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Hydrodesulfurization of Sulfur Heterocyclic Compounds

Reaction Mechanisms

GOPAL H. SINGHAL[1], RAMON L. ESPINO, AND JAY E. SOBEL

Exxon Research and Engineering Company, Corporate Research Laboratories, P.O. Box 45, Linden, New Jersey 07036

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The hydrodesulfurization of sulfur heterocyclic compounds over a commercial Co–Mo/γ-Al_2O_3 catalyst has been studied under close to commercial conditions (300–350°C, 20–40 atm). The compounds were selected on the basis of stability, steric requirement, and resonance interactions and included thianthrene, 1,4,6,9-tetramethylthianthrene, tetraphenylthiophene, dibenzothiophene, and some of its potential intermediates. The study strongly suggests that the pathways followed by the compounds are structure dependent and can be divided into two categories: (1) in compounds where the electron density is localized on the sulfur atom, desulfurization by direct coordination of the sulfur to a catalyst site can take place giving only the aromatic products; (2) in compounds such as dibenzothiophene in which the electron density of the sulfur atom is delocalized over an extensive π system and steric crowding around the sulfur atom is present, the first step in the reaction pathway is probably a π-complex formation which is followed by hydrogenation and desulfurization. In this case, both aromatic and partially saturated compounds are produced. It is proposed that these products result from a common intermediate suggesting a primarily parallel rather than sequential path for the formation of the hydrogenated products.

INTRODUCTION

In the petroleum industry, the long-term trend will be to process heavier feedstocks containing large percentages of sulfur and nitrogen. As the crudes become heavier, the percentage of condensed sulfur heterocyclics increases faster than simpler compounds such as mercaptans and single-ring heterocyclic thiophenes which are relatively easy to desulfurize. In the middle distillates most of the sulfur is present in the form of condensed heterocyclic compounds such as benzothiophenes, dibenzothiophenes, and benzonaphthothiophenes (*1*). To develop improved desulfurization catalysts we believe that it is important to unravel the reaction pathways followed by these molecules during practical hydrodesulfurization (HDS) conditions. Studies of model compounds which are difficult to desulfurize are in our opinion the first steps in attaining a better understanding of sulfur removal.

Our review of the prior art indicated that insufficient mechanistic and kinetic data exist on the desulfurization of complex sulfur heterocyclics (*2–5, 32–35*) and that most of the detailed mechanistic studies have been done with thiophenes, the simplest sulfur heterocyclic compounds at atmospheric pressure. Due to the differences in the chemical nature of the heterocyclic compounds involved, it is very unlikely that the reaction pathways followed by condensed thiophenes under commercial processing conditions are the same as those followed by thiophenes at atmospheric pressure.

In recent years basically two mechanisms have been postulated to explain the HDS of thiophenes. The first one can be considered to be based upon the extensive work of Amberg and co-workers (*6, 7*) and Lipsch and Schuit (*8*). Although there are some differences in the thinking of these

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[1] Present address: Exxon Research and Engineering Company, P.O. Box 4255, Baytown, Tx 77520.

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two groups, the mechanism can be considered to include the following steps:

(a) adsorption of thiophene and coordination of the S atom of thiophene via its lone pair of electrons to an anion vacancy of molybdenum;

(b) transfer of two hydrogen atoms in successive steps from the adjacent Mo · OH(SH) groups, breaking the C–S bonds of thiophene;

(c) desorption of 1,3-butadiene formed after further hydrogenation on the same or different site;

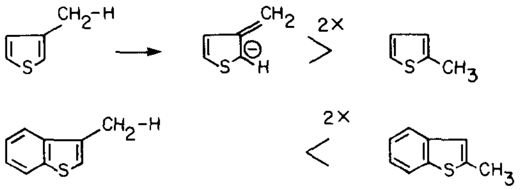
(d) restoration of the original catalyst sites by hydrogen with the desorption of hydrogen sulfide.

Thus, the hydrogen responsible for C–S bond cleavage comes from the catalyst surface.

The second mechanism advanced by Kolboe (*9*) can be considered to be dehydrosulfurization rather than hydrodesulfurization. According to Kolboe the hydrogen required for initial C–S bond breaking comes from a thiophene molecule rather than the catalyst. The diacetylene so formed gives, after hydrogenation, the observed products. Supporting evidence for this mechanism was subsequently provided by Mikovsky and co-workers (*10*).

This picture is complicated by the work of Smith and co-workers (*11*) who find that over Co–Mo catalyst and under the conditions used by Mikovsky and co-workers, thiophene exchanges hydrogen atoms for deuterium atoms extensively in all positions. The only rationalization seems to be that dehydrosulfurization is a much faster reaction than deuterium exchange.

A review of the literature reveals that there is a definite change in the reactivity in going from the derivatives of simple thiophenes to those of benzothiophenes. Thus, Desikan and Amberg (*12*) showed that the rate of conversion of 3-methylthiophene is twice that of 2-methylthiophene. They attributed the greater reactivity of 3-methylthiophene to the combined induction of hyperconjugation effect of the 3-methyl group. This imparts greater electron density (as compared to the 2-methyl group) to the carbon atom α to sulfur and thus greater affinity for the acidic catalyst surface. In the benzothiophene series, however, Givens and Venuto (*13*) found the opposite trend. Thus, the rate of desulfurization of 3-methylbenzothiophene is one half that of 2-methylbenzothiophene.



Kwart *et al.* (*34*) have recently proposed a mechanism for thiophene desulfurization that explains the experimental results that could not be reconciled with the sulfur atom coordination or the dehydrodesulfurization mechanisms. This is a two-point mechanism, with the carbon–carbon double bond interacting with the molybdenum cation and the sulfur atom interacting with a sulfur atom on the sulfided catalyst surface. This mechanism explains the deuterium-exchange results and is consistent with the observed steric effects.

Very recently a number of studies have appeared on the mechanism of desulfurization of condensed thiophenes, particularly dibenzothiophenes, methyl-substituted benzothiophenes, and dibenzothiophenes and their sulfoxides and sulfones. Geneste *et al.* (*33*), based on their kinetic studies in batch autoclaves, concluded that the first step in the desulfurization of benzothiophenes was the hydrogenation of a carbon–carbon double bond in the aromatic ring adjacent to the sulfur atom which was then followed by desulfurization. They also postulated that the methyl derivatives of benzothiophene desulfurized at a slower rate than benzothiophene because of the steric hindrance of the methyl groups. For the sulfones and sulfoxides they also suggested a hydrogenation step followed by deoxygenation and then desulfurization. In the case of dibenzothiophenes, they interpreted results as indicating that the aromatic ring does not need to be hydrogenated before rupture of the C–S bond.

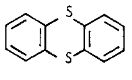
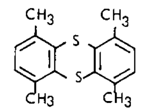
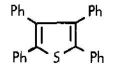
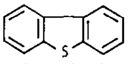
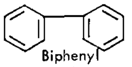
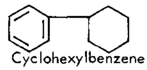
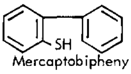
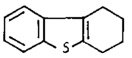
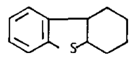
Houalla *et al.* (*35*) studied the hydrodesulfurization of methyl-substituted dibenzothiophenes in a flow reactor packed with sulfided Co/Mo/γ-alumina catalyst. Their kinetic analysis of the results showed noticeable differences in the reactivity of the compounds depending on the location of the methyl group, with 4,6-dimethyldibenzothiophene being the least reactive compound. They have suggested that the reactivity of these sulfur heterocyclics is strongly affected by the rate of hydrogen transfer from the catalyst surface to the reacting molecule and that the steric impact of methyl substitution may explain the low reactivity of molecules with methyl groups close to the sulfur atom.

With this background, we were interested in determining the reaction mechanism of hydrodesulfurization of complex thiophene molecules under close to commercial conditions. Our basic strategy was to study the desulfurization of organic sulfur compounds that were better models of the species present in heavy feedstock in terms of electronic environment and steric crowding. Dibenzothiophene is obviously a better model compound than thiophene. However, we were also interested in studying molecules for which the desulfurization paths proposed in the literature for thiophene were denied or to some extent hindered. This approach was expected to serve the double purpose of testing the literature mechanisms in a conclusive fashion and of providing new leads in understanding the pathways taken by complex sulfur heterocyclic compounds.

The model compounds selected are given in Table 1 along with an explanation for their selection for this study.

TABLE 1

Model Compounds Studied

Compounds	Reasons for Study
 Thianthrene  Tetramethylthianthrene	Steric effects
 Tetraphenylthiophene (TPT)	Steric and electronic effects
 Dibenzothiophene (DBT)	Key-model compound - representative of structures in petroleum feeds boiling above 300°C
 Biphenyl (BiPh)  Cyclohexylbenzene (CHB)  Mercaptobiphenyl  TetrahydroDBT  HexahydroDBT	Probable intermediates in HDS of DBT

EXPERIMENTAL

Analytical Techniques

Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Gas chromatographic analysis was performed on an HP 5830 A gas chromatograph using either a 10-foot, ⅛-in.-o.d. column packed with 3% SP 2250 on 100- to 120-mesh Supelcoport or a 6-foot column packed with 3% Dexsil 300 GC on 100- to 120-mesh Supelcoport. The GC/MS data were obtained on a CEC 21-103/2 mass spectrometer fitted with an all-glass inlet system at an ionization potential of 70 eV.

Materials

Thianthrene, biphenyl, and cyclohexylbenzene (CHB) were obtained from Aldrich Chemical Company and were used without purification. Tetramethylthianthrene was prepared according to the procedure of Buu-Hoi and co-workers (*16*); tetraphenylthiophene was synthesized by the procedure of Baumann and Fromon (*17*). Dibenzothiophene, obtained from Aldrich Chemical Company, was dissolved in tetralin and filtered to remove insoluble impurities. The solution was used without further purification.

Tetrahydrodibenzothiophene (THDBT) was obtained by a modified procedure of Rabindran and Tilak (*18*).

Hexahydrodibenzothiophene (HHDBT) was prepared by the method of Mitra and Tilak (*19*) and was also kindly supplied by Dr. J. Wristers (*20*) of these laboratories.

2-Mercaptobiphenyl was synthesized from *o*-phenylphenol by the general procedure of Newman and Karnes (*21*) for converting phenols to thiophenols. The product was obtained in 52% yield, mp 40–41°C (bp$_{0.5}$ 105°C (*22*)). Anal. Calcd. for $C_{12}H_{10}S$: C, 77.42; H, 5.38; S, 17.20. Found: C, 77.34; H, 5.50; S, 17.10.

General Description of the Experimental Equipment and Procedure

All the HDS runs were carried out in two high-pressure downflow reactors contained in fluidized sand baths. Dimensions were, for Reactor 1: i.d. 1.4 cm, cross-sectional area 1.51 cm^2, and catalyst bed height approximately 5.6 cm; for Reactor 2: i.d. 1.07 cm, cross-sectional area 0.91 cm^2, and catalyst bed height approximately 2.5 cm. The nature of products and the extent of conversion in both reactors were similar. The runs at 310°C and 4.14 MPa (600 psig) were carried out in the larger reactor while the runs at lower pressure (3.1 MPa) were made in both reactors.

In all runs a typical Co–Mo/γ-Al_2O_3 (CoO, 3.7%; MoO_3, 13%; SiO_2, 1.8%) catalyst was used. The surface area of the catalyst, prior to sulfidation, was 250 m^2/g with an average pore volume of 0.5 ml/g. The catalysts were sulfided in a uniform manner with a 10% H_2S/H_2 mixture while gradually heating to 300°C in 2 hr. The heating rate during sulfiding was then changed to 25°C/hr for 2 hr and finally the catalyst was held at 350°C for 1 hr in the sulfiding atmosphere.

In all runs a large excess of hydrogen was used and the residence time was held constant. The flow rate of the liquid feed was maintained at an LHSV value of approximately 6.0. The gas feed rate was held constant at a value of ~700 cm^3 of H_2/cm^3 of liquid feed (4000 SCF/Bbl). The feed consisted of a 10% solution by weight of the sulfur compound in tetralin. In the case of thianthrenes, due to their low solubility, a 5 wt% solution in tetralin was used.

DISCUSSION OF RESULTS

Thianthrenes

The use of thianthrenes as model compounds for HDS study and as precursors for dibenzothiophenes is not without precedent. Given and co-workers (*23*) have postulated that in coal, thiophenic structures may arise from thianthrene-type precursors. They have also shown that while DBT is desulfurized to the extent of 59% upon refluxing with lithium in dioxane, thian-

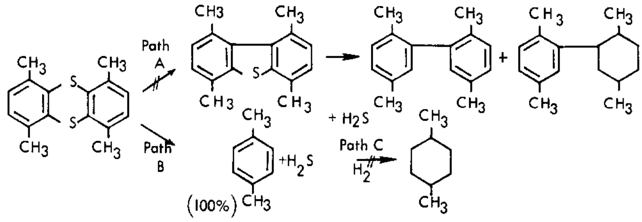


FIG. 1. HDS of thianthrenes at 310°C and 4.1 MPa.

threne, which is less aromatic in character than DBT, is unexpectedly unchanged. Badger and co-workers (*24*) found that desulfurization of thianthrene with hydrogen-poor Raney nickel gives DBT as one of the products. Finally, Benjamin and co-workers (*25*) have recently shown that thianthrene upon heating in tetralin at 400°C is quantitatively converted to DBT.

We were interested in correlating these observations to petroleum feedstocks. Could the difficult to desulfurize compounds in the heavy petroleum fractions arise from the thianthrenes? As shown in Fig. 1, tetramethylthianthrene during HDS could conceivably go through Path A. A planar tetramethyldibenzothiophene is first produced by sulfur extrusion followed by further hydrodesulfurization to the tetramethylbiphenyl and its corresponding cyclohexyl derivative. Alternatively, it could directly hydrodesulfurize (Path B) to give *p*-xylene which on further hydrogenation should give 1,4-dimethylcyclohexane. It should be pointed out that polyalkyl-substituted dibenzothiophenes have been isolated from Kuwait crudes (*26*) but that the synthesis of these compounds has been achieved only through long reaction sequences and low yields (*27*). Therefore, tetramethylthianthrene also provided a possibility for *in situ* preparation of polyalkyl-substituted dibenzothiophenes.

When tetramethylthianthrene and thianthrene were hydrodesulfurized at 310°C and 4.1 MPa, and at a space velocity of 6 hr^{-1} we observed 100% conversion to *para*-xylene and benzene, respectively. These results, though surprising at first, can be explained when it is realized that tetramethylthianthrene and thianthrene have a folded structure along the axis joining the two sulfur atoms in which the two benzene rings are in the planes at an angle of 128° to each other. The tetramethylthianthrene structure is shown in Fig. 2. The net result is that (a) the lone pairs of electrons are fairly localized on the sulfur atoms and (b) the sulfur atoms are relatively exposed and can thus coordinate to vacant sites for direct HDS. Another noteworthy observation is that *p*-xylene is not further hydrogenated to 1,4-dimethylcyclohexane. These results are consistent with the findings of Hoog (*2*): under his HDS conditions (375°C and 750 psig) octylbenzylsulfide is exclusively desulfurized to toluene without further reduction to methylcyclohexane.

Tetraphenylthiophene (TPT)

Tetraphenylthiophene is known to be one of the most stable of the thiophene compounds. According to Sergienko and Per-

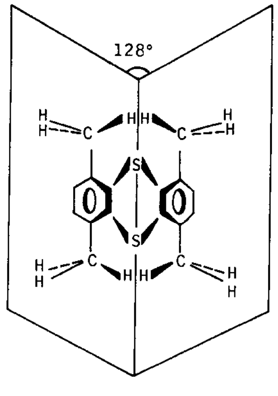


FIG. 2. Molecular model of tetramethylthianthrene.

chenko (*28*) it failed to be desulfurized completely over Ni and W sulfides at 200°C and 200 atm of hydrogen. Using MoS_2, Landa and Mrnkova (*29*) were able to desulfurize TPT. It seems that HDS studies of TPT over Co–Mo catalyst have not been reported. Our interest in the selection of TPT as a model was based upon the realization that in this compound the phenyl groups conjugated with thiophene should drain away the electron density from the C atoms α to sulfur atom and thus reduce its interaction with the catalyst (*12*), thus making its conversion difficult. Also the lack of β-hydrogen atoms would not allow the reaction to proceed without prior hydrogenation by the dehydrosulfurization mechanism of Kolboe (*9*). The results of HDS of TPT and DBT are given in Table 2.

Though TPT gave a much higher conversion than DBT the product mixture was very complex as determined by GC/MS analysis. Products in which one or more phenyl rings had been saturated were obtained. The materials present in the mixture having a molecular weight above 180 along with probable assignments of the structures (tentative) are given in Table 3.

If the HDS takes place by sulfur coordination and hydrogenation (Lipsch and Schuit's model), it is difficult to visualize why further reduction of highly conjugated aromatic rings should take place. Moreover, with four electron-withdrawing phenyl groups, it is doubtful that the S atom has enough localized electron density to coordinate with the vacant site on Mo. The steric bulk of the phenyl group should also hinder this coordination even though the phenyl rings may not be in the plane of the thiophene ring.

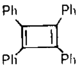
TABLE 2

HDS of TPT and DBT at 310°C and 4.1 MPa Total Pressure

Compound	Percentage conversion	Products (wt%)
TPT	94	93.6% tetraphenyl derivatives of butane, butene, butadiene, and cracked products 6.4%, with phenyl saturation (cyclohexyltriphenyl C_4, dicyclohexyldiphenyl C_4)
DBT	40–45	Biphenyl 86%, cyclohexylbenzene 14%

TABLE 3

HDS of Tetraphenylthiophene (MW = 388)

	COMPOUND	M/E	REMARKS
1.	$PhCH{=}CH\text{-}Ph$	180	
2.	$PhCH_2\text{-}CH_2Ph$	182	
3.	 $\text{-}CH_2\text{-}CH_2Ph$	188	
4.	$PhCH{=}C(Ph)CH_2Ph$	270	
5.	$PhCH{=}C(Ph)\text{-}CH_2\text{-}$ 	276	AND ISOMERS
6.	$C_6H_{11}CH{=}C(Ph)CH_2C_6H_{11}$	282	AND ISOMERS
7.		356	(?)
8.	$PhCH{=}C(Ph)C(Ph){=}CHPh$	358	
9.	$PhCH{=}C(Ph)\text{-}CH(Ph)CH_2Ph$	360	
10.	$PhCH_2CH(Ph)CH(Ph)CH_2Ph$	362	
11.	$PhCH{=}C(Ph)CH(Ph)CH_2C_6H_{11}$	366	AND ISOMERS
12.	$C_6H_{11}CH{=}C(Ph)CH(Ph)CH_2C_6H_{11}$	372	AND ISOMERS

It seems that the hydrodesulfurization of TPT is easier than that of DBT but proceeds by a very complicated reaction pathway. In our opinion, the first step in the sequence shown in Fig. 3 is probably π-complex formation through one of the phenyl rings. The sulfur atom of the thiophene ring can now transfer its electron density to the electron-deficient phenyl ring polarizing the double bonds in the process. This facilitates the addition of one molecule of hydrogen to give a dihydro intermediate such as (**B**). This intermediate can then aromatize by breaking the C–S bond to give a mercaptan (**C**) or, being a dienic structure, can be further hydrogenated to give (**D**) which in turn can give the mercapto intermediate (**E**). These mercapto intermediates are then desulfurized by the catalyst.

The proposed mechanism, therefore, can explain the formation of products in which one or more of the phenyl rings of TPT have been hydrogenated without invoking

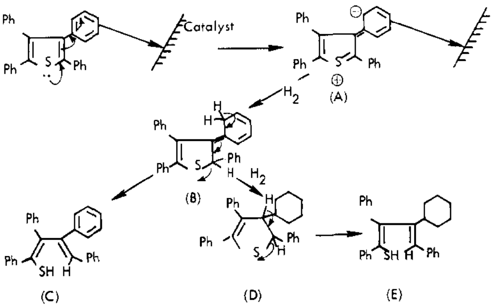


FIG. 3. Proposed mechanism for HDS of tetraphenylthiophene (TPT).

the reduction of desulfurized aromatic compounds. This is also consistent with Hoog's data (*2*) and our thianthrene result that alkylaromatics are not hydrogenated further under HDS conditions employed. It should be pointed out that many forms such as (A) for the polarization of the double bonds, including the ones in which only the thiophene ring is involved, can be postulated without altering the products formed.

Dibenzothiophene and Derivatives

The formation of compounds containing saturated phenyl rings from TPT and cyclohexylbenzene from DBT in hydrodesulfurization prompted us to investigate these reactions further.

There seems to be a lack of agreement on the products formed as well as on the path taken by DBT on HDS over a standard Co–Mo catalyst. Thus, Hoog (*2*) found that DBT on HDS at 375°C and 750 psig gave a mixture of products consisting of 35% biphenyl and 65% cyclohexylbenzene and bicyclohexyl. Commenting on Hoog's results, Cawley (*30*) proposed that during the process one of the benzene rings of DBT is first hydrogenated followed by ring opening and desulfurization to give cyclohexylbenzene. This mechanism does not account for the formation of a major reaction product, biphenyl. Obolentsev and Mashkina (*31*) under a variety of conditions and Bartsch and Tanielian (*3*) at atmospheric pressure found only biphenyl as the reaction product. Very recently Gates and co-workers (*4, 35*) have carried out the HDS of DBT and substituted DBTs at 102 atm and 300°C. They imply that the HDS of DBT also needs 2 moles of hydrogen per molecule of DBT giving biphenyl which can be further hydrogenated to give cyclohexylbenzene. These two processes are summarized in Fig. 4. The situation is further complicated by the statement of Obolentsev and Mashkina (*31*) and the observation of Rollman (*32*) that under their experimental conditions biphenyl is not converted to cyclohexylbenzene.

Our objective was to determine the reaction pathway taken by DBT during HDS and to establish whether cyclohexylbenzene is formed by further hydrogenation of biphenyl or if the latter is produced by the dehydrogenation of the former. It should be pointed out that the absence of β-hydrogen atoms in DBT requires, if Kolboe (*9*) is correct, the formation of benzyne intermediates for desulfurization to occur. On the other hand, Lipsch and Schuit's mechanism as applied by Gates and co-workers would require hydrogenation of biphenyl (BiPh) to give cyclohexylbenzene (CHB).

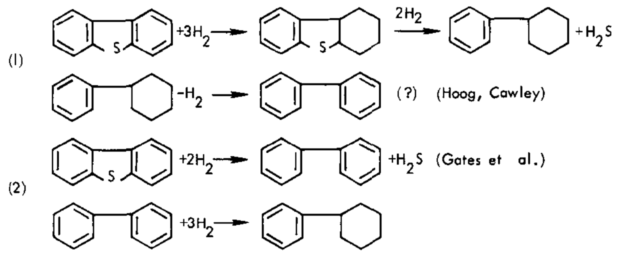


FIG. 4. Literature pathways for DBT hydrodesulfurization.

TABLE 4

Reactions of DBT and Products[a]

Starting material	Conditions		Percentage conversion	Mole% products		
	T (°C)	P (MPa)		DBT	BiPh	CHB
DBT[a]	300	3.1	40	60	37.0	3.0
	310	3.1	55	45	50.0	5.0
	325	3.1	85	15	76.5	8.5
BiPh[b]	300	3.1	0.3		99.7	0.3
	310	3.1	0.7		99.3	0.7
	325	3.1	1.8		98.2	1.8
CHB[b]	325	3.1	0.0			100

[a] 10% in tetralin.

[b] 3% thiophene, 10% reactant, balance tetralin.

Our results for DBT, biphenyl, and cyclohexylbenzene are given in Table 4.

It is clear that the amount of cyclohexylbenzene formed from biphenyl under HDS conditions is much less than observed from DBT. Similarly, cyclohexylbenzene is not converted under the reaction conditions to biphenyl at all. Thus, the hypothesis that the CHB is produced from BiPh seems doubtful. We also believe that the hydrogen atoms in the 4 and 6 positions of DBT might sterically interfere with the bulky SH groups on Mo making coordination through the sulfur atom of DBT difficult. Also, the electron density of the sulfur atom of DBT is distributed over the entire π system, making the coordination of the vacant site on Mo rather unfavorable.

These apparent discrepancies can be accounted for by the mechanism we propose in Fig. 5 which consists of the following steps:

(1) π-complex formation of DBT through one of the benzene rings;

(2) polarization of the double bonds of the complexed ring followed by hydrogenation to give a dihydro intermediate (**B**).

(3) ring opening of the intermediate (**B**) (Path a) to give mercaptobiphenyl (**C**);

(4) further hydrogenation of (**B**) (Path b) followed by ring opening to give (**E**), or rearrangement of (**B**) to (**F**) (Path b′) followed by hydrogenation to (**G**) followed by further hydrogenation, ring opening to give (**E**).

(5) interaction of the mercaptans (**C**) or (**E**) with a vacant site on Mo to give biphenyl and cyclohexylbenzene, respectively.

Obviously, the transformation of DBT to (**B**) involves the loss of a great amount of resonance energy (~36 kcal, calculated by Benson's additivity rule) but once (**B**) is formed, it can be hydrogenated under high hydrogen pressure (since it is a dienic intermediate) to give hexahydro-DBT or tetrahydro-DBT via Paths b and b′. The intermediate (**B**) can also undergo ring opening to give (**C**) (Path a), which is a more favorable process since in going from (**B**) to (**C**), most of the resonance energy is recovered by aromatization. Since Path a is an energetically more favorable route, it can now

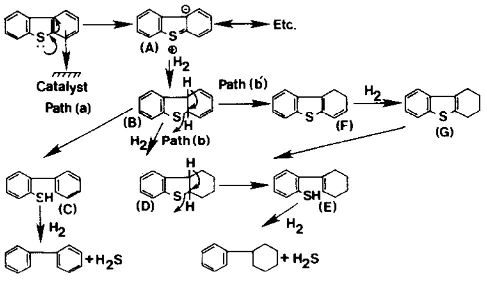


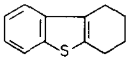
FIG. 5. HDS of DBT.

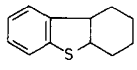
TABLE 5

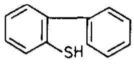
Reactions of DBT and Probable Intermediates

Starting material	Conditions		Mole% conversion	Mole% products			
	T (°C)	*P* (MPa)		DBT	BiPh	CHB	THDBT
DBT	325	3.1	85	15	76.5	8.5	
THDBT	325	3.1	100	—	Tr	99+	—
	275	3.1	87.5	4.3	1.3	80	12.5
HHDBT	290	3.1	100	1.4	4	92	1.3
Mercapto-BiPh	290	3.1	100	5.5	93.2	1.3	

Note. Feed 10% in tetralin.


THDBT


HHDBT


MERCAPTOBIPHENYL

be explained why some of the investigators such as Bartsch and Tanielian (*3*) working at atmospheric pressure have obtained only BiPh in the HDS of DBT.

Our mechanism implies that the HDS of compounds such as tetrahydrodibenzothiophene or hexahydrodibenzothiophene should proceed at a faster rate since the loss of resonance energy would be less than in the case of DBT. Mercaptobiphenyl should desulfurize at a faster rate too and should give mostly biphenyl while partially hydrogenated compounds such as tetrahydrodibenzothiophene or hexahydrodibenzothiophene should be the source of cyclohexylbenzene. This is what was found experimentally. The results are summarized in Table 5.

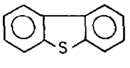
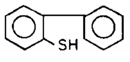
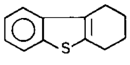
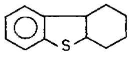
Finally, according to our mechanism the reactive intermediate (**B**) in Fig. 5 should also lead to the formation of hexahydrodibenzothiophene, directly or through tetrahydrodibenzothiophene, and to 2-mercaptobiphenyl. We were not able to detect the presence of these compounds in our earlier work. However, a more detailed analysis by GC/MS of the products from one of the HDS runs showed the presence of some of these intermediates. These results are given in Table 6.

It should be pointed out that the problem of identification of tetrahydrodibenzothiophene is complicated since its peak in GC was not resolved from that of DBT. The amount was estimated from the parent ion current detected by a DuPont 21-491 mass spectrometer.

The mechanistic conclusions of our study are in disagreement with those of Geneste *et al.* (*33*) and Houalla *et al.* (*35*) since we propose a parallel pathway for the formation of the two major products, biphenyl and cyclohexylbenzene, while these two groups favor a sequential pathway for the products. We believe that the reaction con-

TABLE 6

Estimated Relative Abundance of Intermediates in HDS Reaction of DBT[a]

Compound	Structure [S4h]	Relative abundance
Dibenzothiophene		100
2-Mercapto-biphenyl (**A**)		—
Tetrahydro-dibenzothiophene (**B**)		0.5–0.7
Hexahydro-dibenzothiophene (**C**)		0.01–0.02

[a] *T*, 310°C; *P*, 3.1 MPa; LHSV, 6 hr^{-1}.

ditions can account for the discrepancy. At high pressures and with the sulfur heterocyclic in the liquid phase, conversion of biphenyl to cyclohexylbenzene is to be expected. Our kinetic studies reported in Part II show that biphenyl hydrogenation, under those conditions, can account for a measurable fraction of the cyclohexylbenzene in the product.

CONCLUSIONS

Our studies on the hydrodesulfurization of sulfur heterocyclics at temperatures between 300 and 350°C, pressures below 40 atm, and with a sulfided Co–Mo/γ-Al_2O_3 have shown that the reaction rates and pathways are strongly dependent on the steric and electronic environments of the sulfur compounds. Thus, in the case of thianthrene and its tetramethyl derivative which have molecular dimensions similar to DBT but have the electron density localized on the sulfur atoms, direct desulfurization via sulfur coordination with the active sites of the catalyst seems to occur. Consequently, the products consist of only aromatic molecules such as benzene and xylene, respectively. Their hydrogenated derivatives, namely, cyclohexane and 1,4-dimethylcyclohexane, were not observed. It can also be concluded from this study that aromatic or alkylaromatic compounds, once formed, are not further hydrogenated over this catalyst and under the reaction conditions.

If on the other hand the electron density of the sulfur atom is delocalized over an extensive π system, the first step in the reaction pathway seems to be the hydrogenation of a carbon–carbon double bond in the aromatic ring. This intermediate can further hydrogenate and desulfurize. The reaction products from these compounds include aromatic and saturated cyclic compounds. This is the case for tetraphenylthiophene and dibenzothiophene. Studies of the reactivity of the proposed intermediates in DBT desulfurization strongly support this mechanism. A detailed kinetic study of the desulfurization of dibenzothiophene has been carried out which also supports this mechanism. This study is the subject of Part II of this paper.

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