitive to changes in pressure. Assuming a relationship of the form

$$k_j \alpha p^{n_j}$$

The values of n_j were calculated and are also listed in Table 4. The high values of n_j for some rate constants could be due to the estimation based on power law model. The true values of n_j can be obtained by application of a Langmuir-Hinshelwood type model which was not feasible in this study due to the failure to detect some of the intermediates.

Effect of Initial Concentration of Dibenzofuran

The effect of the initial concentration of dibenzofuran upon the various steps in the approximate network was evaluated at initial concentrations of 9.787×10^{-5}, 14.345×10^{-5} and 21.393×10^{-5} g mol/g oil. The rate constants are given in Table 5. Among the primary reactions involved, the reaction dibenzofuran $\xrightarrow{k_1}$ biphenyl is affected to a lesser extent than the reactions dibenzofuran $\xrightarrow{k_2}$ cyclohexyl benzene and dibenzofuran $\xrightarrow{k_3}$ phenyl hexanol by an increase in the initial concentration of dibenzofuran.

The above results do not enable us to ascertain the nature of the catalyst sites involved in the various individual steps of the reaction. However, a comparison of the rate constants k_1 and k_5 indicates that the reaction biphenyl $\xrightarrow{k_5}$ cyclohexyl benzene is retarded to a greater extent. Desikan and Amberg (1964) have reported the presence of strong and weak acid sites in their studies on thiophene hydrodesulfurization on a $CoMo/Al_2O_3$ catalyst. They note that the strongly acidic sites were responsible for hydrogenation whereas the weakly acidic sites promoted desulfurization. Lipsh and Schuit (1969) on the basis of their studies on hydrodesulfurization of thiophene on a $CoMo/Al_2O_3$ catalyst reported that the strongly acidic sites could adsorb poison such as H_2S, H_2O and pyridine, thereby making them unavailable for hydrogenation of olefins. On this basis, we speculate that catalyst sites with two levels of acidity also exist on the NiMo catalyst used in the present study. The removal of oxygen could be occurring primarily on the weakly acidic sites with some reaction taking place on the strongly acidic sites. The strong adsorption of oxygen containing compounds on the hydrogenation sites could explain the greater extent to which the reaction biphenyl $\xrightarrow{k_5}$ cyclohexyl benzene is retarded when compared to the reaction of dibenzofuran $\xrightarrow{k_6}$ biphenyl, with increasing concentration of dibenzofuran.

TABLE 5. EFFECT OF INITIAL CONCENTRATION OF DIBENZOFURAN ON THE RATE CONSTANTS IN ITS APPROXIMATE REACTION NETWORK AT 10.34 MPA AND 638K

Initial Conc., g mol/g oil $\times 10^5$	9.787	14.435	21.393
Rate Const., g-oil/g-cat, min			
Dibenzofuran $\xrightarrow{k_1}$ Biphenyl	0.0394	0.034	0.0374
Dibenzofuran $\xrightarrow{k_2}$ Cyclohexyl Benzene	0.116	0.1	0.084
Dibenzofuran $\xrightarrow{k_3}$ Phenol Hexanol	0.0426	0.0395	0.0344
Dibenzofuran $\xrightarrow{k_4}$ Products	1.138	0.979	1.118
Biphenyl $\xrightarrow{k_5}$ Cyclohexyl Benzene	2.675	1.874	2.108
Cyclohexyl Benzene $\xrightarrow{k_6}$ Products	0.474	0.425	0.433
Phenyl Hexanol $\xrightarrow{k_7}$ Products	0.328	0.354	0.311

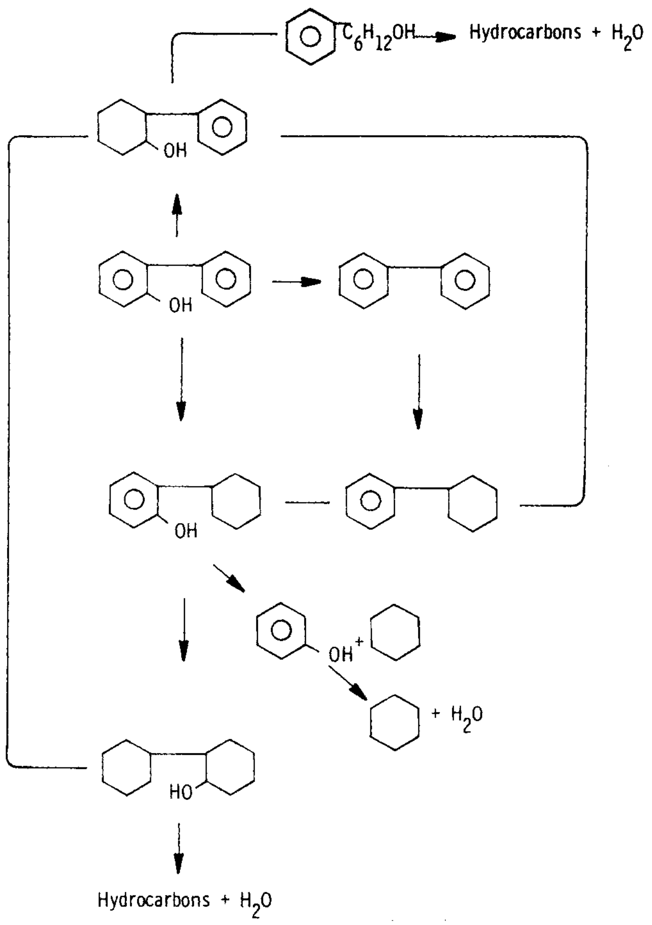

Figure 6. Reaction network for the HDO of o-phenyl phenol.

Reaction Network for the HDO of O-Phenyl Phenol

Biphenyl, cyclohexyl benzene, phenyl hexanol, bicyclohexyl, cyclohexyl methyl cyclopentane and cyclohexane were detected in the reaction products from the HDO of o-phenyl phenol. The absence of hydrogenated phenols is speculated to be due to their rapid decomposition. Weisser and Landa (1973) have reported the dehydration of cyclic alcohols to be by far the most rapid reaction under conditions favoring a high degree of conversion to hydrocarbons. Based on the above findings, the network in Figure 6 is proposed for the HDO of o-phenyl phenol.

For purposes of kinetic analysis, the reaction network shown in Figure 7 was used. The rate constants, for the various steps in the approximate network shown in Figure 7 at 598, 611, 627, 641K assuming first order kinetics and the corresponding activation energies, are given in Table 6.

The experimental and predicted concentration profiles for the above network at 595K are shown in Figure 8. A reasonably good agreement is observed for this case. The agreement for the other cases was equally good and is shown elsewhere

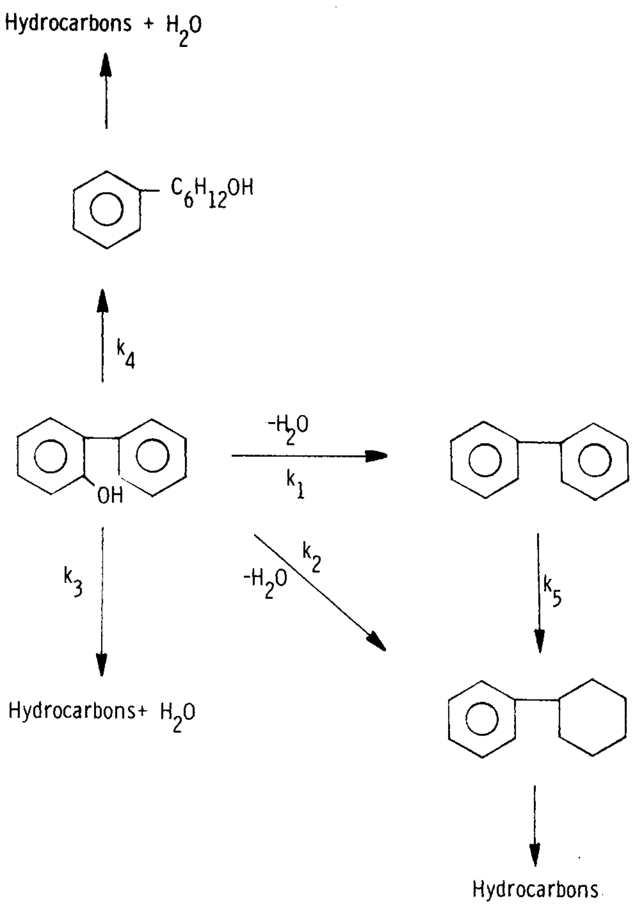

Figure 7. Approximate reaction network for the HDO of o-phenyl phenol.

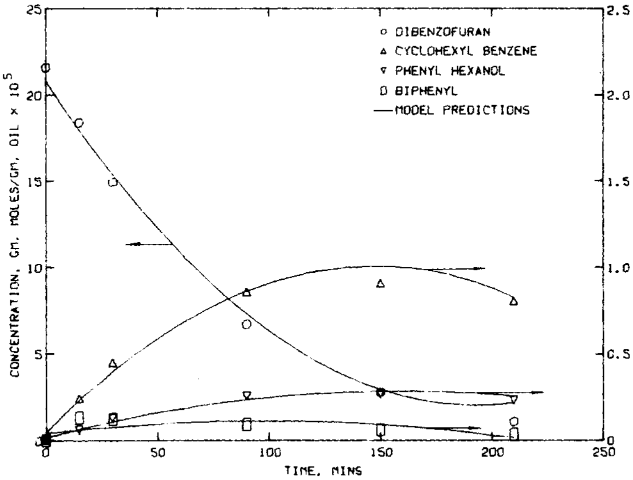

Figure 8. Comparison of experimental and predicted concentration profiles for the various reacting species in the approximate reaction network for o-phenyl phenol at 598K and 10.34 MPa with a reactant to catalyst ratio of 1:0.25.

TABLE 6. EFFECT OF TEMPERATURE ON THE RATE CONSTANTS IN THE APPROXIMATE REACTION NETWORK FOR O-PHENYL PHENOL AT 10.34 MPA AND A REACTANT TO CATALYST RATIO OF 1:0.25

Temperature, K	598	611	627	644	*E* kJ/mol
Rate Const., g-oil/g-cat, min					
O-Phenyl Phenol $\xrightarrow{k_1}$ Biphenyl	0.3204	0.4356	0.6902	1.082	85.59
O-Phenyl Phenol $\xrightarrow{k_2}$ Cyclohexyl Benzene	1.346	1.808	2.73	3.672	71.09
O-Phenyl Phenol $\xrightarrow{k_3}$ Hydrocarbons	0.846	1.029	1.428	1.84	55.32
O-Phenyl Phenol $\xrightarrow{k_4}$ Phenyl Hexanol	0.2616	0.4474	0.6484	0.9258	86.02
Biphenyl $\xrightarrow{k_5}$ Cyclohexyl Benzene	1.139	1.215	1.199	1.426	13.81

TABLE 7. EFFECT OF TEMPERATURE ON THE RATE CONSTANTS IN THE APPROXIMATE REACTION NETWORK FOR O-CYCLOHEXYL PHENOL AT 10-34 MPA AND A REACTANT TO CATALYST RATIO OF 1:0.2

Temperature, K	561	568	598	624	E kJ/mol
Rate Constant g-oil/g-cat, min					
O-Cyclohexyl Phenol $\xrightarrow{k_1}$ Phenol + Cyclohexane	0.4296	0.5726	3.462	11.542	155.53
O-Cyclohexyl Phenol $\xrightarrow{k_2}$ Cyclohexyl Benzene	0.0606	0.0722	0.2656	0.7454	118.13
O-Cyclohexyl Phenol $\xrightarrow{k_3}$ Bicyclohexyl	0.789	0.8946	1.9648	3.890	74.42
Phenol $\xrightarrow{k_4}$ Products	2.43	2.71	7.002	13.048	80.19
Cyclohexyl Benzene $\xrightarrow{k_5}$ Bicyclohexyl	—	—	—	—	—
O-Cyclohexyl Phenol $\xrightarrow{k_6}$ Products	0.958	1.2148	5.748	15.68	132.51

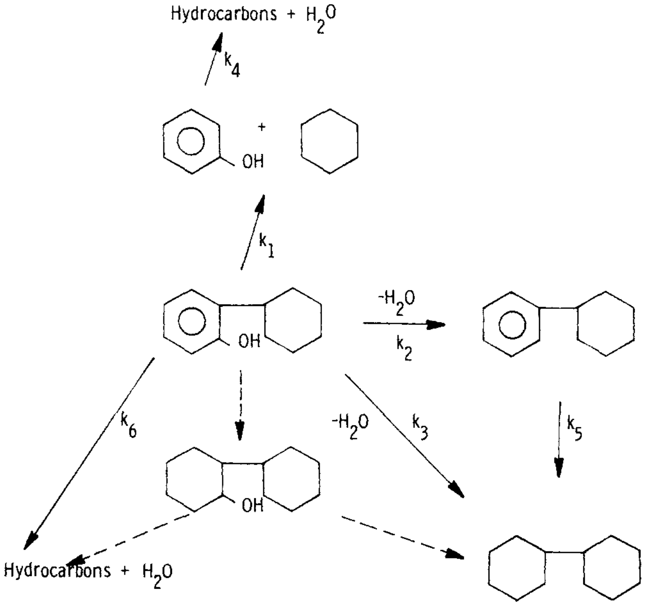

Figure 9. Reaction network for the HDO of o-cyclohexyl phenol (dotted lines show the approximate network used for kinetic analysis).

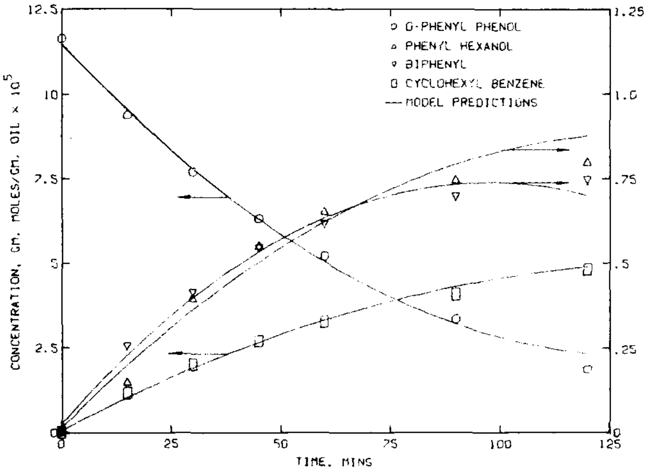

Figure 10. Comparison of experimental and predicted concentration profiles for the various reacting species in the approximate reaction network for o-cyclohexyl phenol at 560K and 10.34 MPa with a reactant to catalyst ratio of 1:0.2.

(Krishnamurthy, 1980). A comparison of the rate constants indicates that hydrogenation of at least one of the aromatic rings enhances the removal of oxygen. The rates of the reactions o-phenyl phenol $\xrightarrow{k_1}$ biphenyl and o-phenyl phenol $\xrightarrow{k_4}$ phenyl hexanol are comparable and are much slower than the other steps. The step o-phenyl phenol $\xrightarrow{k_3}$ products represents reaction to form products other than cyclohexyl benzene through the formation of o-cyclohexyl phenol as well as o-phenyl cyclohexanol. The yield of bicyclohexyl was high even at low reaction times. The rate constant for the reaction cyclohexyl benzene to products was, however, found to be zero. It was, therefore, postulated that the formation of bicyclohexyl proceeded through the step o-phenyl phenol $\xrightarrow{k_3}$ products. Thus, rapid hydrogenation of o-phenyl phenol prior to oxygen removal appears to be favored on this catalyst. This is also supported by the fact that $k_2 > k_1 > k_3$ at all temperatures indicating the preferred formation of cyclohexyl benzene through o-cyclohexyl phenol. The activation energy for o-phenyl phenol $\xrightarrow{k_1}$ biphenyl is slightly higher than that for dibenzofuran → biphenyl. This could be due to combining the reactions dibenzofuran → o-phenyl phenol → biphenyl into a single step. The activation energy for biphenyl $\xrightarrow{k_3}$ cyclohexyl benzene is low and comparable to the value reported earlier for the same reaction in the dibenzofuran network.

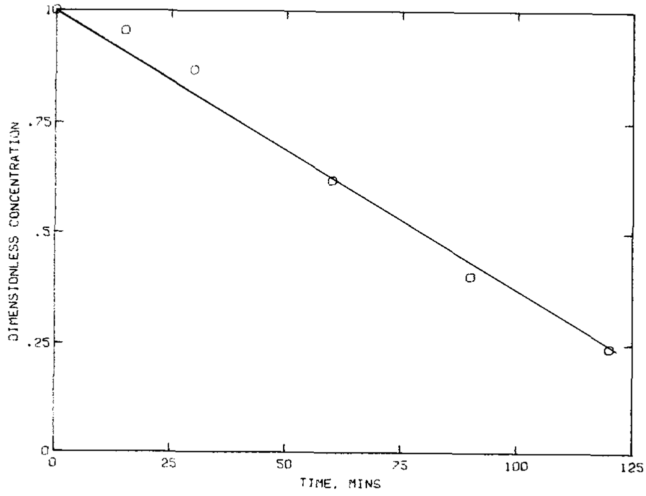

Figure 11. Zero order kinetic plot for the thermal decomposition of o-cyclohexyl phenol at 624K and 10.34 MPa.

Reaction Network for the HDO of O-Cyclohexyl Phenol

Cyclohexyl benzene, bicyclohexyl, phenol, cyclohexyl methyl cyclopentane and cyclohexane were detected in the reaction products from the HDO of o-cyclohexyl phenol. Once again, cyclohexyl cyclohexanol and cyclohexanol were not detected. On this basis, the network in Figure 9 was postulated. A kinetic analysis was made using reaction steps represented by dark lines. The rate constants for the various steps in the network at 561, 568, 598 and 624K assuming first order kinetics along with the corresponding activation energies are given in Table 7. Figure 10 shows the comparison between the experimental and predicted concentration profiles at 561K. The agreement is seen to be reasonably good for this case. The agreement for the other cases was equally good and is shown elsewhere (Krishnamurthy, 1980). The rate constant for the step cyclohexyl benzene $\xrightarrow{k_5}$ bicyclohexyl is zero at all temperatures, indicating that bicyclohexyl was formed entirely through an alternate route, namely, o-cyclohexyl phenol $\xrightarrow{k_3}$ bicyclohexyl. The rate constant for the step o-cyclohexyl phenol $\xrightarrow{k_2}$ cyclohexyl benzene is much lower than all other rate constants. It may be speculated on the basis of earlier findings (Weisser and Landa, 1973) that the removal of oxygen from phenol, under the conditions employed in present study, proceeds via rapid hydrogenation of phenol to cyclohexanol followed by decomposition to cyclohexane and water. A comparison of the activation energy for the step o-cyclohexyl phenol $\xrightarrow{k_2}$ cyclohexyl benzene with the value reported for the step o-phenyl phenol → cyclohexyl benzene indicates that the lower value of the latter could be due to combination of the reactions o-phenyl phenol → o-cyclohexyl phenol → cyclohexyl benzene. A similar observation was made in the previous section. It may be noted here that the reaction o-cyclohexyl phenol $\xrightarrow{k_1}$ phenol has an unusually high activation energy for a catalytic reaction indicating the high sensitivity of this reaction step to changes in temperature. In order to ascertain the effect of catalyst on the above reaction, o-cyclohexyl phenol was reacted at 624K and 10.38 MPa in the absence of the catalyst. The above reactant was converted to an extent of 60% in two hours thereby indicating the non-catalytic nature of this reaction. Phenol and cyclohexane were the main products formed under the above conditions. The reaction was found to be well described by zero order kinetics with a rate constant of 0.00641 g oil/g mol, min (Figure 11). A similar experiment with o-phenyl phenol at 644K resulted in a conversion of less than 3% in two hours indicating that the above compound is fairly resistant to decomposition under purely thermal conditions.

The catalytic hydrodeoxygenation of dibenzofuran on a NiMo/γ-Al_2O_3 catalyst is seen to proceed via direct extrusion of oxygen without ring hydrogenation as well as through the oxygen without ring hydrogenation as well as through the formation of hydrogenated intermediates such as 1,2,3,4 tetrahydrodibenzofuran, with the latter mode of oxygen removal being more prevalent under conditions examined in the present study. In the sequence involving the removal of oxygen through the formation of hydrogenated intermediates the first step dibenzofuran → 1,2,3,4 tetrahydrodibenzofuran appeared to be rate limiting. This is due to the absence of reaction intermediates such as o-cyclohexyl phenol, phenol, cyclohexyl cyclohexanol and cyclohexanol and the high yields of cyclohexane, cyclohexyl benzene, bicyclohexyl and cyclohexyl methyl cyclopentane even at short reaction times. A comparison of the rate constants in Table 3 indicates that $k_2 > k_1$ implying that most of cyclohexyl benzene could not have been formed through the reaction sequence dibenzofuran $\xrightarrow{k_1}$ biphenyl $\xrightarrow{k_5}$ cyclohexyl benzene and $k_4 >> k_1$ indicates that the most of formation of bicyclohexyl occurs through dehydration of cyclohexyl cyclohexanol and not through hydrogenation of cyclohexyl benzene. The effect of initial concentration of dibenzofuran upon the various steps in the reaction network indicates strong adsorption of some of reacting species on the active catalyst sites. The exact nature of the catalyst sites, the extent to which they were affected, and the nature of the reacting species affecting these sites could not be ascertained in the present study.

The removal of oxygen from o-phenyl and o-cyclohexyl phenols is seen to proceed via extensive ring hydrogenation prior to -C-O- bond scission. The formation of biphenyl and phenyl hexanol from o-phenyl phenol is in agreement with the results reported for the hydrodeoxygenation of dibenzofuran, thereby indicating the formation of the phenolic intermediate to be a probable step in the latter network. The hydrogenation of the phenyl group in o-phenyl phenol weakens the -C-C- bond linking the aryl groups thereby facilitating its scission even under purely thermal conditions. The decomposition of both phenols showed a high degree of temperature sensitivity, which could explain their absence in the reaction products from dibenzofuran.

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NOTATION

C = concentration, g mol/g oil
E = activation energy, kJ/mol
k = pseudo-first order rate constant, g-oil/g-cat, min
T = temperature, K
n = hydrogen pressure dependence
p = hydrogen pressure, MPa
r = reaction rate, g mol/g cat, min

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