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KINETICS AND MECHANISM OF DESULFURIZATION AND
DENITROGENATION OF COAL-DERIVED LIQUIDS

Twelfth Quarterly Report, March 21—June 20, 1978

MASTER

By
Bruce C. Gates
James R. Katzer
Jon H. Olson
Harold Kwart
Alvin B. Stiles

October 20, 1978
Date Published

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Departments of Chemical Engineering and Chemistry
University of Delaware
Newark, Delaware

FOSSIL
ENERGY



U. S. DEPARTMENT OF ENERGY

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Under Contract No. E(49-18)-2028

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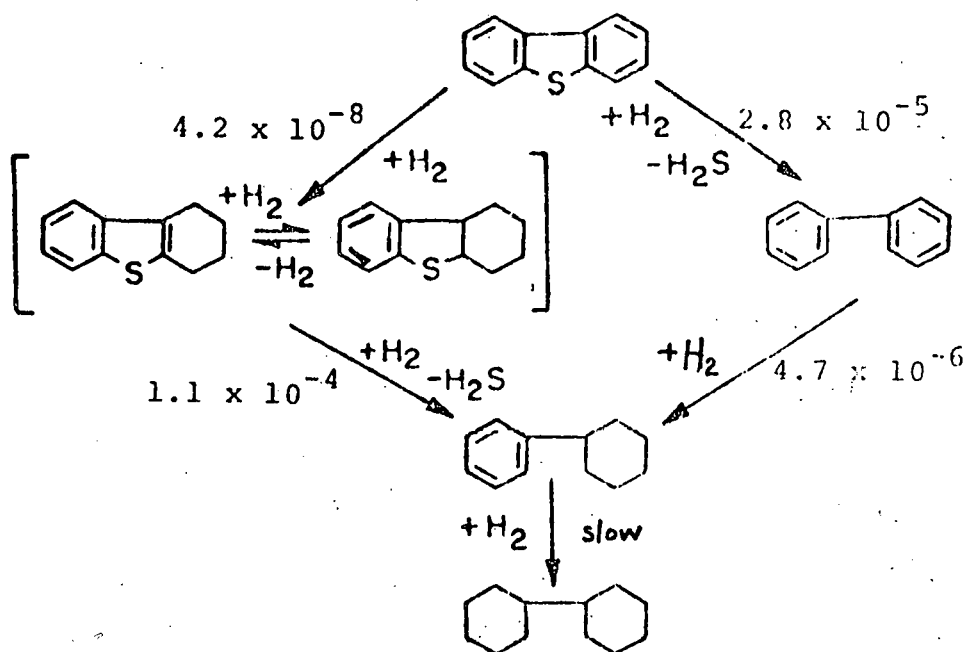
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ABSTRACT

All the data reported in previous quarterly reports have been reevaluated to determine the quantitative reaction network for dibenzothiophene hydrodesulfurization at about 100 atm and 300°C. The results are summarized as follows, where the numbers next to the arrows represent pseudo first-order rate constants in units of m^3/kg of catalyst \cdot s:



This network shows the high selectivity of the catalyst for simple hydrodesulfurization (biphenyl + H_2S formation). When methyl groups are present in the 4 and 6 positions of dibenzothiophene, the primary hydrogenation reaction is approximately as fast as the primary hydrodesulfurization reaction. Ni and Mo or Ni and W used instead of Co and Mo in the catalyst, or H_2S in the reactant mixture, also favor hydrogenation relative to hydrodesulfurization.

The results obtained in the earlier periods of this research have been evaluated in light of the recent literature to provide a new interpretation of the reaction mechanism of catalytic hydrodesulfurization on surfaces of sulfided Co-Mo/Al₂O₃.

It has often been assumed that catalytic hydrodesulfurization of thiophene and related compounds proceeds via a one-point "end-on" adsorption involving bonding of the sulfur atom with Mo ions at an anion vacancy on the catalyst surface. This interpretation is inadequate, failing to account for deuterium-exchange results, the reactivities of benzothiophene and dibenzothiophene, and the small steric effects of methyl substituents affecting the adsorption and reaction of compounds in the thiophene, benzothiophene, and dibenzothiophene families of homologs. An alternative mechanism, presented here, involves a multi-point adsorption of the reactant, with a C=C bond interacting with the Mo cation and the S atom of the reactant interacting with a S ion on the surface. The new mechanism accounts for the observed deuterium exchange and hydrodesulfurization reactions and is consistent with the observed steric effects.

II. OBJECTIVES AND SCOPE

The major objectives of this research are as follows:

- i) to develop high-pressure liquid-phase microreactors for operation in pulse and steady-state modes to allow determination of quantitative reaction kinetics and catalytic activities in experiments with small quantities of reactants and catalyst.
- ii) To determine reaction networks, reaction kinetics, and relative reactivities for catalytic hydrodesulfurization of multi-ring aromatic sulfur-containing compounds found in coal-derived liquids.
- iii) To determine reaction networks, reaction kinetics, and relative reactivities for catalytic hydrodenitrogenation of multi-ring aromatic nitrogen-containing compounds found in coal-derived liquids.
- iv) To obtain quantitative data characterizing the chemical and physical properties of aged hydroprocessing catalysts used in coal liquefaction processes and to establish the mechanisms of deactivation of these hydroprocessing catalysts.
- v) To develop reaction engineering models for predicting the behavior of coal-to-oil processing and of catalytic hydroprocessing of coal-derived liquids and to suggest methods for improved operation of hydrodesulfurization and hydrodenitrogenation processes.
- vi) In summary, to recommend improvements in processes for the catalytic hydroprocessing of coal-derived liquids.

SCOPE

A unique high-pressure, liquid-phase microreactor is being developed for pulse (transient) and steady-state modes of operation for kinetic measurements to achieve objectives ii) through iv). The relative reactivities of the important types of multi-ring aromatic compounds containing sulfur and nitrogen are being measured under industrially important conditions (300-450°C and 500-4000 psi). The reaction networks and kinetics of several of the least-reactive multi-ring aromatic sulfur-containing and nitrogen-containing compounds commonly present in coal-derived liquids will be determined. Catalyst deactivation is an important aspect of the commercial scale upgrading of coal-derived liquids. Accordingly, the chemical and physical properties of commercially aged coal-processing catalysts are being determined to provide an understanding of catalyst deactivation; these efforts can lead to improved catalysts or procedures to minimize the problem. To make the results of this and related research most useful to DOE, reaction engineering models of coal-to-coal processing in trickle-bed and slurry-bed catalytic reactors including deactivation will be developed to predict conditions for optimum operation of these processes. Based on the integrated result of all of the above work, recommendations will be made to DOE for improved catalytic hydrodesulfurization and hydrodenitrogenation processing.

III. SUMMARY OF PROGRESS TO DATE

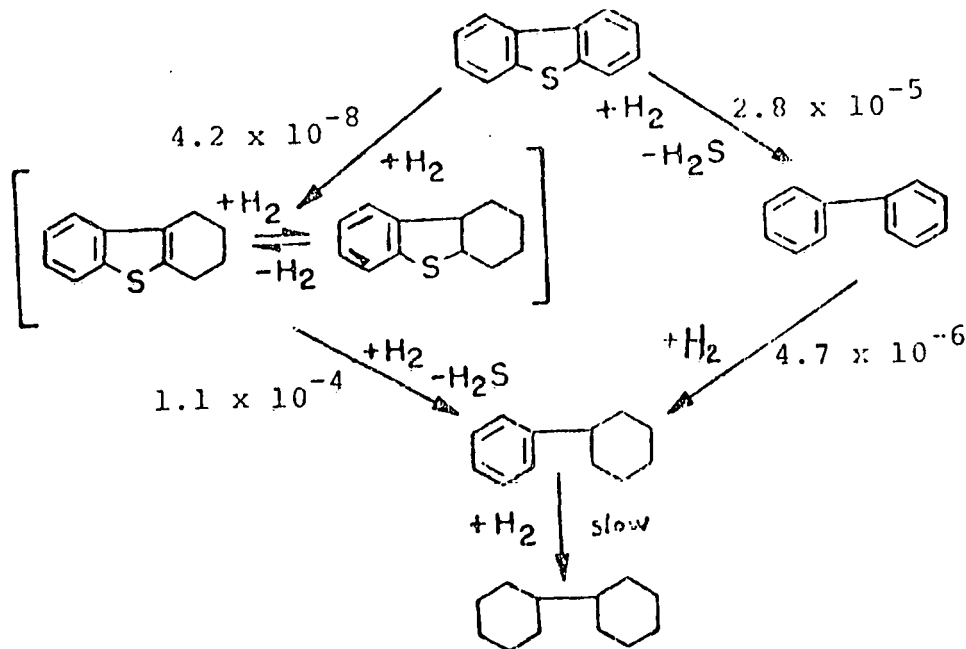
This summary is organized to parallel the task statements of the contract. A milestone chart is provided at the end of this section.

Microreactor Development

Three continuous-flow, liquid-phase, high-pressure microreactors have been built and operated under this contract. The work in this report confirms the success of these microreactors; the data from the batch autoclave runs are effectively identical to data from the flow microreactors. This task has been completed.

Catalytic Hydrodesulfurization

The hydrodesulfurization of dibenzothiophene (DBT) has been examined with a high-pressure microreactor and in batch, stirred-autoclave experiments. The range of data show that the reaction network is slightly more complex than the direct reduction of dibenzothiophene (DBT) to hydrocarbon products; the network is the following at 300°C and 100 atm where the rate constants for units of m^3/kg of catalyst·s:



The relative rates of hydrodesulfurization of a variety of the important sulfur-containing compounds in coal-derived liquids have been determined. The compounds include methyl-substituted dibenzothiophenes, which evidently are among the least reactive compounds in hydrodesulfurization. The relative rate constants for the various reactants are the following: DBT, 1; 4-MeDBT, 0.16; 4,6-diMeDBT, 0.10; 3,7-diMeDBT, 1.7; and 2,8-diMeDBT, 2.6. These results are largely explained by steric and inductive effects. Groups located β to the sulfur atom restrict its interaction with a surface anion vacancy and lower the reactivity. Inductive effects explain the higher reactivities of the compounds having methyl substituents where they exert no steric influence.

The reactivities of the compounds have been determined with individual sulfur-containing compounds and with pairs of these compounds. The reactivities of these compounds are influenced by competitive adsorption determined by the previously mentioned steric and inductive effects.

More detailed study of the hydrodesulfurization of 4,6-dimethyl-dibenzothiophene, which is the least reactive sulfur-containing compound found so far, shows that the reaction network is similar to that of dibenzothiophene but that hydrogenation of the aromatic ring is more pronounced than for dibenzothiophene.

Results from batch-autoclave reactor studies on the hydrodesulfurization of multi-ring sulfur-compounds (with sulfided Co-Mo/ γ -Al₂O₃, 300°C and 70 ± 2 atm of H₂) show that the reactivity decreases from 1-ring to 3-ring compounds and then it increases for the 4-ring compound. Thus the three-ring sulfur-compound, dibenzothiophene, its methyl derivatives are the least reactive compounds studied so far. The first-order rate constants for the hydrodesulfurization of these compounds are given below:

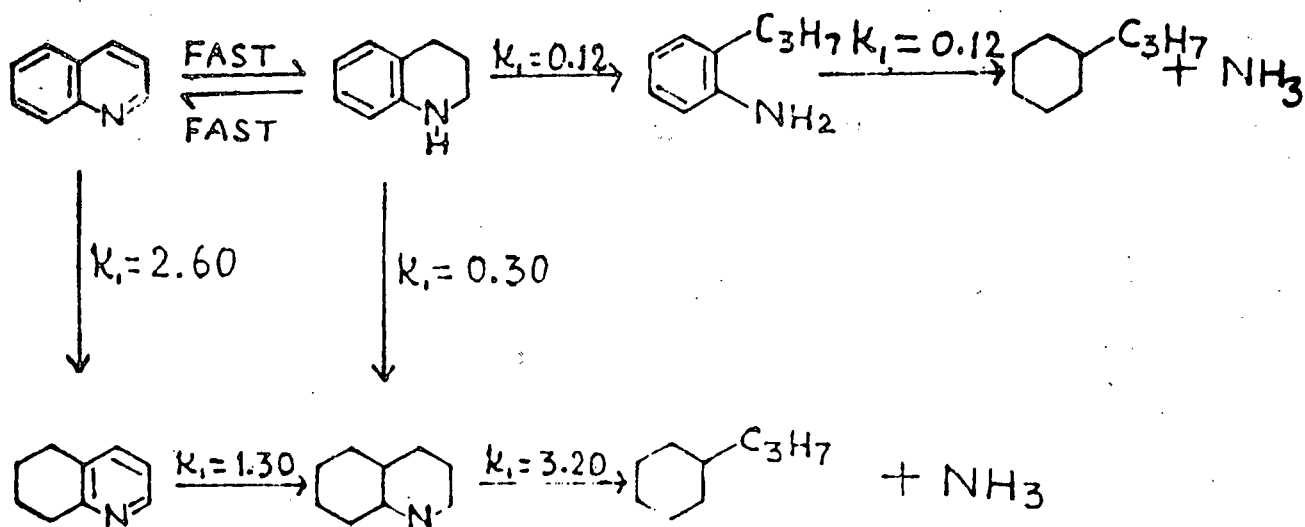
<u>Reactant</u>	<u>Pseudo first-order rate Constant, cm³/g cat h</u>
thiophene	5000
benzothiophene	2900
dibenzothiophene	200
benzonaphthothiophene	600
7,8,9,10-tetrahydrobenzo-naphthothiophene	280

Three different catalysts, namely Co-Mo/ γ -Al₂O₃, Ni-Mo/ γ -Al₂O₃ and Ni-W/Al₂O₃ have been tested for the hydrodesulfurization of dibenzothiophene. The activities of these catalysts have been found to decrease in the order: Ni-Mo > Ni-W ≥ Co-Mo.

A new "three-point" adsorption of thiophenic compounds has been suggested to be important in the surface-catalyzed hydrodesulfurization mechanism. The new mechanism accounts for the observed substituent effects and the effects of the number of rings in the reactant; it also accounts for results of H-D exchange studies reported in the literature. ⁶

Catalytic Hydrodenitrogenation

The hydrodenitrogenation of quinoline has been studied to yield a nearly complete identification of the reaction network and partial identification of the rate parameters in this network. The network is as follows:



This network shows that usually both the benzene and pyridine rings are saturated before the C-N bond in the (now) piperidine ring is broken. Thus, the hydrodenitrogenation of quinoline requires a large consumption of hydrogen before the nitrogen atom is removed from the hydrocarbon structure. The lack of selectivity encountered in hydrodenitrogenation stands in sharp contrast to the high selectivity in hydrodesulfurization.

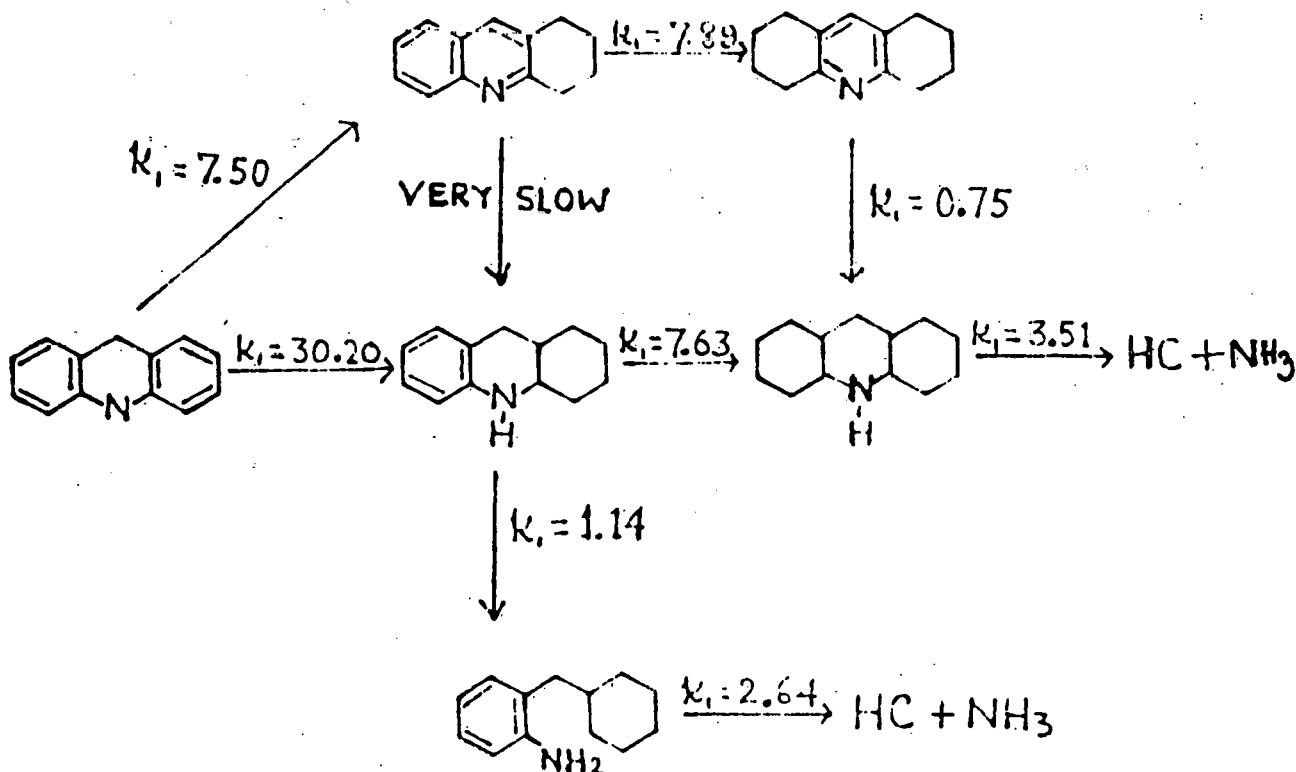
The total rate of hydrodenitrogenation shows a maximum with respect to hydrogen partial pressure. This is because the pseudo first-order rate constant for the C-N bond scission step is reduced by increasing hydrogen pressure and the rate constants for the hydrogenation steps, which increase with hydrogen pressure at lower hydrogen pressures, pass through a maximum and decrease with increasing hydrogen pressure at the high hydrogen pressures.

Also in hydrodenitrogenation of acridine, a large amount of hydrogenation precedes nitrogen removal, and the carbon-nitrogen bond breaking reactions are relatively slow. In the presence of Co-Mo/ γ -Al₂O₃ catalyst, heteroaromatic ring hydrogenation is favored, and with a Ni-Mo/ γ -Al₂O₃ catalyst, aromatic ring hydrogenation is favored. For both acridine and quinoline, little effect of replacing Co with Ni could be detected in the nitrogen removal reaction, although Ni-Mo/ γ -Al₂O₃ is roughly twice as active for hydrogenation as Co-Mo/ γ -Al₂O₃.

The hydrodenitrogenation of carbazole has been examined under conditions similar to those used for acridine. Both carbazole disappearance and total nitrogen removal can be represented as first-order reactions. Tetrahydrocarbazole was the major intermediate compound present in the dry column extract. Both cis-hexahydrocarbazole and octahydrocarbazole were identified as minor products. Reactivity of carbazole is slightly less than that of quinoline and acridine is the least reactive. Hydrodenitrogenation of four- and five-ring nitrogen-containing compounds are currently being studied.

Preliminary experiments have been carried out to characterize hydrodenitrogenation of substituted quinolines. The conditions used were similar to those used for quinoline hydrodenitrogenation. 2,6-, 2,7- and 2,8-dimethylquinolines were studied and products identified were analogous to those observed in the quinoline network. The reactivity of these compounds to hydrodenitrogenation is comparable to that of quinoline.

The reaction network for the hydrodenitrogenation of acridine (in White Oil) catalyzed by Ni-Mo/ γ -Al₂O₃ catalyst is as given below:



The pseudo first-order rate constants are for 367°C and 136 atm. The pseudo first-order rate constants for hydrodenitrogenation (total nitrogen removal) at 367°C and 136 atm catalyzed by Ni-Mo/ γ -Al₂O₃ falls in the following order:

<u>Reactant</u>	<u>Pseudo first-order rate constant for total nitrogen removal, min⁻¹</u>
Dibenz[c,h]acridine	3.79
Quinoline	2.52
Carbazole	2.43
Acridine	1.62
Benz[c]acridine	1.54
Benz[a]acridine	1.08

Preliminary studies of competing hydroprocessing reactions catalyzed by Ni-Mo/ γ -Al₂O₃ and involving quinoline, indole and naphthalene in White Oil show that marked interactions exist. The naphthalene hydrogenation rate is markedly reduced by the presence of quinoline; whereas the reactivity of quinoline is virtually unchanged by the presence of naphthalene. Similarly the rate of hydrodenitrogenation of indole, a non-basic nitrogen-containing compound, is strongly reduced by the presence of quinoline, whereas the rate of hydrodenitrogenation of quinoline, a basic nitrogen-containing compound, is unaffected by the presence of indole. Studies involving combinations of nitrogen- and sulfur-containing compounds and aromatic hydrocarbons are underway.

Catalyst Deactivation

A variety of physical techniques have been used to identify the aging process for catalysts used in synthetic liquid fuel processes. Catalyst samples from three processes have been examined: a proprietary fixed-bed process, Synthoil, and H-Coal^R. The spent fixed-bed catalysts show the formation of an external crust which appears to be formed by columnar grain growth combined with the deposition of coal mineral matter, particularly clays and rutile. This external crust is absent from the H-Coal^R catalyst. The interior of the catalyst is altered by several processes: coking, reactive deposition of mineral matter, passive deposition of mineral matter, and crack enhancement. These four processes are found in catalysts from all three processes. Coking fills the micro-pore volume of the catalyst. Reactive deposition of mineral matter penetrates about 200 μ m from the outer surface into the interior of the catalyst. The concentration profile is approximately exponentially decreasing from the exterior surface. Passive cementing occurs within 50 μ m of the surface unless the irregular concentration profiles. Finally, grain growth can occur inside the catalyst near the surface and tends to increase these cracks. When the surface cracks become a significant portion of the pore volume, passive deposition can penetrate further into the interior of the catalyst.

The activity of aged catalyst from the H-Coal^R process has been measured in batch experiments with dibenzothiophene and with quinoline. The activity was reduced 20-fold for hydrodesulfurization of dibenzothiophene and five-fold for hydrodenitrogenation of quinoline. Burning off of carbonaceous deposits increased the activity of the aged catalyst only

three-fold for dibenzothiophene hydrodesulfurization, which implies that irreversibly deposited inorganic matter was responsible for most of the loss of catalytic activity.

Microreactor Engineering

The use of moments as a tool in interpreting pulse data from microreactors has been extended to fairly complex reaction networks. This work is now complete. The complex data from quinoline and acridine reactions have been reduced to rate parameters by extension of nonlinear regression analysis. Reaction engineering concerned with coal hydro-processing is now underway.

TIME PLAN* AND MILESTONE CHART**

Year	0	1	2	3
ACCOMPLISHMENT				
A. APPARATUS CONSTRUCTION				
1st High-Pressure Microreactor	Completed	month 6	100%	
2nd High-Pressure Microreactor	Completed	month 10		
Batch Reactors	Completed	month 4		
B. MICROREACTOR STUDIES OF HDS & HDN				
Definition of reaction procedures and operating conditions	Choice of HDN Catalyst	month 8	100%	
Reaction Studies For:				
Benzothiophene	month 6	month 12	Started	100%
Quinoline			90%	100%
Dibenzothiophene	month 12		month 18	95%
Carbazole	50%		50%	100%
Naphthobenzothiophene	Synthesis Underway	month 18	month 24	Started 95%
Acridine			85%	month 24 month 28 100% month 30
Higher molecular weight and methyl-substituted nitrogen and sulfur compounds	Synthesis Underway	month 12	75%	month 28 month 30 100%
Reaction Kinetics Reaction Networks and Inhibitor Studies of Least Reactive Sulfur and Nitrogen Compounds			75%	85% 90%
		month 18	month 24	month 28 month 30
HDS-HDN: Simultaneously, Effect of Inhibitors	month 16		Started 20%	50% 60% month 36

TIME PLAN* AND MILESTONE CHART** (Continued)

Year	0	1	2	3
C. CATALYST DEACTIVATION SYNTHOIL CATALYST:				
Physical Properties	month 6	100%		
Chemical Properties	month 6		month 16 75%	80%
Other Deactivated Catalysts	90% month 10			month 24 80%
Catalyst Deactivation Studies	50%	month 14 70%		100% month 30
D. REACTION ENGINEERING				
Reactor Models for Pulse and Flow Microreactors	75%	month 14 90%	95%	100%
Process Reaction Engineering	5%	month 14 15%	30%	70% month 36

*Time Plan and Milestone Chart as Presented in Proposal.

**Hatching indicates that activity indicated is under active investigation; number in hatch region indicates the percentage completed; crosshatching indicates that the task has been completed.

CUMULATIVE EXPENDITURES*

Quarter	Personnel	Travel	Supplies & Expenses	Occupancy & Maintenance	Equipment	Information Processing	Transfers (Overhead)
First	\$ 5,807	\$ 28	\$ 4,674	\$ 6,110	\$ 610	--	--
Second	20,740	528	10,007	9,208	17,978	--	\$ 10,202
Third	37,396	1,152	19,582	10,108	30,704	--	20,035
Fourth	53,418	1,152	25,735	10,634	34,930	\$ 97	38,710
Fifth	91,593	1,521	37,291	13,755	50,614	154	75,839
Sixth	112,666	2,458	42,341	13,920	54,013	375	93,287
Seventh	132,669	3,140	51,589	14,396	54,013	1,180	113,830
Eighth	146,146	3,814	56,488	14,600	52,295	1,868	123,576
Ninth	167,884	5,119	54,778	16,325	54,977	2,044	117,681
Tenth	192,658	6,113	70,579	18,010	54,977	2,248	134,895
Eleventh	224,941	6,113	76,733	19,635	54,977	2,369	161,208
Twelfth	261,759	7,349	95,041	24,159	57,778	2,454	186,267

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

B. Catalytic Hydrodesulfurization: The DBT Network

INTRODUCTION

The increasing importance of hydrodesulfurization in petroleum processing and the need for alternative fossil-energy sources for production of clean-burning fuels have led to a surge of research on the chemistry and engineering of hydrodesulfurization. Most of the work has focused on catalyst characterization by physical methods (Massoth, 1977), on low-pressure reaction studies of compounds, like thiophene, having relatively high reactivities, or on process development (Gates et al., 1979). There is only fragmentary information about the reactions of relatively unreactive compounds like dibenzothiophene under conditions of practical interest, especially high pressure. The literature of hydrodesulfurization of thiophene, benzothiophene, and dibenzothiophene (compiled by Kilanowski, in preparation) fails to provide definitions of the reaction networks and kinetics, but it is clear that at high pressures, the multiring compounds are the less reactive ones, and dibenzothiophene is especially worthy of study, being one of the least reactive compounds (Nag et al., submitted for publication) and one which is found in significant quantities in petroleum and especially in coal-derived liquids.

The hydrodesulfurization of dibenzothiophene has been investigated by Hoog (1950), Obolentsev and Mashkina (1958, 1959), Landa and Mrnkova (1966), Urimoto and Sakikawa (1972), Bartsch and Tanielian (1974), and Rollmann (1977). The results of these authors, representing a variety of temperatures, hydrogen partial pressures, and catalyst compositions, fail to establish a unique reaction network (Kilanowski et al., to be published). Many authors have found biphenyl, cyclohexylbenzene, and bicyclohexyl among the reaction products, which indicates that hydrogenation reactions are important, and

some authors (e.g., Obolentsev and Mashkina, 1958; 1959) have found that biphenyl was the only product besides H_2S , which indicates that under certain conditions (598-698°K and 10-60 atm with a sulfided $CoO-MoO_3/\gamma-Al_2O_3$ catalyst in the work of Obolentsev and Mashkina), there may be a high selectivity for sulfur removal without prior or subsequent hydrogenation.

The experiments reported here were performed to provide a resolution of the reaction network involving dibenzothiophene and hydrogen. The catalyst was a typical commercial "cobalt molybdate" (sulfided $CoO-MoO_3/\gamma-Al_2O_3$) operated under conditions of practical interest, 573°K and 102 atm. Supplementary experiments were done with sulfided $NiO-MoO_3/\gamma-Al_2O_3$ and with sulfided $NiO-WO_3/\gamma-Al_2O_3$ catalyst and with 4,6-dimethyldibenzothiophene and other methyl-substituted dibenzothiophenes as reactants.

EXPERIMENTAL

The catalyst was sulfided $CoO-MoO_3/\gamma-Al_2O_3$ (HDS 16A, American Cyanamid). The properties of the oxidic form are summarized in Table 1. A few experiments were done with $NiO-MoO_3/\gamma-Al_2O_3$ (HDS 9A, American Cyanamid) and $NiO-WO_3/\gamma-Al_2O_3$ (NT-550, Nalco) having the properties summarized in Table 1.

Dibenzothiophene (95%), cyclohexylbenzene (96%), and bicyclohexyl (> 98%) were used as supplied by Aldrich. Biphenyl (> 98%) was used as supplied by Eastman. The compounds 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene were synthesized according to the methods of Campaigne et al. (1969) and Mitra et al. (1956). Methyl-substituted dibenzothiophenes were prepared by the methods cited by

Houalla et al. (1977). The solvent n-hexadecane was supplied by Humphrey Chemical Co. and was redistilled before use.

A high-pressure flow microreactor, described in detail by Eliezer et al. (1977), was used for steady-state reaction experiments. The catalyst bed had a volume of $3.25 \times 10^{-7} \text{ m}^3$ and a length of $4.1 \times 10^{-2} \text{ m}$. The catalyst ($2.5 \times 10^{-5} \text{ kg}$) was mixed with $6.25 \times 10^{-4} \text{ kg}$ of alundum, an inert reactor packing material. The catalyst particle size was usually 149-178 μm .

The catalyst was presulfided in the reactor for two hours with a flowing mixture of 10 vol % H_2S in H_2 at atmospheric pressure and 673°K. The reactant solution usually contained about 0.13 mol % dibenzothiophene in n-hexadecane. Before operation, the solution ($2.6 \times 10^{-4} \text{ m}^3$) was saturated with hydrogen (or occasionally with hydrogen + H_2S) in a stirred autoclave by first purging with hydrogen for two hours at atmospheric pressure to remove air and then saturating with hydrogen at room temperature and 69 atm for three hours. It was estimated from hydrogen solubility data that under these conditions the mole fraction of hydrogen in the solution was 0.036. After saturation, the reactant solution was transferred to the feed reservoir, care being taken that the pressure never fell below 69 atm. The catalyst in the meantime had been flushed with helium and presulfided, then the reactor was cooled to 573°K and the liquid flow was begun at a rate of typically $(2-20) \times 10^{-10} \text{ m}^3/\text{s}$ (the inverse weight hourly space velocity varied between 18.6 and 223 kg of feed/kg of catalyst·h). The reactor pressure was maintained at 102 atm, ensuring that all the reactants remained in the liquid phase, and the temperature was held constant within $\pm 1^\circ\text{K}$.

The first product samples were collected after about $3 \times 10^{-5} \text{ m}^3$ of the reactant had passed through the catalyst bed, and samples were thereafter taken periodically. After a change in feed flow rate, several hours elapsed before sampling was begun again. The flow rate was finally adjusted to the initial value to allow a check for possible catalyst deactivation (which was not observed).

The reaction of dibenzothiophene with hydrogen was also carried out in a batch autoclave reactor; the apparatus and procedure were nearly identical to those described by Shih *et al.* (1977). The catalyst was brought in contact with reactants only after they had been heated up to reaction conditions, so that conversion during the heat-up period was negligible. Under typical operating conditions, the concentration of dibenzothiophene in *n*-hexadecane (before H_2 saturation) was 0.37 mol %. The mass of catalyst was $2.21 \times 10^{-4} \text{ kg}$ and the volume of liquid reactant was $3.5 \times 10^{-4} \text{ m}^3$. The reaction temperature was $573 \pm 1^\circ\text{K}$ and the pressure was 71 atm. The relatively high reactant concentrations and the large reactant volume used in the batch experiments provided relatively large amounts of reaction products, aiding in the analysis and identification of minor products.

Reaction products were analyzed with a Hewlett-Packard 5750 (or an Antek 400) gas chromatograph equipped with a flame ionization detector and an electronic integrator. A gas chromatograph was interfaced to a mass spectrometer, and each product was identified by its mass spectrum. Occasionally, products were concentrated by solvent extraction and dry-column chromatography prior to analysis by gas chromatography-mass

The first product samples were collected after about $3 \times 10^{-5} \text{ m}^3$ of the reactant had passed through the catalyst bed, and samples were thereafter taken periodically. After a change in feed flow rate, several hours elapsed before sampling was begun again. The flow rate was finally adjusted to the initial value to allow a check for possible catalyst deactivation (which was not observed).

The reaction of dibenzothiophene with hydrogen was also carried out in a batch autoclave reactor; the apparatus and procedure were nearly identical to those described by Shih et al. (1977). The catalyst was brought in contact with reactants only after they had been heated up to reaction conditions, so that conversion during the heat-up period was negligible. Under typical operating conditions, the concentration of dibenzothiophene in n-hexadecane (before H_2 saturation) was 0.37 mol %. The mass of catalyst was $2.21 \times 10^{-4} \text{ kg}$ and the volume of liquid reactant was $3.5 \times 10^{-4} \text{ m}^3$. The reaction temperature was $573 \pm 1^\circ\text{K}$ and the pressure was 71 atm. The relatively high reactant concentrations and the large reactant volume used in the batch experiments provided relatively large amounts of reaction products, aiding in the analysis and identification of minor products.

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spectrometry. The routine analyses were carried out by gas chromatography; response factors were measured for standards of each compound in n-hexadecane. The organic reactants and products were separated in 3.4-m stainless-steel column having a 2.3×10^{-3} -m ID and packed with 3% SP-2100 DB (methyl silicone fluid--the basic sites were deactivated) on 100-200 mesh Supelcoport (Supelco) at 423°K with a helium carrier-gas flow rate of about 5×10^{-7} m³/s. The H₂S product was not determined quantitatively. The same column was used in a Perkin-Elmer 3920 B gas chromatograph equipped with a sulfur-specific detector to test for any sulfur-containing compounds in the products or sulfur-containing impurities in the feeds in addition to those detected with the flame ionization detector; none was found. An open tubular column coated with OV-101 was occasionally used in the Perkin-Elmer instrument to provide an improved separation of cyclohexylbenzene from bicyclohexyl.

RESULTS

Preliminary experiments were done to ensure the lack of influence of mass transfer on reaction rates: changing the catalyst particle size from 125 to 250 μm led to no change in the rate of dibenzothiophene conversion. Standard tests confirmed the appropriateness of the assumption of piston flow in the microreactor. Blank runs with alundum packing and no catalyst in the reactor under typical conditions gave conversions less than 0.5% compared with about 80% when 2.5×10^{-5} kg of catalyst were used.

The conversion of dibenzothiophene (Fig. 1) gave predominantly biphenyl; yields as high as 87 mol % were observed. The other organic products included cyclohexylbenzene and, in trace amounts, bicyclohexyl.

These results show that the catalyst was highly selective for hydrodesulfurization but that some hydrogenation also occurred. When the product samples were analyzed with the sulfur-specific detector, no sulfur-containing compounds besides dibenzothiophene were found in concentrations exceeding 50-100 ppm. This result indicates that any sulfur-containing intermediates which might have been formed were too reactive to be isolated.

A more detailed picture of the reaction network emerged from analysis of the batch reactor products; the concentration of dissolved hydrogen was about three times higher than that in the flow microreactor. The batch experiments provided evidence of low yields of 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene. These were formed from the beginning and were therefore primary reaction products, formed directly from dibenzothiophene and in parallel with biphenyl. These batch-reactor results show that some hydrogenation precedes hydrodesulfurization in one path of the dibenzothiophene-hydrogen reaction network.

The selectivity for hydrodesulfurization vs. hydrogenation was different when a Ni-Mo or a Ni-W catalyst was used instead of Co-Mo. Typical product distribution data contrasting the three catalysts are shown in Fig. 2. The yield of cyclohexylbenzene at a given conversion was usually about three times higher with Ni-Mo catalyst than with Co-Mo catalyst. The activity of Ni-Mo catalyst per unit surface area (of the original oxidic form) was about twice as high as that of the Co-Mo catalyst.

The product distribution also depended on the concentration of H_2S in the reactant solution. Results summarized in Table 2 show that H_2S

suppressed the dibenzothiophene hydrodesulfurization (hydrogenolysis) reaction relative to the hydrogenation reaction forming cyclohexylbenzene. At high feed H_2S concentrations ($C_{H_2S}/C_{H_2} = 0.2$), 1,2,3,4-tetrahydrodibenzothiophene was detected in the flow-reactor product, providing further evidence of increased selectivity for hydrogenation.

Other results (not shown) demonstrate that increased hydrogen concentration also increased the rate of hydrogenation relative to hydrogenolysis, but quantitative data are lacking.

To confirm which were primary and which were secondary products in the dibenzothiophene-hydrogen reaction network and to determine independently quantitative kinetics of the individual reactions, a set of experiments was carried out with each of a series of individual products of the dibenzothiophene conversion used as the reactant with hydrogen; the compounds used were *o*-phenylthiophenol, biphenyl, 1,2,3,4-tetrahydrodibenzothiophene, and 1,2,3,4,10,11-hexahydrodibenzothiophene.

Conversion data were generally consistent with pseudo first-order reaction of each of the organic reactants, as shown in Fig. 3, and the data are therefore summarized as pseudo first-order rate constants having dimensions of m^3/kg of catalyst $\cdot s$; the rate equation is

$$\underline{r} = \underline{k}_i C_i \quad (1)$$

where C_i is the concentration of organic reactant i .

Biphenyl was the major organic product of the dibenzothiophene conversion, and an obvious possibility is that *o*-phenylthiophenol was an intermediate in the biphenyl formation, although this compound was not

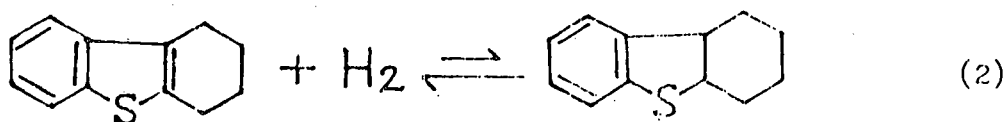
detected in the product. To check the reactivity of *o*-phenylthiophenol, one run was carried out under typical conditions with the flow reactor; the feed contained 0.07 mol % of *o*-phenylthiophenol prior to saturation with hydrogen. Even at the highest flow rate, it was completely desulfurized, giving primarily biphenyl and a minor amount of cyclohexylbenzene. Since *o*-phenylthiophenol is highly reactive in comparison with dibenzothiophene, it remains an open question whether it is an intermediate in the hydrodesulfurization of dibenzothiophene.

Although the rate constant for the hydrodesulfurization of *o*-phenylthiophenol could not be determined, the results of this experiment were useful in providing an estimate of the rate constant for the hydrogenation of biphenyl. The value was calculated to be $1.2 \times 10^{-6} \text{ m}^3/\text{kg}$ of catalyst•s (the underlying assumption is that *o*-phenylthiophenol was converted instantaneously into biphenyl and H_2S).

Two experiments were done with biphenyl as the reactant. In the first, biphenyl (0.12 mol %) was dissolved in *n*-hexadecane and the run was carried out in the usual way. Conversion of as much as 7% of the biphenyl was observed, and the product contained not only cyclohexylbenzene but a small amount (up to 10% of total conversion) of bicyclohexyl. In all the preceding experiments, H_2S was generated during the hydrodesulfurization reaction, and since it had been found (Broderick *et al.*, 1978) that some H_2S is needed to maintain the activity of the catalyst, another experiment was conducted with biphenyl reactant mixed with 3,7-dimethyldibenzothiophene. The average conversion of the latter was about 35% (varying between 23 and 49%), generating enough H_2S to prevent the catalyst from slowly deactivating.

The first-order rate constant for the conversion of biphenyl under these conditions was $1.1 \times 10^{-6} \text{ m}^3/\text{kg} \cdot \text{s}$, in good agreement with the value estimated from the aforementioned *o*-phenylthiophenol experiment.

Both 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene were hydrodesulfurized under typical conditions. The major product with each reactant was cyclohexylbenzene, the yield being about 70%; small quantities of bicyclohexyl were determined in the product, but there was no detectible biphenyl. Each of the sulfur-containing reactants was converted into the other, and the ratio of the concentrations of the two remained virtually constant at 5.6, regardless of which was used as the feed. We conclude that the following equilibrium was achieved rapidly:



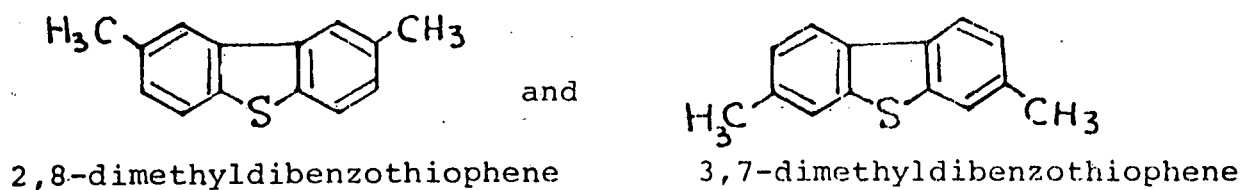
In all the experiments, the hydrogen was present in stoichiometric excess, and its concentration was virtually constant. Therefore, the concentration equilibrium constant

$$K = \frac{C_{1,2,3,4,10,11\text{-hexahydrodibenzothiophene}}}{C_{\text{H}_2} \cdot C_{1,2,3,4\text{-tetrahydrodibenzothiophene}}}$$

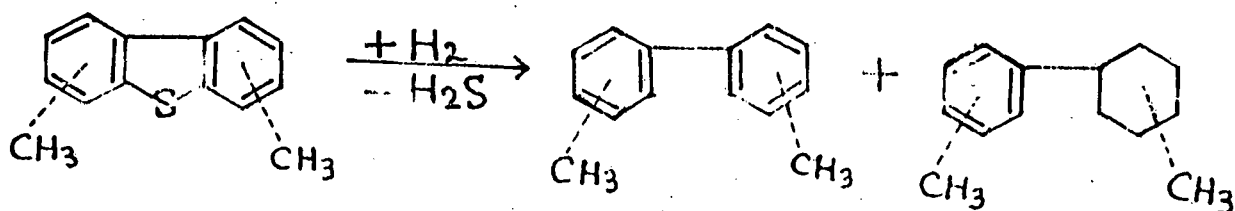
was estimated to be about $1.5 \times 10^{-3} \text{ m}^3/\text{mole}$ at 573°K .

Since it was not possible to ascertain the individual rate constants for ^{conversion of} these compounds into cyclohexylbenzene, we lump the two, representing the kinetics with the average rate constant of $1.12 \times 10^{-4} \text{ m}^3/\text{kg} \cdot \text{s}$ of catalyst·s.

The experiments done with methyl-substituted dibenzothiophenes as reactants were only preliminary in the sense that full product analyses were not performed; nonetheless, the results are sufficient to define a pattern in the reaction network: compounds having the methyl groups in the 2 and 8 or the 3 and 7 positions,

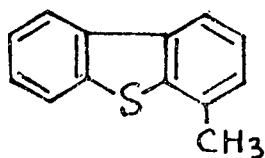


were studied under conditions cited earlier; their concentrations in the reactant solution were about 0.6 mol %. These compounds were found to have nearly the same reactivity as dibenzothiophene (Houalla *et al.*, 1977). The product distribution with each was similar to that expected from the results with dibenzothiophene (Fig. 2):

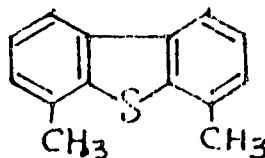


The substituted biphenyl was the predominant organic product in each case, and the ratio of the concentration of that product to the concentration of the substituted cyclohexylbenzene was nearly the same for each as the ratio of the concentration of biphenyl to the concentration of cyclohexylbenzene produced from dibenzothiophene.

A different product distribution was observed when the reactants were



and



4-methyldibenzothiophene

4,6-dimethyldibenzothiophene

These compounds were less reactive than dibenzothiophene (Houalla *et al.*, 1977), and the yields of the substituted cyclohexylbenzene products formed from them were greater than the yield of cyclohexylbenzene formed from dibenzothiophene under comparable conditions. These results suggest that 4-methyldibenzothiophene and especially 4,6-dimethyldibenzothiophene experienced more hydrogenation prior to sulfur removal than dibenzothiophene and the other methyl-substituted dibenzothiophenes, but this suggestion is preliminary and in need of testing by a quantitative determination of the reaction network.

DISCUSSION

The dibenzothiophene conversion data show that both the desulfurized compound biphenyl and the undesulfurized but partially hydrogenated compounds 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene are primary products of the reaction of dibenzothiophene and hydrogen. These are subsequently converted into the secondary product cyclohexylbenzene, which is further hydrogenated to give the tertiary product bicyclohexyl. The mercaptan *o*-phenylthiophenol may be an intermediate in the conversion of dibenzothiophene into biphenyl, but the data fail to establish whether it is.

In the flow microreactor experiments with dibenzothiophene feed, the only product components which could be analyzed quantitatively were dibenzothiophene, biphenyl, and cyclohexylbenzene; there were only trace amounts of bicyclohexyl. To obtain a preliminary quantitative evaluation of the data from the flow-reactor (Fig. 1), the simplest reaction network consistent with the data of Fig. 1 was postulated, as shown in Fig. 4.

The individual rate constants k_i were estimated in the following way:

a) Each reaction in the network of Fig. 4 was assumed to be first-order in the organic reactant.

b) The data of Fig. 1 were smoothed by fitting to the following simple functions:

$$C_{\text{dibenzothiophene}} = A_1 \exp[\underline{A}_2(SV)^{-1}] \quad (4)$$

$$C_{\text{biphenyl}} = \underline{A}_3 \{ \exp[\underline{A}_4(SV)^{-1}] - \exp[\underline{A}_5(SV)^{-1}] \} \quad (5)$$

$$C_{\text{cyclohexylbenzene}} = \underline{A}_6(SV)^{-1} + \underline{A}_7(SV)^{-2} + \underline{A}_8(SV)^{-3} \quad (6)$$

The coefficients \underline{A}_i and \underline{A}_j were determined with a nonlinear least squares program. (We note that the smoothing functions (4) and (5) are the actual solutions of the differential equations for the network of Fig. 4, provided that each reaction is indeed first order. The exact solution for cyclohexylbenzene could not be fitted, since there were too few data.)

c) Points were taken at equal intervals of $(SV)^{-1}$ from the smoothed curves predicted by Eqs. (4)-(6) and used with equal weighting in the Carlton 2 program (Himmelblau et al., 1967) to determine best values of the rate constants characterizing the formation of each of the products except bicyclohexyl, for which the data were too imprecise.

The following values for the pseudo first-order rate constants for the individual steps in the network of Fig. 4 were obtained:

$$k_1 = 2.3 \times 10^{-5} \text{ m}^3/\text{kg of catalyst}\cdot\text{s}$$

$$k_2 = 4.2 \times 10^{-8} \text{ m}^3/\text{kg of catalyst}\cdot\text{s}$$

$$k_3 = 4.7 \times 10^{-6} \text{ m}^3/\text{kg of catalyst}\cdot\text{s}$$

When combined with the flow-reactor data, the batch-reactor data allow an improved interpretation; they show that the undesulfurized but partially hydrogenated compounds 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene are primary products of the dibenzothiophene conversion and provide a route to the secondary product cyclohexylbenzene. Conversion data obtained from the flow-reactor experiments with 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene in the feed establish the pseudo first-order rate constant for the conversion of this pair of compounds into cyclohexylbenzene; the value is $1.1 \times 10^{-4} \text{ m}^3/\text{kg of catalyst}\cdot\text{s}$.

This value is four orders of magnitude greater than the value of k_2 obtained from the foregoing analysis of ^{the} dibenzothiophene conversion data of Fig. 7. It is clear that the value of k_2 is a good representation of the slower reaction in the sequence in which dibenzothiophene is first hydrogenated and then hydrodesulfurized to give cyclohexylbenzene.

Combining these results, we are led to the suggestion of Fig. 5 for the reaction network in the dibenzothiophene-hydrogen conversion. The pseudo first-order rate constants are shown in the figure.

The results summarized in Fig. 5 indicate approximate consistency of the dibenzothiophene conversion data with the ^{results} of the separate experiments with biphenyl (and *o*-phenylthiophenol) in the feed. The four-fold difference in rate constants for the biphenyl hydrogenation reaction is interpreted as an indication of the differences in reaction environments in the separate experiments; the difference in rate constants is explained by competitive adsorption of the various aromatic compounds and H₂S. There are too few data to allow determination of full rate equations indicative of these effects.

The lines in Fig. 1 show the good fit to the dibenzothiophene conversion data obtained with the rate constants of Fig. 5. The analysis could not have been done without prior knowledge of the reaction network; we emphasize the need for study of the various intermediates as reactants to permit an unequivocal statement of the reaction network, to determine the kinetics expression for each reaction, and to determine a precise estimate of the rate constant for each.

The summary of results given in Fig. 5 emphasizes the high selectivity of the Co-Mo/Al₂O₃ catalyst, a primary reason for its wide application in industrial hydrodesulfurization processes; almost all the hydrogen, an expensive reactant, is used in sulfur removal. The Ni-Mo and Ni-W catalysts have comparable activity but are less selective.

The resolution of the reaction network provides a basis for interpreting the apparent inconsistencies in the results of earlier workers, mentioned in the Introduction. Direct conversion of dibenzothiophene into biphenyl and hydrogenation of the aromatic ring are both

primary reactions; under the conditions of this study, the latter reaction is slow compared with the former, and at low pressures it is evidently negligibly slow (Kilanowski *et al.*, 1978). But the hydrogenation becomes relatively fast as H_2S is added to the reactant mixture, as Ni replaces Co in the catalyst, or as methyl groups are incorporated in the 4 or 4 and 6 positions (but not in the 3 and 7 or 2 and 8 positions) in dibenzothiophene. Earlier investigators used a variety of catalysts, different pressures, and different H_2S concentrations, which explains the variety of their product distributions.

The influence of H_2S and of methyl substitution on the reactant provide the basis for some suggestions about the surface chemistry of the catalytic reactions. The effect of H_2S in increasing the rate of hydrogenation relative to hydrodesulfurization indicates differing degrees of inhibition of the two reactions by H_2S , which adsorbs in competition with reactants--the result suggests that there may be more than one kind of catalytic site, perhaps single and double anion vacancies (Gates *et al.*, 1979).

The effect of the methyl groups in the 4 and 6 positions (considered in view of the lack of an effect of methyl groups in the positions farther removed from the sulfur atom) suggests that they sterically hinder the adsorption that leads to hydrodesulfurization--in which the sulfur atom evidently interacts with the surface--but that they do not hinder the adsorption that leads to hydrogenation, in which the benzenoid ring(s) evidently interact(s) with the surface. This suggestion implies that the reactants may bond to the catalyst not vertically, through the interaction

of the sulfur atom with a surface anion vacancy (as has often been supposed), but more or less flat, as the π electrons of the aromatic rings interact with the surface. This subject is considered in detail in the following section (Kwart et al., to be published).

NOMENCLATURE, PART A

<u>A</u> _i	empirical constant, mol/m ³
<u>A</u> _{≡i}	empirical constant, kg of catalyst·s/m ³ of reactant solution
<u>C</u>	concentration, mol/m ³
<u>k</u>	pseudo first-order reaction rate constant, m ³ of reactant solution/kg of catalyst·s
<u>K</u>	concentration equilibrium constant, m ³ /mol
<u>r</u>	reaction rate, moles of organic reactant converted/kg of catalyst·s
<u>SV</u>	space velocity, m ³ of reactant solution/kg of catalyst·s

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TABLE I
CATALYST PROPERTIES*

Catalyst	NiO-MoO ₃ /γ-Al ₂ O ₃ (HDS-9A)	CoO-MoO ₃ /γ-Al ₂ O ₃ (HDS-16A)	NiO-WO ₃ /γ-Al ₂ O ₃ (NT-550)
Supplier	American Cyanamid	American Cyanamid	Nalco
Composition, wt%			
NiO	3.1	---	5.1
CoO	---	5.6	---
MoO ₃	18.3	11.2	---
WO ₃	0.04	---	22.0
Na ₂ O	0.05	0.03	---
Fe		0.04	---
10 ⁻⁵ x surface area, m ² /kg	1.49	1.76	2.50
10 ¹⁰ x pore volume, m ³ /kg	5.1	5.0	5

* The reported values were determined by the catalyst suppliers.

TABLE 2
 EFFECT OF H₂S ON THE SELECTIVITY FOR
 HYDROGENATION vs. HYDRODESULFURIZATION OF
 DIBENZOTHIOPHENE^a

C_{H_2S}/C_{H_2} in feed	Space velocity m ³ of feed/kg of catalyst·s	Yield of cyclohexylbenzene, mol % of hydrocarbon product
0.00	3.52×10^{-5}	7.4
0.00	2.02×10^{-4}	1.9
0.015	3.34×10^{-5}	9.0
0.015	1.92×10^{-4}	2.0
0.20	3.47×10^{-5}	13.3
0.20	1.99×10^{-4}	3.8

^a The catalyst was 1.0×10^{-5} kg of sulfided Co-Mo/ γ -Al₂O₃ diluted with 2.8×10^{-4} kg of alundum. The feed contained 0.15 mol% dibenzothiophene in *n*-hexadecane, which was subsequently saturated with hydrogen at 69 atm. The temperature was $573 \pm 1^\circ\text{K}$ and the pressure was 102 atm.

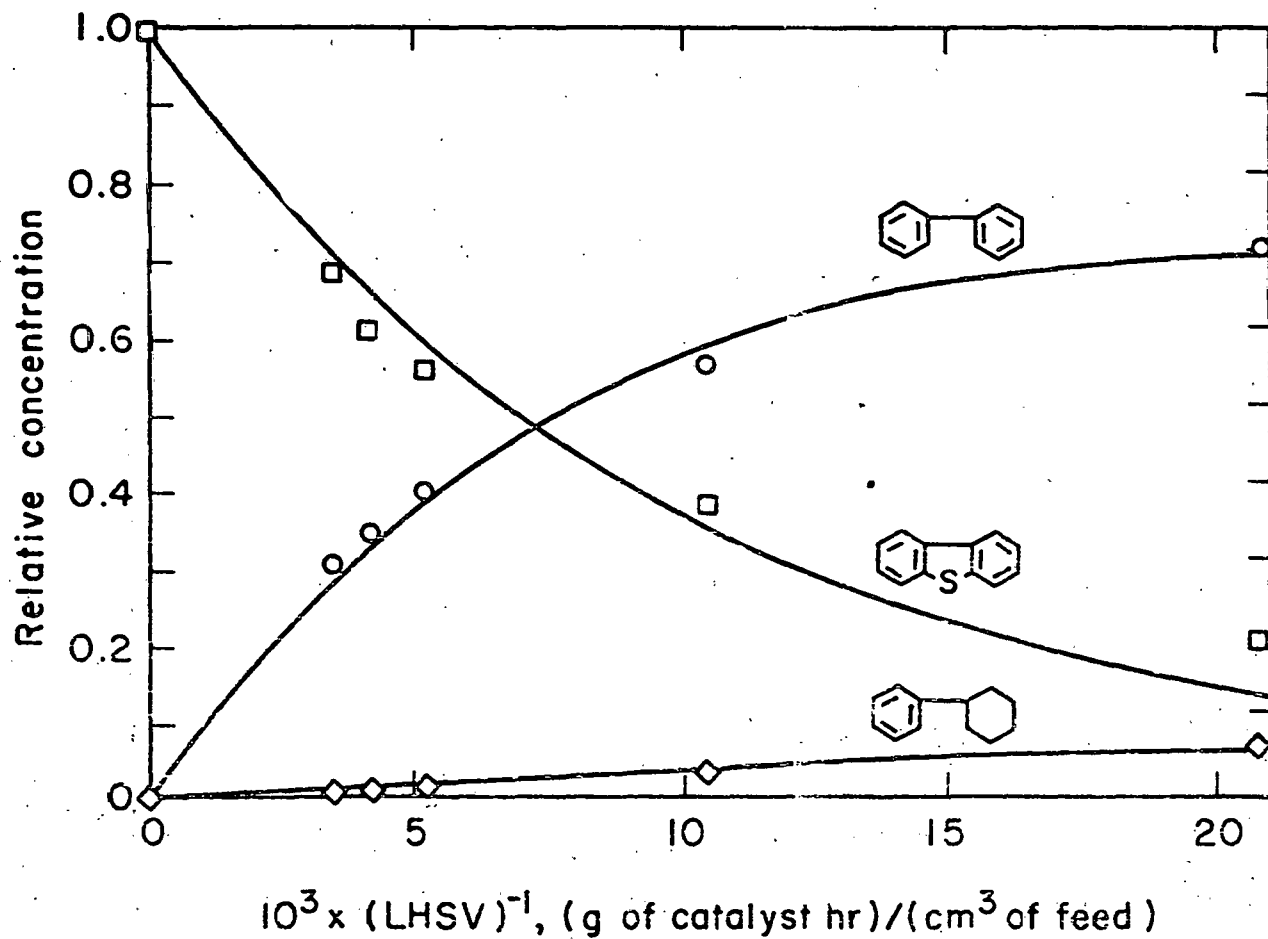


Fig. 1. Product distribution in the reaction of dibenzothiophene with hydrogen catalyzed by sulfided Co-Mo/Al₂O₃ at 573°K and 102 atm. The reactor feed was 0.12 mol % dibenzothiophene dissolved in n-hexadecane, which was saturated with hydrogen at room temperature and 69 atm. The lines correspond to the network of pseudo first-order reactions summarized in Fig. 5.

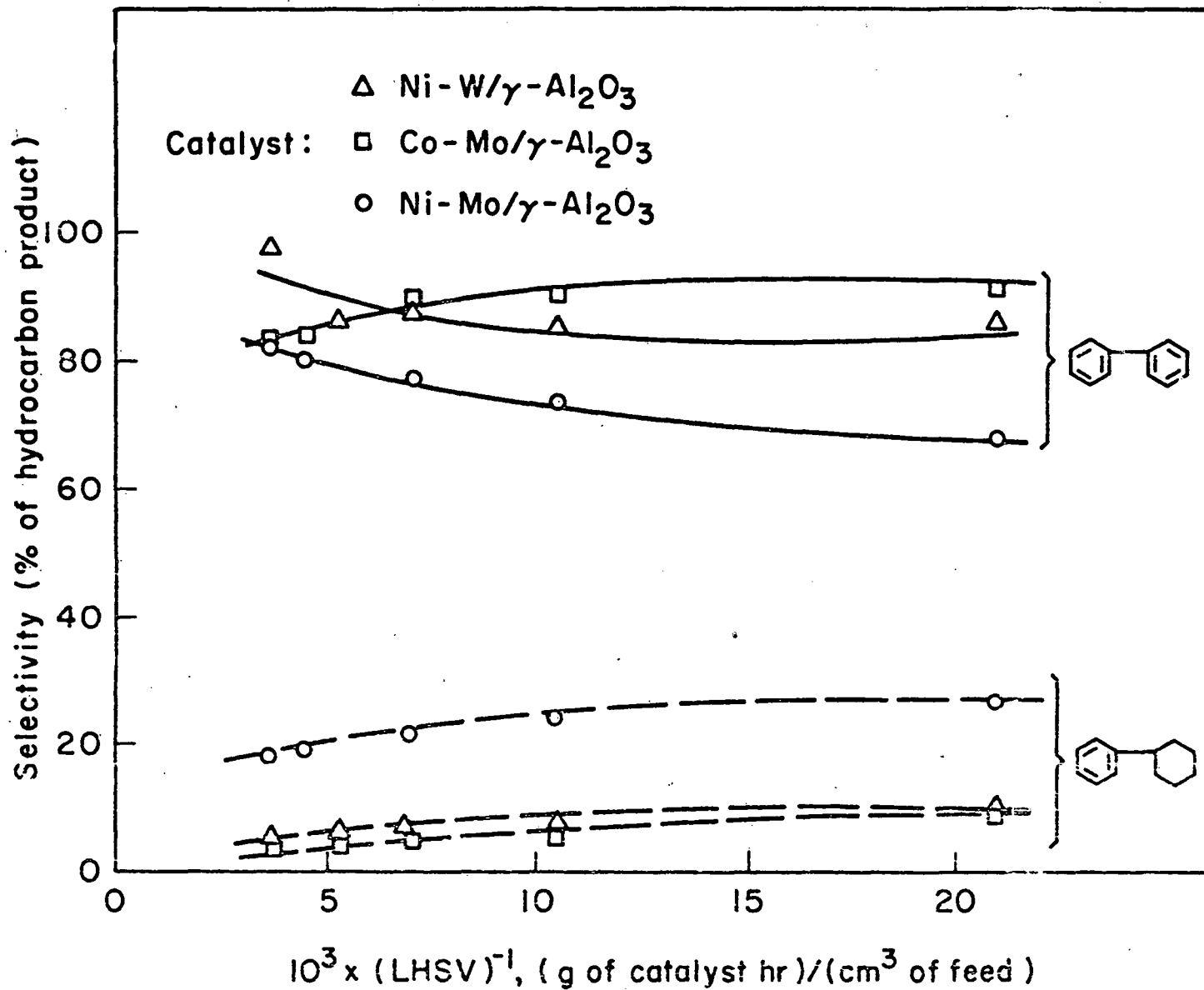


Fig. 2 Effect of catalyst composition on the product distribution in the conversion of dibenzothiophene + hydrogen. The reaction conditions are specified in the text.

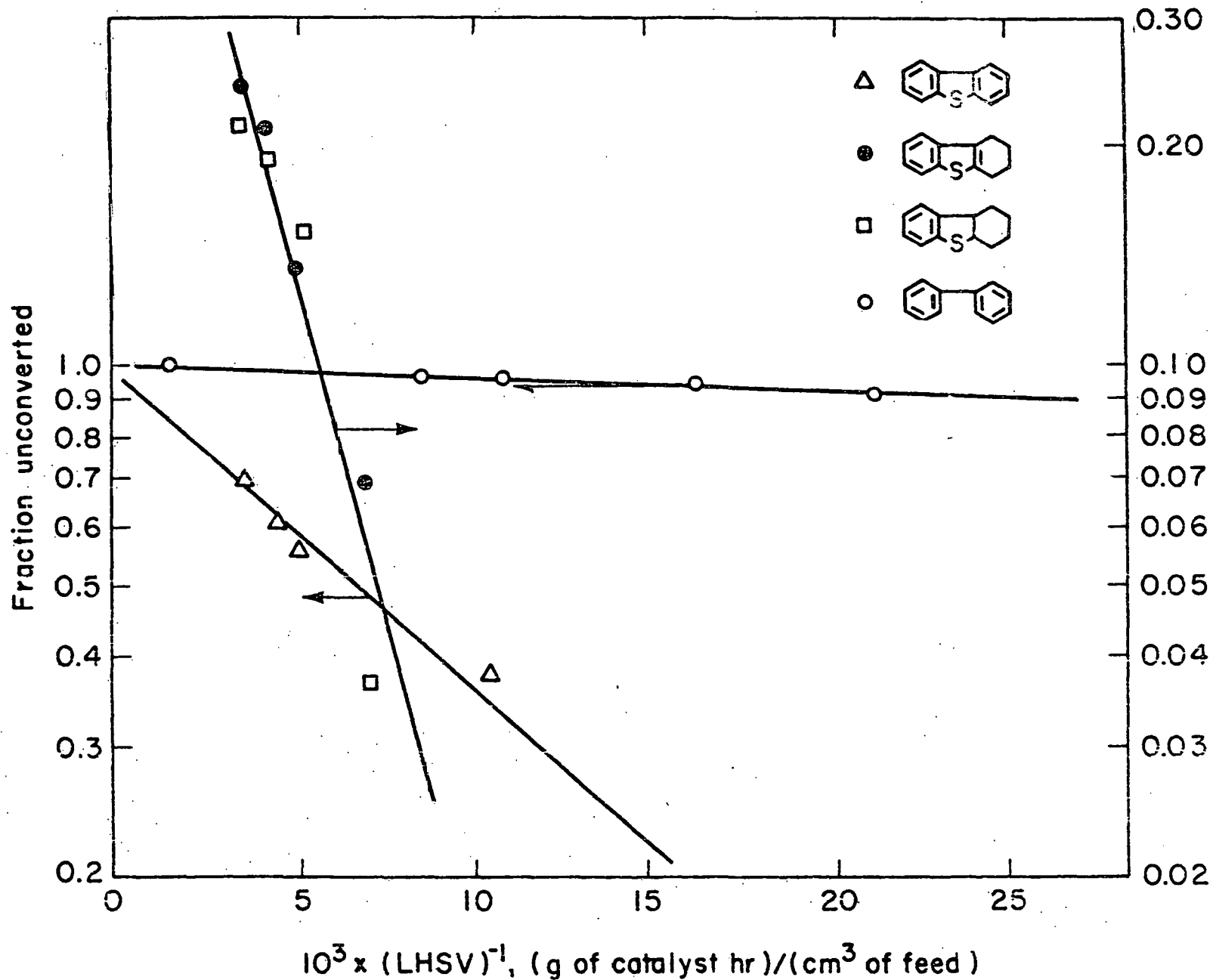


Fig. 3 Pseudo first-order kinetics of the disappearance of each of the reactants shown in the presence of hydrogen and sulfided Co-Mo/Al₂O₃ catalyst under the conditions described in the text. Each reactant was fed separately (with hydrogen) into the flow reactor.

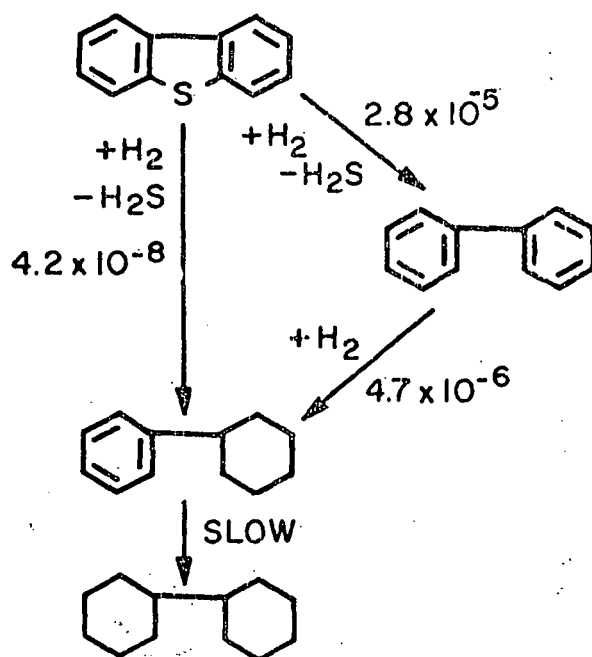


Fig. 4 Approximate reaction network for conversion of dibenzothiophene and hydrogen in the presence of sulfided Co-Mo/ γ - Al_2O_3 at 573° and 102 atm. Each reaction is assumed to be first-order in the organic reactant; the numbers next to the arrows are the pseudo first-order rate constants in m^3/kg of catalyst·s.

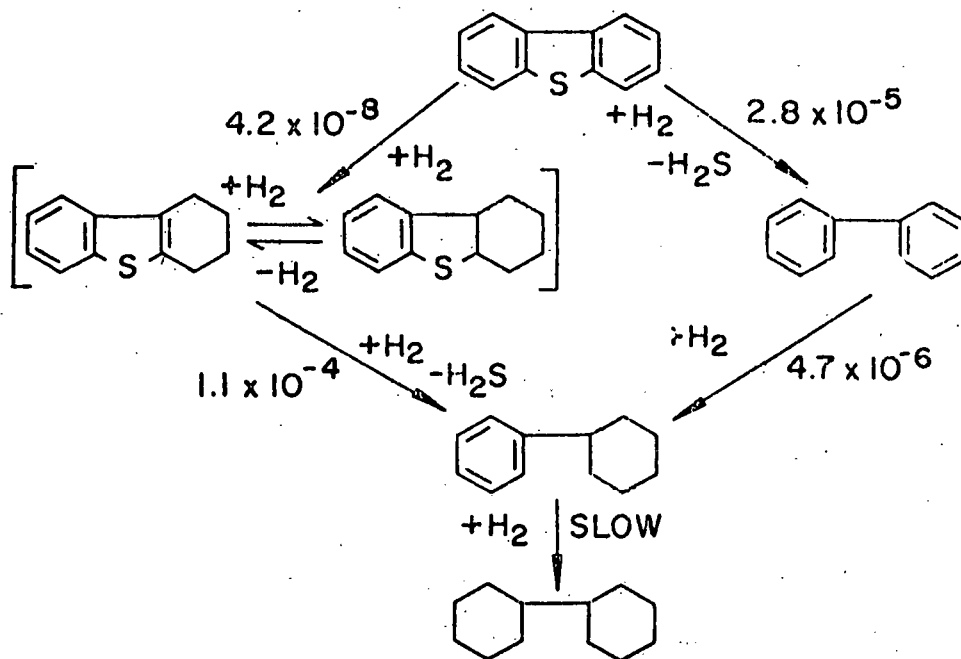


Fig. 5 Conversion of dibenzothiophene and hydrogen in the presence of sulfided Co-Mo/ Al_2O_3 at 573°K and 102 atm: the reaction network. Each reaction is first-order in the organic reactant; the numbers next to the arrows are the pseudo first-order rate constants in m^3/kg of catalyst·s.

B. The Mechanism of Hydrodesulfurization of Thiopenic Compounds

Introduction

Catalytic hydrodesulfurization is a subject of intensive research, most of it centered on the physical characterization of the industrially applied sulfide catalysts. Our objective is to evaluate the literature of hydrodesulfurization of thiopenic compounds, focusing on the neglected subject of the nature of the organic surface intermediates and mechanisms of the catalytic reactions. The following paragraphs include a review of the commonly assumed "one-point" model of the adsorption of thiopenic compounds and a proposed alternative, a "multipoint" adsorption, which more successfully accounts for the available data.

The most widely discussed mechanism proposed for the hydrodesulfurization of thiopenic compounds (Figure 6) has been deduced from studies of the reaction of thiophene itself catalyzed by sulfidic Co-Mo/Al₂O₃ and related solids (1-8). An initial step is assumed to be an end-on adsorption, whereby only the sulfur atom of the reactant experiences chemical interactions with the catalytic sites, assumed to be anion vacancies at the surface. Since the remainder of the thiopenic ring is assumed to stand upright from the sulfur bonded to the surface, the mechanism has been referred to as the "one-point" mechanism (8).

This interpretation was derived largely from kinetics and product distribution data of Amberg and coworkers (6,7), who detected butadiene among the products of thiophene hydrodesulfurization at low pressures (< 1 atm). These authors (7) interpreted the formation of butadiene as an indication that hydrogenation of the thiophene ring need not precede hydrogenolysis of the sulfur-carbon bond. Kieran and Kemball (9), on the other hand, observed butadiene as a product of the hydrodesulfurization of tetrahydrothiophene and suggested its formation via the following pathway:



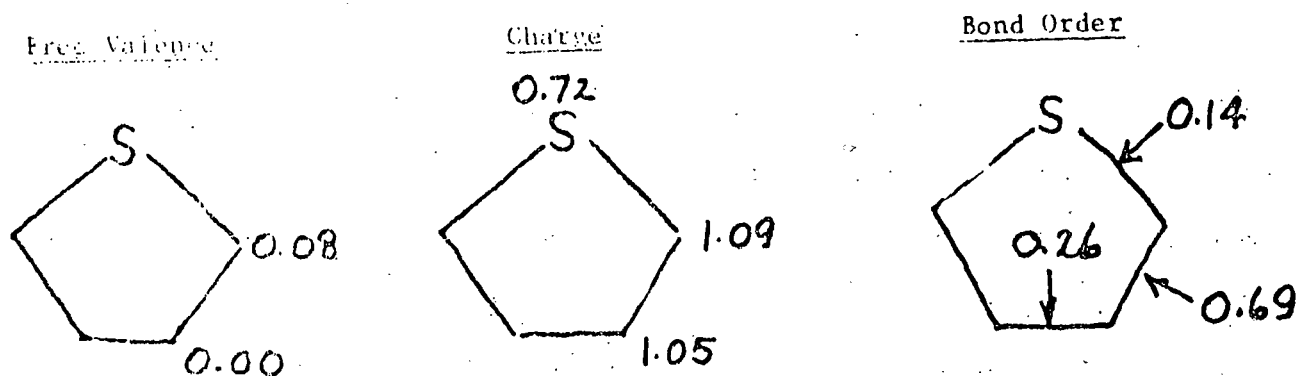
Kolboe (10) observed that the amount of butadiene formed via hydrodesulfurization of tetrahydrothiophene exceeded that arising from hydrodesulfurization of thiophene and suggested that the reaction of thiophene did not occur by a hydrodesulfurization, but instead by a dehydrodesulfurization route, whereby H_2S was removed by a beta-elimination to produce an initial diacetylene product, as shown in Figure 7. Infrared evidence has been presented purporting to indicate an acetylenic intermediate (11). Deuterium tracer experiments by Mikovsky *et al.* (12) have also given rise to results of this nature and a reinterpretation of the earlier results by Cowley (13) suggests that the Kolboe one-point mechanism may not be the only one occurring in the hydrodesulfurization process. Moreover, the hydrodesulfurization of benzothiophene (14) and dibenzothiophene (15) cannot readily be accommodated by the Kolboe mechanism without formation of high-energy benzyne intermediates.

Kinetics data determined recently with dibenzothiophene and related compounds provide new evidence of the reaction mechanisms. The presence of a methyl group in a position adjacent to the sulfur atom (as in 4-methyldibenzothiophene) could restrict access of the reactant to the active site on the catalyst surface. The steric hindrance caused by this methyl substitution in the one-point adsorption would be expected to be even more pronounced in the case of 4,6-dimethyldibenzothiophene (Figure 8). The experimental results obtained with sulfided Co-Mo/ Al_2O_3 catalyst at about 300°C and 100 atm (16) show that 4,6-dimethyldibenzothiophene is about 10 times less reactive than dibenzothiophene, but only about two times less reactive than the 4-methyldibenzothiophene. Results determined at subatmospheric pressures give qualitatively the same reactivity pattern (17). In contrast to these results, however, the steric

features of the one-point mechanism (as shown in Figure 8) would lead us to the expectation, based on the abundant literature illustrating the rate effects associated with model cases of steric hindrance (18), that differences of several orders of magnitude in rate should distinguish these reactants.

Similar conclusions can be drawn from the low-pressure conversion data of Givens and Venuto (14) for benzothiophene and methyl-substituted benzothiophene. They reported, for example, that 3-methylbenzothiophene is slightly less reactive than 2-methylbenzothiophene, which would be regarded as much more sterically hindered on the basis of the one-point mechanism. Similarly, Desikan and Amberg (7) have shown that 2-methyl- and 3-methylthiophene hydrodesulfurization reactions take place in the presence of sulfided Co-Mo/Al₂O₃ with indistinguishable apparent activation energies. And the adsorption studies of Zdrzil (19), who used substituted thiophenes and aromatics contacting Co-Mo/Al₂O₃ in a pulse system, confirm that the bonding with the surface is only slightly affected by the substituent groups and is similar for thiophenic compounds and substituted benzenes having nearly the same molecular weight. All these substituent effects, taken together, strongly suggest the inadequacy of the one-point adsorption model.

Furthermore, the chemistry of thiophene and its polycyclic aromatic homologs does not support a one-point adsorption mechanism. This conclusion can be reasoned from bonding characteristics of thiophene expressed by Daudel et al. (20) in terms of the following bonding parameters: The bond order refers to the "double bond character" of a bond or the sum of the partial bond orders contributed by each π electron. Apparently, the C₂-C₃ bond has, by far, the highest electron availability. The free valence is a measure of the potential for homolytic (free radical) reactivity at each of the ring atoms, and the total charge at



each atom is an expression of the potential for reactivity toward an approaching, polarizing species such as an electron-deficient reagent.

The known bonding characteristics of thiophene and of its polycyclic aromatic homologs therefore indicate that the tendency of the compound to be adsorbed at an anion vacancy on the Co-Mo catalyst would not occur preferentially at the sulfur (say, through an available 3p orbital situated at right angles to the plane of the thiophene ring), but instead at the C₂ and C₃ position--if indeed a one-point mechanism were demanded. The unshared, non-bonded pairs on sulfur are so involved with the resonance of the thiophene nucleus that it has little residual electron availability for direct coordination by the electrophilic catalyst.

Proposed Multipoint Mechanism of Hydrodesulfurization of Thiophene

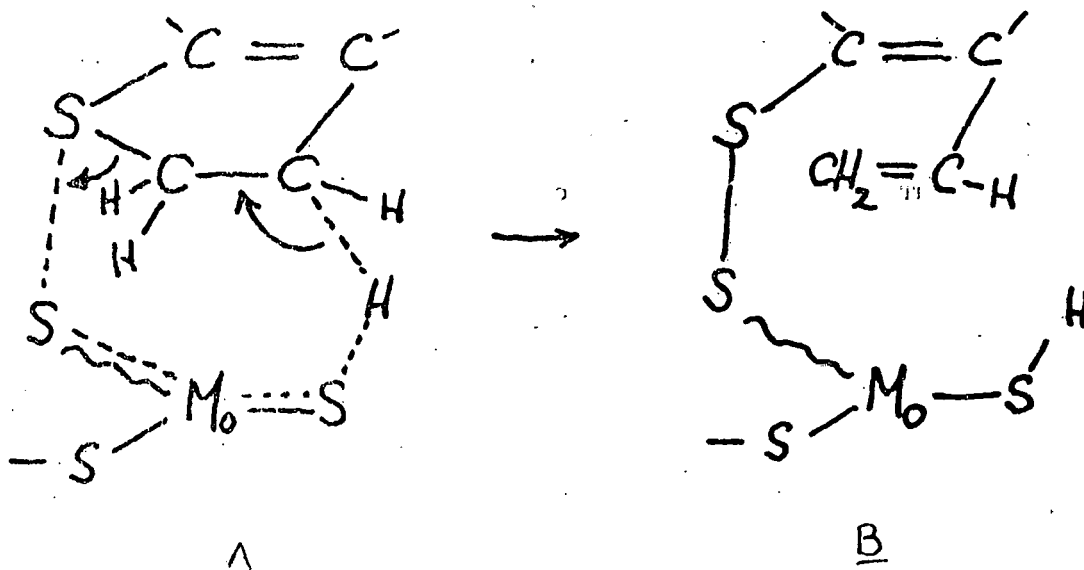
We suggest that thiophenic molecules may be chemisorbed such that the C₂-C₃ bond is coordinated at an anion vacancy of the catalyst, with the adjacent sulfur center then interacting with a neighboring sulfide center on the catalyst surface. When the thiophene ring becomes bonded via its C₂-C₃ positions at the

anion vacancy, the result is expected to be a change in the electron distribution of the thiophene ring, making the sulfur atom electron deficient, and thus promoting the formation of a bonding interaction with either an adjacent or a more remote, electron-dense sulfur site on the sulfided catalyst. This suggestion is depicted in Figure 8.

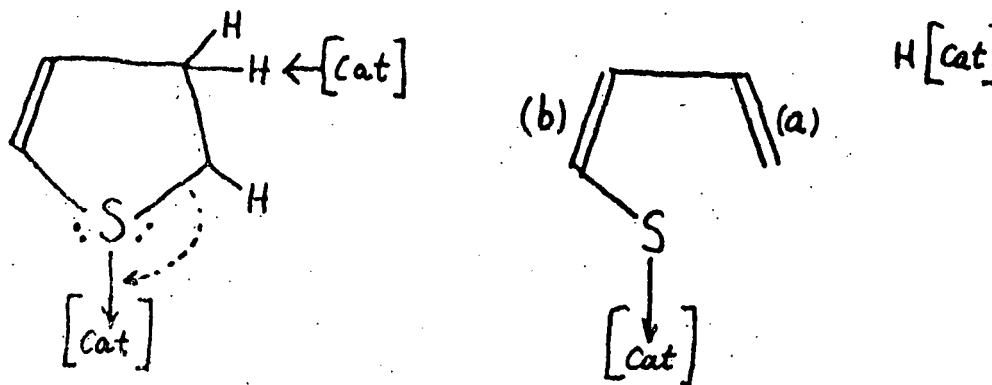
This suggestion brings to mind the analogous case of the enzyme nitrogenase, a molybdenum-centered reducing enzyme (21,22) capable of redox activity toward a wide variety of π -bonded species including molecular nitrogen, acetylenes, and aldehydes. The mechanistic picture proposed for the reduction of acetylenes is typical. This substrate (reactant) coordinates to the Mo^{4+} centers of the enzyme in its fully activated state in a π -type, (side-on) fashion. After the juxtaposition of the coordinated acetylene, the Mo(IV) center, and the amine ligands, this enzyme-substrate complex is ready for the coupled hydrogen- and electron-transfer process illustrated in Figure 8. The two-site theory of the mechanism of reaction involving molybdenum-containing redox enzymes, advocated by Hardy et al. (23), is considered a three-point Ogston mechanism (24) since the acetylenic and related substrates exhibit two points of chemical bonding on the catalyst surface.

Working from the structure of Figure 8, we now recognize several alternative pathways for product-forming steps leading from the substrate-catalyst complex. The dotted lines are intended to represent only a fractional degree of covalency in the bonding of Figure 8. If the C_2 becomes bonded with a full covalency to a proton before a similar process occurs at C_3 (i.e., if partial hydrogenation of the $\text{C}_2=\text{C}_3$ double bond occurs), then, as depicted in A, electron delocalization from the partial covalency to the proton at C_3 can lead to

rupture of the S-C₂ bond, as follows:



If the partially bonded protons in the structure of Figure 4 become involved in covalent bonds to C₂ and C₃ by a more-or-less concerted process, the resulting hydrothiophene C no longer has aromatic properties. Structure C is highly susceptible to thermal β -elimination (as illustrated by the dotted arrows), probably assisted by electrophilic centers on the catalyst to which it is strongly bonded via its sulfur, which has become nucleophilic upon loss of thiophenic aromaticity. The net result is clearly the same as is realized from the pathway involving nonsimultaneous transfer of hydrogen to the chemisorbed substrate in A.



or equivalent

It is clear that B, which is presumably strongly bonded to the catalyst, can experience chemisorption of its olefinic groups to Mo^{4+} at anion vacancies created in its vicinity by hydrogenation (and desorption of H_2S), and this can again lead to rupture of its carbon-sulfur bond. Ultimately, the process will lead to liberation of butadiene or, if the double bond (a) (more remote from the carbon-sulfur bond) is reduced prior to reduction of the vinylic sulfide double bond (b), butene will be formed directly without butadiene.

All these mechanistic possibilities can be invoked to account for the product compositions and reaction networks observed in hydrodesulfurization. Thus, the predominance of biphenyl as the product in the hydrodesulfurization of dibenzothiophene (15) correlates well with the preference for product formation via the pathway analogous to those involving A, B, C, and D, in which only the ring carbon to which the sulfur is attached becomes covalently bonded to a proton; electron delocalization similar to the step transforming A into B occurs rapidly to restore the aromatic energy of the ring with formation of o-mercaptobiphenyl before a dihydro product can be realized. This picture, which assumes that thiophenes are bonded to the catalyst surface through coordination involving their π electrons, accounts for steric effects of substitution arising from planar adsorption of the ring. It eliminates the necessity of assuming orbital interaction with the surface perpendicularly to the plane of the thiophenic π orbitals as demanded by the one-point model. Thus, a 4-methyl substituent in dibenzothiophene exerts a mild steric influence inhibiting coplanar adsorption of the reactive centers because the hydrogens of a methyl group (bonded to the C_4 position, which is one of the three centers involved in the coplanar adsorbate), rotating about the axis of its bond to the ring, sweeps out a sphere of revolution above and below the plane of the sigma framework of the ring. The effect of the

methyl substituent is to diminish slightly the degree of coordination of these reaction centers with the catalyst, as depicted in Figure 10. Since dibenzothiophene is a planar structure, however, a second methyl group at the 6-position would not significantly increase the difficulty of achieving an interaction with the catalyst, since it creates no greater steric separation of the ring plane from the planar catalyst surface.

On the other hand, methyl groups at the 3,7 and 2,8 positions, which have no proximate relationship to the three adsorbate centers, would have little steric effect since the normal bending vibrations of the ring would readily accommodate any possible interference with coplanarity of these centers. Instead, we observe a small rate enhancement resulting from hyperconjugative electron release by the 3,7 and 2,8 methyls to the sulfur and the ring carbon to which it is linked in the substrate (16); increased electron density at the centers of adsorption presumably increases the catalytic reaction rate through increased ease of coordination at the anionic vacancies of the catalyst.

A recent proposal by Cowley (17) has been made to overcome some of the shortcomings of the model of end-on adsorption of thiophene through the sulfur atom. Cowley's proposal holds that thiophene is adsorbed flat on the catalyst surface in a π -complex, as Zdražil also concluded (19). The π -complex is presumed to be subsequently converted to a sigma-complex in which sulfur orbitals perpendicular to the plane of the ring become bonded to the Mo^{3+} center of the anion vacancy. The hydrodesulfurization reaction process is presumed to be completed with the reactant in this posture.

This planar modification of the end-on, one-point mechanism is based largely on the finding that the deuterodesulfurization products of 2,5-dideutero-

thiophene contain major amounts of D_2S . Such results have been interpreted by Cowley as an indication that the α -deuterium exchange reaction occurs by a pathway different from that of the normal hydrodesulfurization. Cowley reasoned that the initially formed π -complex, in which the ring is bound parallel to the surface, becomes equilibrated with a series of sigma-complexes, in all of which there exists substantial bonding between an α -carbon and an electron-deficient Mo^{3+} center. The hydrogen-deuterium exchange reaction in thiophene, benzothiophene, and dibenzothiophene has been visualized as occurring in these sigma-complexes, with the hydrodesulfurization reaction taking place in sigma-complexes in which the sulfur has become coordinated by sigma bonding to Mo^{3+} centers. Hydrogenolysis of the carbon-sulfur bond with release of butadiene is presumed to be the consequence of altering the nature of the sulfur through its coordination by the Mo^{3+} , while adjacent $Mo^{4+}S^{2-}$ sites provide the hydrogen, as shown in Figure 11.

It is apparent, however, that the multi-point model discussed above directly provides an explanation for both the observed exchange at α (preferred) and β positions and the hydrogenolysis reactions, without the necessity of assuming the intervention of two different sigma complexes for the two respective reactions. In the multipoint mechanism it is the π orbital on carbon at which the available electron density of the aromatic (thiophenic) system can be coordinated by the electron-deficient molybdenum centers of the catalyst. The very act of bonding to these centers destroys the aromaticity of the ring sufficiently to induce a degree of electron deficiency on the ring sulfur, thereby creating the opportunity for its back-bonding with one of the sulfur atoms localized in the coordination sphere of the molybdenum center, as shown in Figure 12.

Regarding the hydrodesulfurization reaction of saturated sulfides such as tetrahydrothiophene, it is important to focus on the sigma-complex E in Figure 2. It expresses the understanding that with a properly sulfided Co-Mo catalyst, a sigma-complex can be formed with, for example, tetrahydrothiophene, in which a sulfur-sulfur bond steers the subsequent events leading to formation of complex F and ultimate loss of butene or butadiene and H_2S . That is, a highly probable series of steps involving β -elimination accompanied by hydrogen transfer to the catalyst is postulated on the premise of the ready formation of a S-S covalency (as in E) involving one of the sulfur ligands of a molybdenum center which, in turn, is also capable of complexing with the resulting carbon-carbon π -bond in forming F. This picture is in accord with the results of Kolboe (10) accounting for the previously puzzling observation that the amount of butadiene produced by desulfurization of tetrahydrothiophene exceeds that arising from desulfurization of thiophene; there is no need for invoking an unprecedented dehydrodesulfurization route (Figure 7).

We recognize, however [as suggested by Cowley (13)], that the coordination of the sulfur atom of tetrahydrothiophene at the anion vacancy must also be regarded as a competing possibility. Therefore, the one-point mechanism for tetrahydrothiophene (as advanced by Cowley) cannot be excluded as a possible course of reaction; both the one-point and the multipoint mechanisms must be accepted as consistent with the experimental results.

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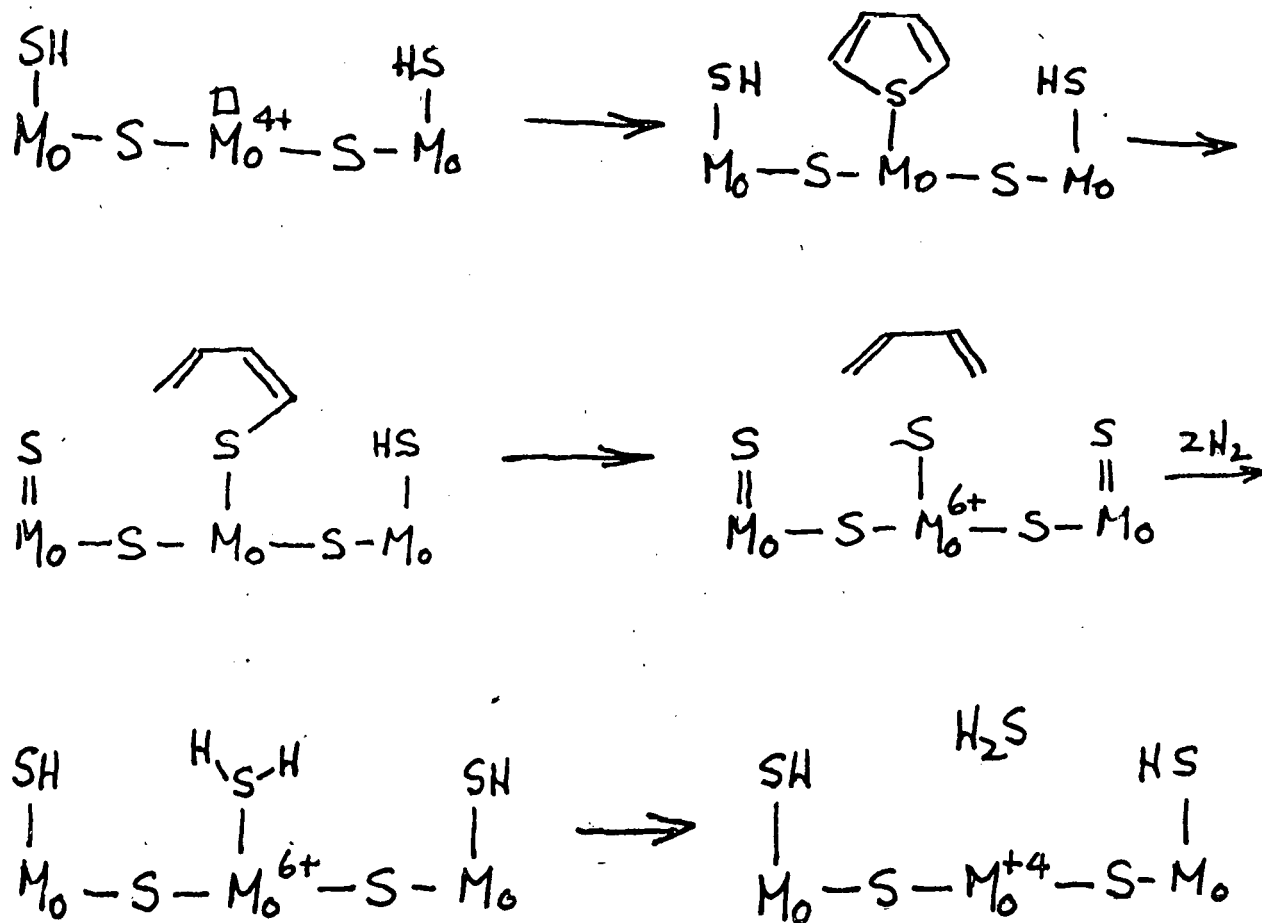


Fig. 6 The suggested one-point mechanism of thiophene hydrodesulfurization on sulfided Co-Mo/Al₂O₃ and related catalysts.

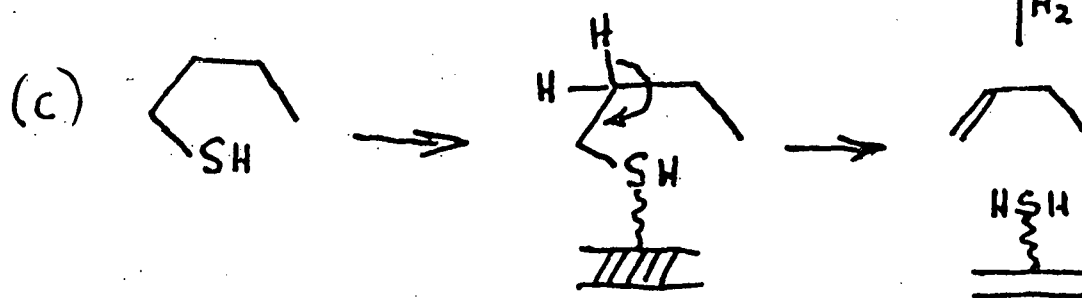
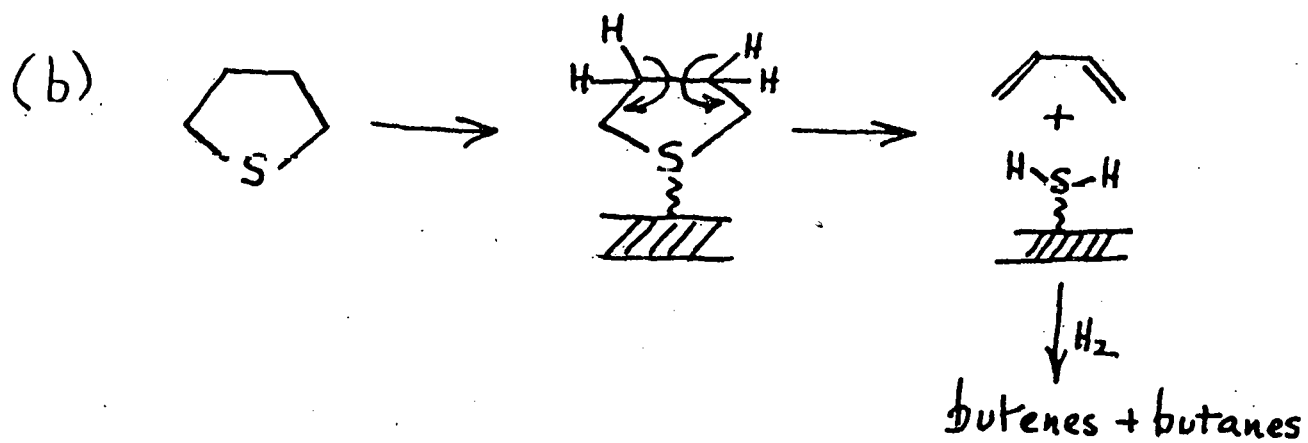
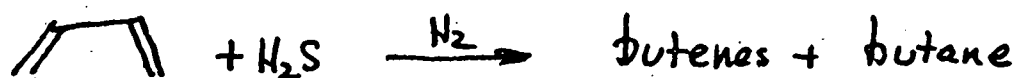
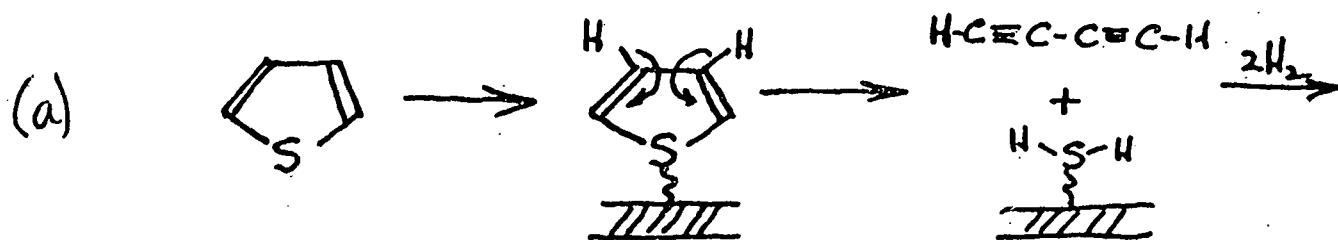


Fig. 7 The Kolbe one-point mechanism for thiophene hydrodesulfurization.

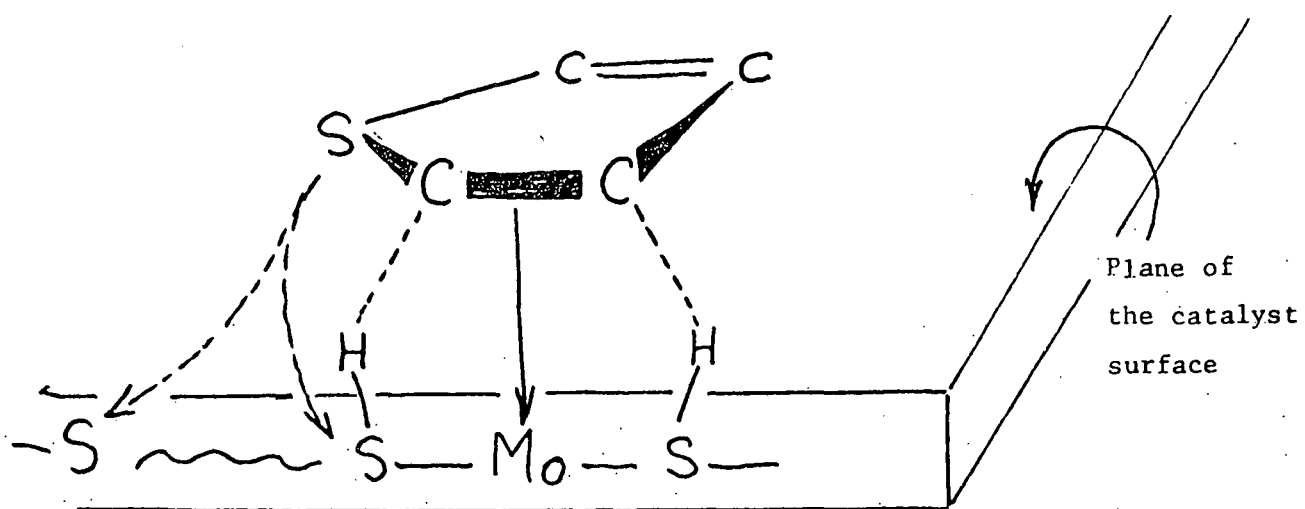


Fig. 8 Suggested structure of chemisorbed thiophene in the three-point mechanism. The dashed line indicates a weaker interaction between center than the full line. The wavy line indicates a longer or more remote bond between centers.

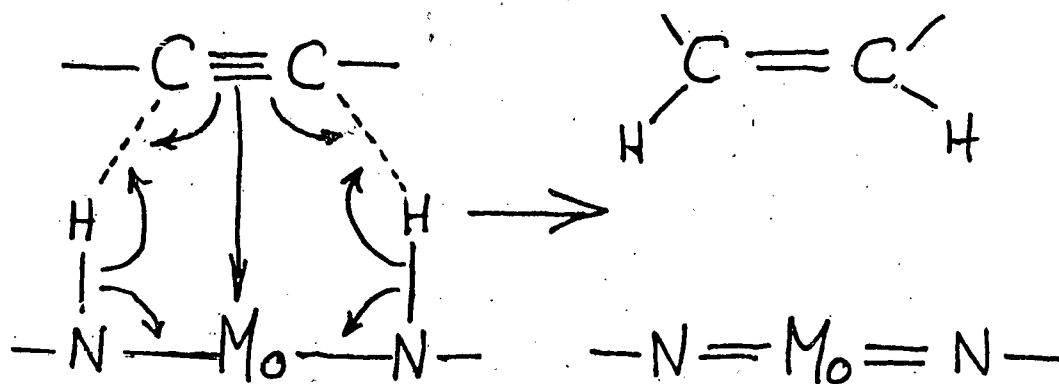


Fig. 9 A three-point mechanism for the catalytic action of nitrogenase on an acetylenic substrate.

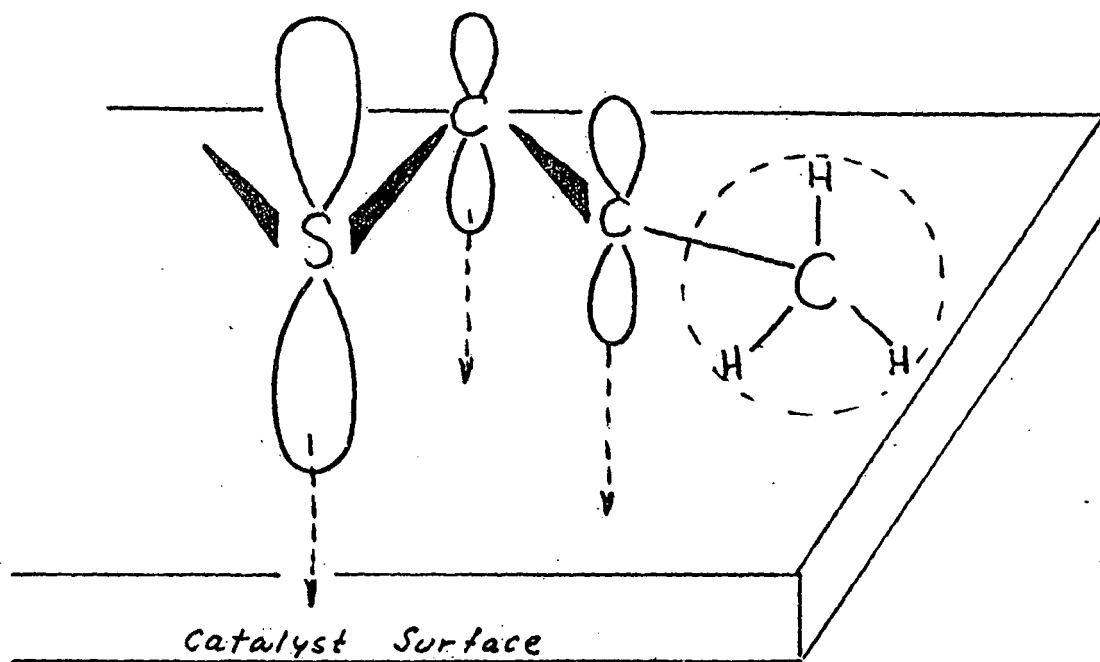


Fig. 10 Schematic representation of the steric effects of a methyl substituent in the 4-position of dibenzothiophene on the adsorption on the catalyst.

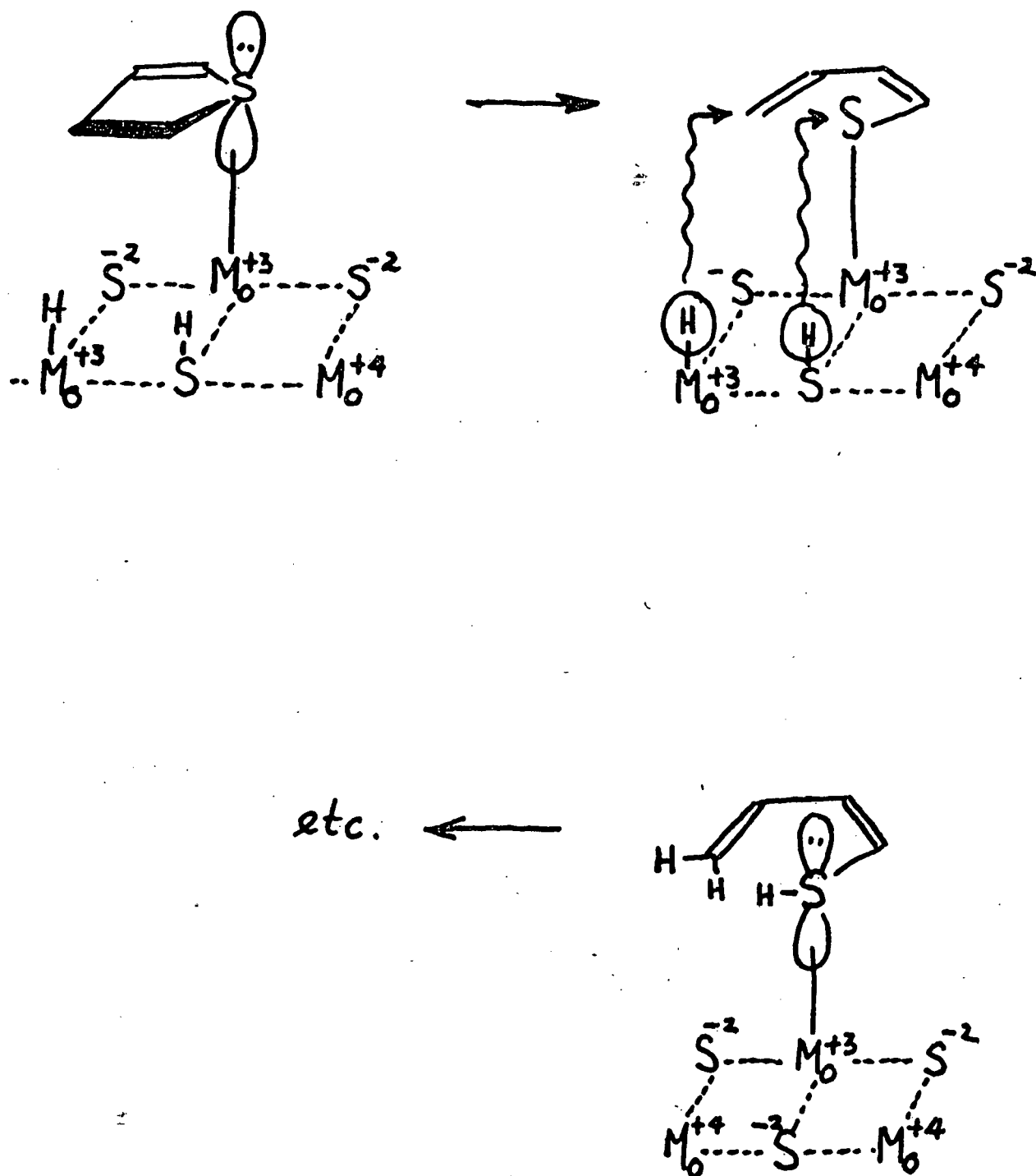


Fig. 11 Mechanism suggested for the hydrogenolysis of the carbon-sulfur bond in adsorbed thiophene.

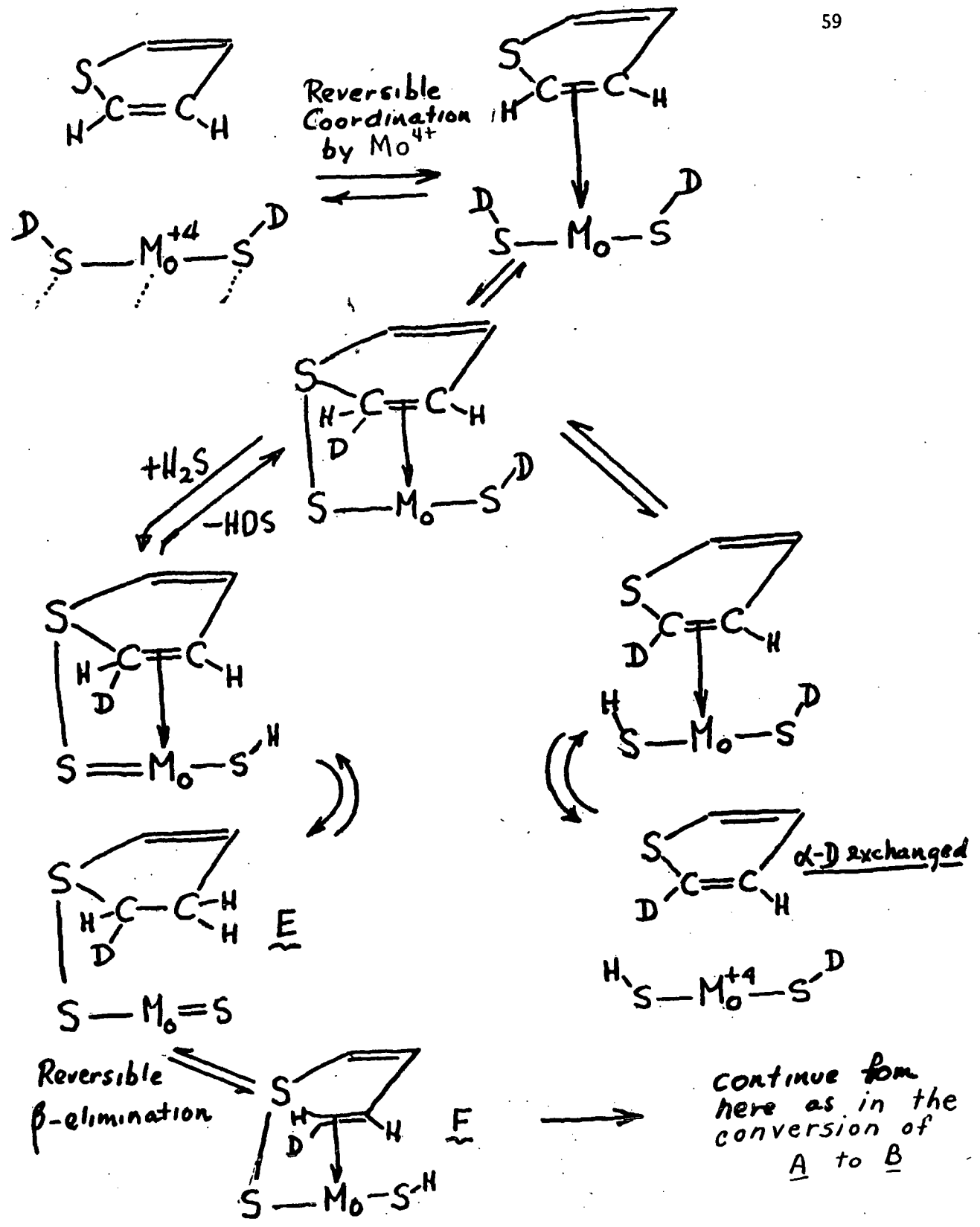


Fig. 12 Details of the suggested mechanisms of simultaneous deuterium exchange and hydrodesulfurization of thiophene adsorbed by the multipoint model.

V. PUBLICATIONS

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VI. PERSONNEL

There have been no changes in personnel during this quarter.