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Hydrodesulfurization of Sulfur Heterocyclic Compounds

Kinetics of Dibenzothiophene

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A kinetic analysis of the hydrodesulfurization (HDS) of dibenzothiophene (DBT), a representative model of the condensed sulfur heterocyclics found in heavy petroleum feeds, has been carried out. Kinetic data were generated over standard Co–Mo/γ-Al_2O_3 catalyst at temperatures of 285 to 350°C by varying hydrogen partial pressure, liquid hourly space velocity, and DBT feed concentration. From the data, models obeying Langmuir–Hinshelwood kinetics were developed to account for the rate of disappearance of DBT as well as for the selectivity of product formation. The models imply that two types of sites on the catalyst surface are involved in the HDS reaction, on one of which dibenzothiophene and the reaction products biphenyl, cyclohexylbenzene, and hydrogen sulfide competitively adsorb and a second site on which hydrogen adsorbs. The kinetic models developed to account for the appearance of the products indicate that product formation proceeds predominantly by a parallel path mechanism. However, there is a small contribution to the cyclohexylbenzene production from the sequential hydrogenation of biphenyl which becomes significant at higher temperatures.

NOMENCLATURE

E_a	energy of activation (kcal/g mole)
F	molar flow rate of fluid at reactor inlet (g moles fluid/hr)
ΔH_{ads}	heat of adsorption of hydrogen (kcal/g mole)
K_i	adsorption equilibrium constant of *i*th species in Langmuir–Hinshelwood expression for surface reaction rate (MPa^{-1})
k	intrinsic reaction-rate constant for surface reaction (g moles fluid/hr-g catalyst)
k', k'', k'''	reaction-rate constants
LHSV	liquid hourly space velocity (cm^3 liquid feed/hr-cm^3 catalyst)
P_i	partial pressure of *i*th species (MPa)
P_i^0	partial pressure of *i*th species at reactor inlet (MPa)
r	reaction rate (g moles reactant/g catalyst-hr)
t	time (hr)
T	absolute temperature (°K)
X	molar conversion of dibenzothiophene: $X = ([DBT_0]\ [DBT])/[DBT_0]$ and $X_{BiPh} = ([BiPh_0]\text{-}[BiPh]/[BiPh_0])$
W	weight of catalyst in reactor (g catalyst)
α	relative amount of dibenzothiophene converted to biphenyl: $\alpha = [BiPh]/([DBT_0] - [DBT])$
θ_i	fractional coverage of catalytic sites of *i*th species in Langmuir–Hinshelwood expression for surface reaction rate
BiPh	biphenyl
DBT	dibenzothiophene

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CHB	cyclohexylbenzene
Prod	reaction products of dibenzothiophene hydrodesulfurization, i.e., cyclohexylbenzene, hydrogen sulfide, and biphenyl
o	value of parameter at inlet to reactor

INTRODUCTION

The growing concern with the impact of sulfur emissions on the environment, coupled with the need to desulfurize feedstocks to minimize poisoning of noble metal catalysts, has made hydrodesulfurization (HDS) a major petroleum process. Although HDS achieves the desired sulfur level in the products, the process consumes hydrogen in excess of the stoichiometric requirements for sulfur removal (*1*). This excess consumption is greater when heavier feeds and residua with higher levels and complexity of sulfur compounds are processed to meet growing demands for clean liquid fuels.

In order to minimize the hydrogen consumption in HDS, an understanding of the routes for desulfurization and hydrogenation of condensed sulfur heterocyclics is required. To date, most studies of the HDS mechanism over Co–Mo/Al_2O_3 catalysts have been limited to the atmospheric pressure reaction of thiophene (*2-4*). This molecule, however, is not representative of the condensed sulfur heterocyclics in heavier feeds (*5*).

Considerable insight into the HDS mechanism was gained from our previous study of the chemistry of condensed sulfur heterocyclics (*6*). Thus for thianthrene and its tetramethyl derivative, both of which desulfurize easily, the reaction appears to occur by direct coordination of the sulfur with the active site of the catalyst. Analysis of the reaction products indicates that no further hydrogenation of the aromatics or alkylaromatic products occurs. But when dibenzothiophene (DBT), which is more difficult to desulfurize, is the feed, both hydrogenated and unhydrogenated products are observed. We have proposed that these compounds are produced from a common intermediate suggesting a parallel rather than sequential path for the reaction.

In recent years the kinetics of DBT hydrodesulfurization has been receiving increasing attention. Obolentsev and Mashkina (*7*) report data for the hydrodesulfurization of DBT in the presence of added biphenyl (BiPh) and H_2S. For contact times up to 6 sec, the addition of biphenyl significantly decreased conversion while H_2S had little effect. These results suggest that the rate of DBT desulfurization is product inhibited. There was no indication, however, that the catalyst was presulfided or that the results represented steady-state operations.

Bartsch and Tanielian (*8*) studied DBT hydrodesulfurization at atmospheric pressure, and detected only BiPh and H_2S as reaction products. The kinetic model developed to account for the disappearance of DBT indicated a first-order dependence on DBT and H_2 concentration with an activation energy of 5 kcal/mole. This low value for the activation energy suggests that the reaction of DBT was pore diffusion limited.

Aguilar Rios *et al.* (*9*) extended Bartsch and Tanielian's study by operating with a finely divided catalyst to overcome pore diffusion limitations and studied hydrodesulfurization of DBT in the gas phase at atmospheric pressure and low temperature, 220–240°C. Under these conditions the primary products were biphenyl and H_2S. They correlated their data in terms of a Langmuir–Hinshelwood kinetic model with inhibition between the DBT and the H_2S. They explain the production of a small amount of cyclohexylbenzene in terms of the sequential hydrogenation of biphenyl. Unfortunately these conditions are not representative of those of commercial significance and offer little insight into the mechanisms under those conditions.

Houalla *et al.* (*10*) report that the hydrodesulfurization of DBT is first order with respect to DBT. The study was conducted at 300°C and 10 MPa with a feed containing 0.06 wt% DBT. Under these conditions, the only product observed was BiPh. The low concentration of the reactants in their study makes it difficult to extend their findings to the present study. Houalla *et al.* (*11*) in a subsequent study of the hydrodesulfurization of methyl-substituted dibenzothiophenes reported pseudo-first-order kinetics for the HDS reaction. This study was carried out at a low concentration of the sulfur heterocycle as was their previous study. They also report data on the effect of methyl substitution on product selectivity which they could not reconcile with their sequential mechanism.

In a study of the catalytic hydrogenation of mixed nitrogen, sulfur, and oxygen compounds, Rollman (*12*) found that the disappearance of DBT was first order with respect to H_2 and DBT. The reactions were run at temperatures of 290–430°C and pressures of 2–10 MPa with a crushed Co–Mo/Al_2O_3 catalyst. At these conditions the principal products were biphenyl and H_2S. There was some production of cyclohexylbenzene (CHB), which increased with temperature. Rollman concluded that this CHB production did not result from the sequential hydrogenation of BiPh. This conclusion was based on his observation that BiPh added to the mixed feed did not hydrogenate. But no kinetic model was developed to account for the formation of the observed products.

Geneste *et al.* (*13, 14*) in studies of the hydrodesulfurization of DBT and its oxidized sulfur analogs report conflicting data for the order of the reaction and reaction mechanism. Hence they explain the appearance of cyclohexylbenzene in terms of a sequential mechanism, but report data for the hydrogenation of biphenyl which show that the cyclohexylbenzene they produced could not be accounted for solely by the sequential reaction. Moreover in their study they sulfided their catalyst *ex situ* and then transferred it to an autoclave. Since these catalysts are extremely air sensitive it is difficult to know if they achieved a stable catalyst structure or steady state in their study.

EXPERIMENTAL

Apparatus

The runs were made in two downflow stainless-steel reactors contained in fluidized sand baths. The details of the reactors and flow system are shown in Fig. 1.

Procedure

The standard operating conditions and process variables are summarized in Table 1. A presulfided Co–Mo/Al_2O_3 catalyst was used for both hydrogenation and desulfurization studies. In the desulfurization study the liquid feed was a solution of DBT in tetralin. The liquid feed was modified for the hydrogenation studies of cyclohexylbenzene and biphenyl. In this case, the feed contained 10 wt% of the reactant in tetralin, to which 4 wt% thiophene was added to maintain the catalyst in the sulfided state. In all cases, the thiophene was completely desulfurized.

A standard operating procedure was employed for all desulfurization and hydrogenation studies. DBT was hydrodesulfurized by passing a DBT solution in tetralin over the sulfided catalyst at the standard conditions of 3.1 MPa, 310°C, 4000 SCF/Bbl,

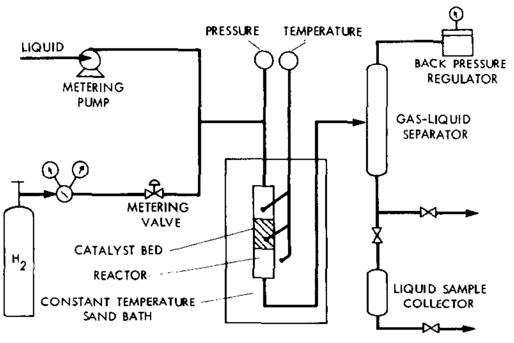


FIG. 1. Schematic drawing of experimental apparatus. Reactor A i.d. = 1.07 cm; reactor B i.d. = 1.39 cm.

TABLE 1

Operating Conditions

Process variable	Level
Reactor loading	2.5, 5.0, 10.0 cm^3 catalyst
Particle size	$\frac{1}{16}$-in. extrudates: 20/40, 40/60, and 60/80 mesh
Temperature	285–350°C
LHSV (total flow)	1–15 hr^{-1}
DBT in tetralin	2–10 wt%
H_2 concentration in He	50–100 mole%
H_2S concentration in H_2	0.5, 1.0 mole%
Standard conditions	
Total pressure	3.1 MPa
Gas flow	4000 SCF/Bbl
Temperature	310°C
LHSV (total flow)	6 hr^{-1}
DBT concentration in tetralin	10 wt%

and 6.0 hr^{-1} LHSV until conversion and product distribution reached steady state. This required 2 to 3 days of continuous operation. At that time, operating conditions were changed and the run continued until a steady state was reestablished (8–24 hr). At the steady state, a minimum of three hourly samples of the effluent were analyzed. Periodically, a run was made at the standard conditions for 24 hr to monitor catalyst activity. No catalyst deactivation was observed in any of the runs.

The molar flow rate of DBT was varied in two ways. For most runs the concentration of DBT was maintained at 10 wt% and the total liquid flow rate varied. For several runs the total flow rate was maintained at a LHSV of 6.0 hr^{-1} and the concentration of DBT in the feed varied.

Catalyst

The catalyst was Co–Mo/λ-Al_2O_3 containing 3.7% CoO, 13.0% MoO_3, and 1.8% SiO_2. Before each run the catalyst was sulfided with a 10% H_2S/H_2 mixture by heating at a rate of 140°C/hr to 300°C and then 25°C/hr for 2 hr. The catalyst was maintained at the maximum temperature of 350°C for 1 hr. This sulfiding procedure coupled to the high H_2S concentrations produced by the desulfurization of DBT assures that the catalyst is not subject to the long-term structural changes noted by Broderick *et al.* (*15*) when the H_2S level is very low.

Analysis

The products were analyzed on an HP 5830 A gas chromatograph equipped with a thermal conductivity detector using either a 10-foot, $\frac{1}{8}$-in.-o.d. column packed with 3% SP 2260 on 100- to 120-mesh Supelcoport or a 6-foot, $\frac{1}{8}$-in.-o.d. column packed with Dexsil 300 G.C. on 100- to 120-mesh Supelcoport. Standard solutions of the reactant and products in tetralin were run for comparative purposes.

Materials

Biphenyl, cyclohexylbenzene, thiophene, and dibenzothiophene were obtained from Aldrich Chemical Company. The first three were used without purification. Dibenzothiophene was dissolved in tetralin and filtered to remove insoluble impurities. The solution was used without further purification. Tetralin was obtained from Aldrich Chemical Company and Matheson, Coleman and Bell and was found to contain toluene,

TABLE 2

Reactions of DBT and Products[a]

Starting material	Temperature (°C)	Mole% conversion	Mole% products		
			DBT	BiPh	CHB
DBT[b]	300	40	60.0	37.0	3.0
	310	55	45.0	50.0	5
	325	85	15.0	76.5	8.5
	350	99+	—	89.0	11.0
BiPh[c]	300	0.3	—	99.7	0.3
	310	0.7	—	99.3	0.7
	325	1.8	—	98.2	1.8
	350	3.8	—	96.2	3.8
CHB	300–350	0	—	—	100

[a] Reaction conditions: 4000 SCF/Bbl, 6 LHSV, 3.1 MPa.

[b,c] Feed: [b] 10% in tetralin; [c] 10% in tetralin and 4% thiophene.

decalin, and naphthalene as impurities. Since these compounds did not interfere with the product analysis, no attempt was made to remove them.

RESULTS AND DISCUSSION

Results

In this investigation the only products observed were biphenyl (BiPh), cyclohexylbenzene (CHB), and H_2S.

Typical levels of DBT, BiPh, and CHB conversion and product distributions are given in Table 2. These results are the basis for the development of the parallel path mechanism.

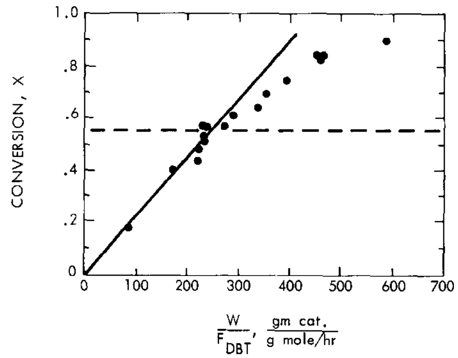


FIG. 2. The conversion of dibenzothiophene as a function of space velocity. Reaction conditions: 310°C, 2.6 MPa H_2 partial pressure, 20/40- and 40/60-mesh catalysts.

Kinetic rate data were obtained by varying the space velocity and monitoring conversion at steady-state operation. The space velocity was varied by either (i) changing total liquid flow rate at constant DBT feed concentration or (ii) changing DBT feed concentration at a constant total liquid flow rate. The conversion was found to be independent of the method of chang-

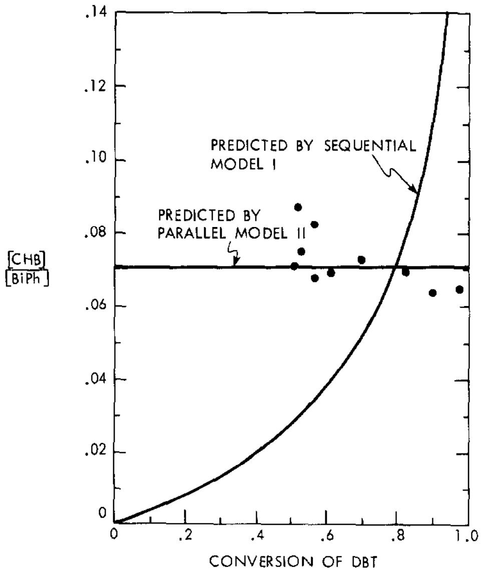


FIG. 3. The effect of conversion on product ratio. Reaction conditions: 310°C, 2.6 MPa H_2 pressure, 40/60-mesh, catalyst, $k''/k' = 0.07$.

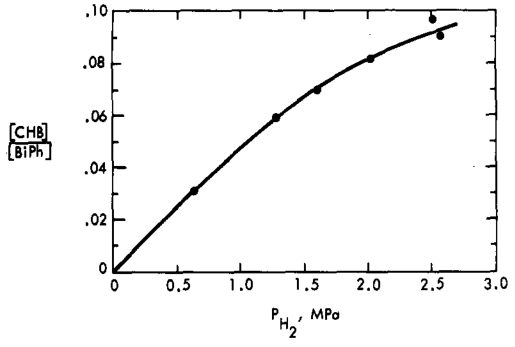


FIG. 4. The effect of hydrogen partial pressure on the product ratio. Reaction conditions: 325°C, 3.1 MPa total pressure, 6.0, hr^{-1} LHSV.

ing the DBT flow rate and dependent solely on the space velocity. These results are shown in Fig. 2.

Although conversion of DBT is a function of space velocity, selectivity, as shown in Fig. 3, is not. The selectivity is, however, a function of hydrogen partial pressure and temperature as shown in Figs. 4 and 5, respectively.

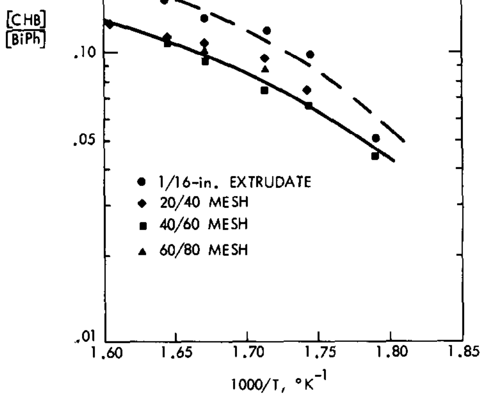


FIG. 5. The effect of temperature on product ratio. Reaction conditions: 2.6 MPa hydrogen pressure, 6.0 hr^{-1} LHSV total.

TABLE 3

Effect of H_2S on Reaction of DBT[a]

Mole% H_2S in H_2	Mole% conversion	[CHB]/[BiPh]
0	61.3	0.068
0.052	52.7	0.065
0.97	49.3	0.077

[a] Reaction conditions: 300°C, 3.1 MPa, 6.0 LHSV, 10% DBT, 4000 SCF/Bbl.

Product inhibition in the hydrodesulfurization of DBT was investigated by operating with H_2S added to the feed. These results are summarized in Table 3. It is evident that under these conditions H_2S inhibits the rate of the DBT reaction, but has no significant effect on selectivity.

In reactions over porous catalysts, such as Co–Mo/Al_2O_3, the overall rate of reaction may be influenced by the following transport steps: (i) bulk mass transfer, (ii) axial dispersion, and (iii) pore diffusion. The absence of any bed height or fluid velocity effects on conversion or product selectivity indicates that there are no bulk mass transfer or axial dispersion effects in these experiments. These data are summarized in Table 4. There does, however, appear to be some pore diffusional limitation on reactant disappearance and product formation as shown by the data in Table 5.

In these experiments hydrogen is present

TABLE 4

Bed Height Effects in DBT Reaction[a]

Volume of catalyst bed (cm^3)	Mole% conversion of DBT	[CHB]/[BiPh]
2.5[b]	45.0	0.138
5.0[b]	43.5	0.136
10.0[c]	47.8	0.141

[a] Reaction conditions: 310°C, 4000 SCF/Bbl, 6 LHSV, 3.1 MPa, 10 wt% DBT in tetralin.

[b] 1.07-cm-i.d. reactor.

[c] 1.39-cm-i.d. reactor.

TABLE 5

Particle Size Effects in DBT Reaction[a]

Particle size	Mole% conversion of DBT	[CHB]/[BiPh]
$\frac{1}{16}$-in. extrudate catalyst	47.8	0.141
20/40–mesh catalyst	55.5	0.096
40/60–mesh catalyst	53.5	0.083
60/80–mesh catalyst	53.1	0.090

[a] Reaction conditions: 6 LHSV,, 3.1 MPa, 10 wt% DBT in tetralin.

in great excess (the molar ratio of H_2 : DBT is greater than 50 : 1). In the kinetic analysis the hydrogen partial pressure is assumed to be constant throughout the reactor.

Product Formation—Kinetic Model

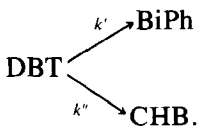
The sole products of DBT hydrodesulfurization are BiPh and CHB.

The two simplest models to account for the appearance of products are:

Model I
(Sequential)

$$\mathrm{DBT} \xrightarrow{k'} \mathrm{BiPh} \xrightarrow{k''} \mathrm{CHB},$$

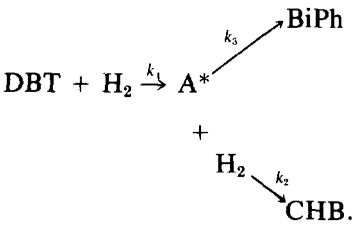
Model II
(Parallel)



Following the procedures outlined by Carberry (*16*), the product ratio can be expressed as a function of k'/k'' and conversion. The experimental results and theoretical distributions for those two models are shown in Fig. 3. The data clearly demonstrate the superiority of the parallel path mechanism for describing this reaction.

In developing these models for product distribution the dependence of k' and k'' on hydrogen partial pressure was ignored since the data were generated at constant hydrogen pressure. As shown in Fig. 4, the product ratio, CHB/BiPh, is strongly dependent on hydrogen partial pressure. This dependence suggests Langmuir–Hinshelwood kinetics, in which the catalyst sites become increasingly saturated at higher pressure. This requires the following modification of the parallel path mode:

Model III



The model assumes there is an active intermediate A* which is a precursor to the formation of BiPh and CHB. This is the mechanism postulated in our earlier paper. Expressing the rates in terms of Langmuir–Hinshelwood kinetics gives

$$\frac{\mathrm{CHB}}{\mathrm{BiPh}} = \frac{k_2}{k_3}\left[\frac{K_{H_2}P_{H_2}}{1 + K_{H_2}P_{H_2}}\right]. \qquad (1)$$

This model assumes that H_2S does not adsorb competitively with hydrogen. This assumption is based on the experimental

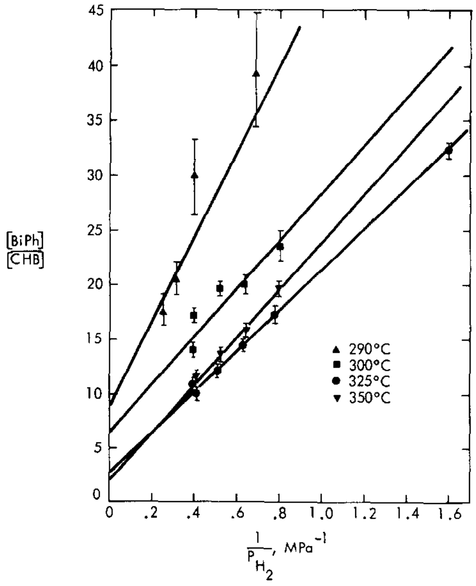


FIG. 6. Fit to product ratio to kinetic Model III.

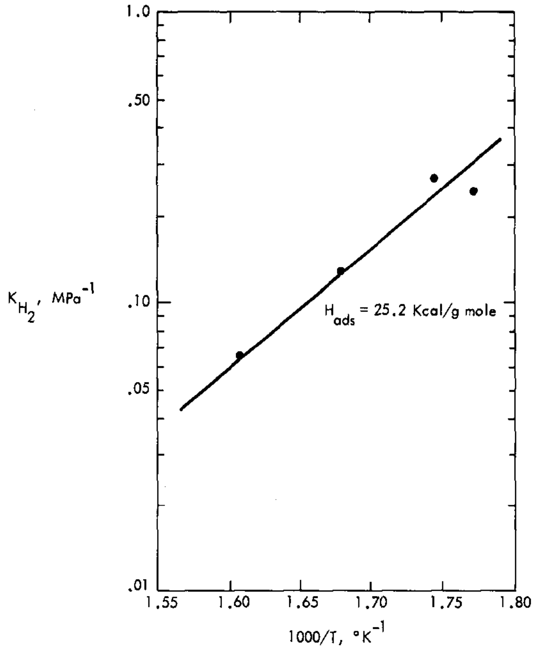


FIG. 7. Plot of the hydrogen adsorption coefficient vs. reciprocal temperature.

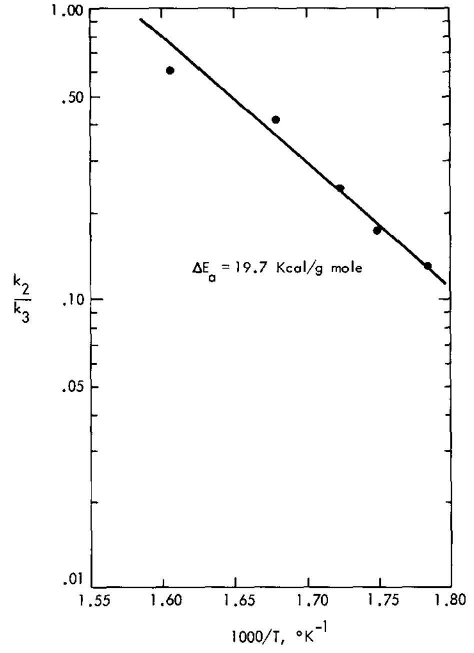


FIG. 8. The Arrhenius plot of the ratio of intrinsic rate constants for the reactions: $A + H_2 \xrightarrow{k_2} CHB$; $A^* \xrightarrow{k_2} BiPh$.

observation that H_2S does not affect product selectivity.

The agreement between the model and the data is shown in Fig. 6. The seemingly poorer fit at low temperatures is a result of the increased error in determining [CHB] at low concentrations. This is reflected in the larger confidence limits for these data.

The values for K_{H_2} and k_2/k_3 were calculated from the intercepts and slopes of the lines in Fig. 6, and are plotted as functions of reciprocal temperature in Figs. 7 and 8, respectively. From these data the heat of adsorption of hydrogen was found to be 25.2 kcal/g mole. Values between 20 and 60 kcal/g mole for the heat of adsorption of hydrogen have been reported in the literature (*17*, *18*). These values were obtained from chemisorption studies made over unsulfided Co and Mo catalysts under nonreactive conditions. From the variation of k_2/k_3 with temperature, an activation energy difference $E_2 - E_3 = \Delta E = 19.7$ kcal/g mole was calculated.

DBT Disappearance—Kinetic Model

The disappearance of DBT was modeled by fitting to Langmuir–Hinshelwood kinetics. The suitability of these kinetics to HDS of simpler thiophenes has been shown by Lee and Butt (*19*). The following models were evaluated.

Model IV

$$\frac{-d(\mathrm{DBT})}{dt} = \frac{kH_{H_2}K_{DBT}P_{DBT}P_{H_2}}{(1 + K_{H_2}P_{H_2} + K_{prod}P_{prod} + K_{DBT}P_{DBT})^2}, \tag{2}$$

i.e., dual site with competitive adsorption on a single type of site.

Model V

$$\frac{-d(\mathrm{DBT})}{dt} = \frac{kK_{H_2}K_{DBT}P_{H_2}P_{DBT}}{(1 + K_{DT}P_{DBT} + K_{prod}P_{prod})(1 + K_{H_2}P_{H_2})}, \tag{3}$$

i.e., two sites with competitive adsorption of DBT and products on one site, adsorption of H_2 on a second type of site.

These models were evaluated utilizing a broad range of assumptions on the relative magnitudes of adsorption of the reactants and products.

Of these models the best fit was obtained with Model V when it was assumed that reactants and products adsorb strongly ($K_{DBT}P_{DBT} + K_{prod}P_{prod} > 1$). This model gives the following integrated rate expression for a plug flow reactor:

$$\frac{1}{X}\ln\frac{1}{1-X} = \frac{kK_{H_2}P_{H_2}}{(1+K_{H_2}P_{H_2})}\,\frac{K_{DBT}}{K_{prod}}\,\frac{W}{F_{DBT}}\,\frac{1}{X} + \left(1-\frac{K_{DBT}}{K_{prod}}\right). \quad (4)$$

The conversion data were fitted to Eq. (4), using values of K_{H_2} obtained from the model for product formation, and are shown in Fig. 9. These data were generated over the range of temperatures, hydrogen partial pressures, and space velocities described in Table 1.

The intrinsic rate constant, k, and ratio of adsorption coefficients, K_{DBT}/K_{prod}, were obtained from the slopes and intercepts of the lines in Fig. 9. The Arrhenius plot for the rate constants is shown in Fig. 10. The activation energy for the disappearance of DBT calculated was 39 kcal/g mole. This agrees with the value of 36 kcal/g mole calculated by Rollman (*12*).

When the ratio of adsorption coefficients, K_{DBT}/K_{prod}, was plotted as a function of $1/T$ the expected linear relationship was not observed. This suggests that the difference in heats of adsorption, $\Delta H_{DBT} - \Delta H_{prod}$, is changing with temperature. This change can be accounted for when the contributions of the different products to the overall adsorption coefficient are considered.

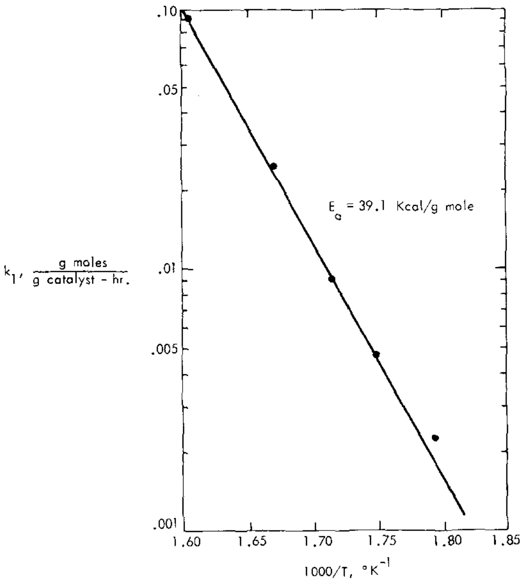


FIG. 10. Arrhenius plot of the intrinsic reaction rate constant for the reaction: DBT + $H_2 \xrightarrow{k_1}$ A*.

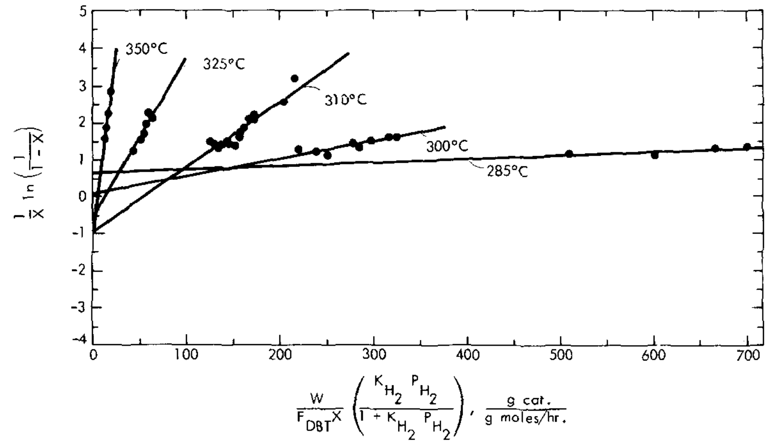


FIG. 9. The fit of the DBT conversion data to kinetic Model V.

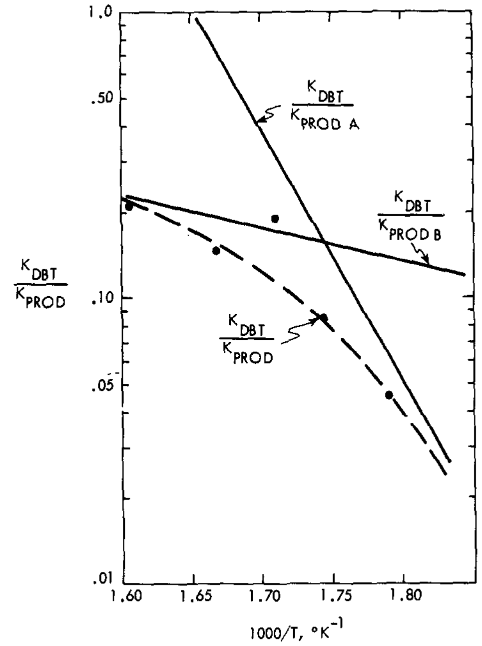


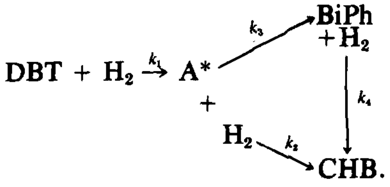
FIG. 11. Theoretical contributions of multiple products to the ratio of adsorption coefficients K_{DBT}/K_{prod}.

At low temperature, it appears that K_{prod} is dominated by a product with a heat of adsorption considerably greater than DBT. This contribution decreases rapidly with increasing temperature, becoming negligible at high temperature. At these temperatures K_{prod} is controlled by a product having a heat of adsorption comparable to DBT. This effect is illustrated in Fig. 11.

Sequential Reaction—Kinetic Model

The models developed thus far do not account for the observed effects of particle size on product selectivity. From the data in Table 5 it is apparent that there are significant diffusional effects for the larger $\frac{1}{16}$-in. extrudate catalyst particles. Since intraparticle diffusion is characterized by a concentration gradient through the catalyst pellet, the effective BiPh concentration in the pores should be greater than the bulk liquid. This higher concentration of BiPh in the pores leads to increasing production of CHB by the sequential reaction pathway. The model developed for product selectivity allows only for the formation of products by the parallel path mechanism. A more complete model which allows for both parallel and sequential reactions is:

Model VI



The integrated rate equations for a plug flow reactor at constant hydrogen pressure are

$$\frac{[\mathrm{BiPh}]}{[\mathrm{DBT}_0]} = \frac{K_2}{K_1 - 1}((1 - X) - (1 - X)^{K_1}), \quad (5)$$

$$\frac{[\mathrm{CHB}]}{[\mathrm{DBT}_0]} = \left(\frac{K_2K_1 + K_1K_3 - K_3}{K_1 - 1}\right) X - \left(\frac{K_2}{K_1 - 1}\right)(1 - (1 - X)^{K_1}), \quad (6)$$

where

$$K_1 = \frac{K_{\mathrm{BiPh}}k_4}{K_{\mathrm{DBT}}k_1},\quad K_2 = \frac{k_3}{k_3 + k_2\Theta_{\mathrm{H}_2}},\quad K_3 = \frac{k_2\Theta_{\mathrm{H}_2}}{k_3 + k_2\Theta_{\mathrm{H}_2}},$$

and

$$\Theta_{\mathrm{H}_2} = \frac{K_{\mathrm{H}_2}P_{\mathrm{H}_2}}{1 + K_{\mathrm{H}_2}P_{\mathrm{H}_2}}.$$

The reaction rate constant, k_4, was evaluated from data on the hydrogenation of BiPh over a crushed Co–Mo/Al_2O_3 catalyst using the following Langmuir–Hinshelwood model:

$$\frac{-d(\mathrm{BiPh})}{dt} = \frac{k_4K_{\mathrm{BiPh}}P_{\mathrm{BiPh}}K_{\mathrm{H}_2}P_{\mathrm{H}_2}}{(1 + K_{\mathrm{BiPh}}P_{\mathrm{BiPh}} + K_{\mathrm{CHB}}P_{\mathrm{CHB}})(1 + K_{\mathrm{H}_2}P_{\mathrm{H}_2})}. \quad (7)$$

Assuming BiPh is strongly adsorbed and $K_{CHB}P_{CHB}$ can be neglected at low conver-

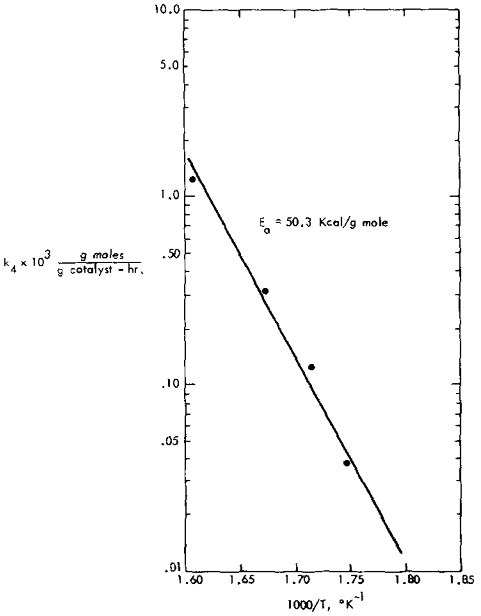


Fig. 12. Arrhenius plot for the intrinsic rate constant for biphenyl hydrogenation: BiPh + $H_2 \xrightarrow{k_4}$ CHB.

sion, for a plug flow reactor Eq. (7) yields

$$\frac{k_4 K_{H_2} P_{H_2}}{1 + K_{H_2} P_{H_2}} = \frac{F_{BiPh}}{W} X_{BiPh}. \qquad (8)$$

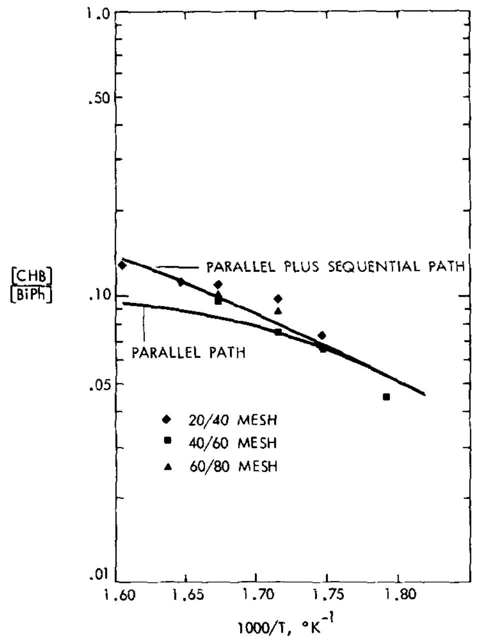


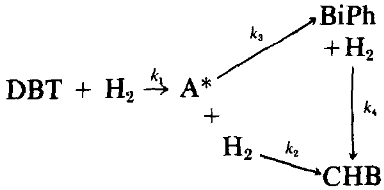
Fig. 13. Product ratio predicted by parallel path model, and parallel plus sequential path model.

Values of k_4 were calculated from Eq. (8) and are plotted in Fig. 12.

The product distribution predicted by Model VI can be calculated if it is assumed that $K_{DBT}/K_{prod} = 1$. A plot of the product ratio, [CHB]/[BiPh], versus temperature is shown in Fig. 13. Included in the plot are the distributions predicted by the parallel path model and the parallel plus sequential path model. The latter model clearly provides a better fit to the data.

CONCLUSIONS

Hydrodesulfurization of dibenzothiophene to biphenyl, cyclohexylbenzene, and H_2S over a Co–Mo/Al_2O_3 catalyst fits the kinetic model:



where A* is a steady-state intermediate. Most CHB is produced by reaction of A*; however, there is a finite contribution from the sequential reaction of BiPh which increases with temperature. This model accounts for the observation by Rollman (*12*) that the production of CHB increases with temperature. The proposed mechanism also accounts for the product distribution reported by Bartsch and Tanielian (*8*) and Aguilar Rios *et al.* (*9*) who found primarily H_2S and BiPh at atmospheric pressure. The model predicts a product ratio, [CHB]/[BiPh], of 0.09 at 325°C and 3.1 MPa and a ratio of 0.005 at atmospheric pressure.

The rate for DBT disappearance is described best by the Langmuir–Hinshelwood expression:

$$\frac{-d(\mathrm{DBT})}{dt} = \frac{k_1 K_{DBT} K_{H_2} P_{DBT} P_{H_2}}{(1 + K_{DBT} P_{DBT} + K_{prod} P_{prod})(1 + K_{H_2} P_{H_2})}.$$

This expression becomes first order with respect to DBT as its concentration decreases. This accounts for the first-order dependence observed by Houalla *et al.* (*10, 11*) at the low DBT concentration they studied.

The rate expression implies that the surface reaction involves two sites on the catalyst surface, one site on which DBT and products competitively adsorb and a second site for H_2 adsorption. This concept of two sites is further established by studies in which the addition of H_2S decreased the rate of conversion but did not affect product selectivity. The competitive adsorption by more than one reaction product can be deduced from the ratio of adsorption coefficients $K_{\mathrm{DBT}}/K_{\mathrm{prod}}$ which indicates that more than one product contributes to K_{prod}. This model is similar to one proposed by Massoth (*20*) for thiophene who reported that desulfurization involves dual sites, one upon which thiophene and H_2S competitively adsorb and one upon which H_2 adsorbs.

The kinetic models developed to account for product selectivity and rate of DBT disappearance support the reaction mechanisms proposed in our earlier paper on the chemistry of condensed sulfur heterocyclics.

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