Hydrodesulfurization of Dibenzothiophene Catalyzed by Sulfided CoO-MoO$_3$$\gamma$-Al$_2O_3$: The Reaction Network

MARWAN HOUALLA
N. K. NAG
A. V. SAPRE
D. H. BRODERICK
and
B. C. GATES

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

Kinetics experiments have determined the reaction network in the hydrodesulfurization of dibenzothiophene catalyzed by sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ at 573°K and 102 atm. The predominant reaction is a direct sulfur extrusion, giving biphenyl and hydrogen sulfide; the biphenyl is subsequently hydrogenated slowly to give cyclohexylbenzene and then bicyclohexyl. Dibenzothiophene also undergoes a primary hydrogenation reaction preceding sulfur removal, but it is about one thousand times slower than the sulfur extrusion reaction.

SCOPE

Catalytic hydrodesulfurization of petroleum is widely practiced on an industrial scale to produce clean burning, low-sulfur fuels, and there is a clear need for extending the technology to other fuels, including coal. The chemistry of hydrodesulfurization of the relatively unreactive compounds in petroleum and coal derived liquids, for example, dibenzothiophene, is poorly defined. The research described here resolves the reaction network prevailing when dibenzothiophene and hydrogen contact fresh, sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ catalyst at 573°K and 102 atm; the data define the catalytic activity and selectivity, providing quantitative kinetics of the hydrogenation and hydrodesulfurization (hydrogenolysis) reactions. They also establish the influence on selectivity of methyl substituents on the reactants, hydrogen sulfide in the reactant mixture, and nickel and molybdenum or nickel and tungsten instead of cobalt and molybdenum in the catalyst.

CONCLUSIONS AND SIGNIFICANCE

The reactions of dibenzothiophene with hydrogen catalyzed by sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ have been determined at 573°K and 102 atm. The results are summarized in Figure 5, in which the numbers next to the arrows represent pseudo first-order rate constants having dimensions of cubic meters per kilogram of catalyst per second.

Figure 5 shows the high selectivity of the catalyst for simple hydrodesulfurization (biphenyl + hydrogen sulfide formation). When methyl groups are present in the four and six positions of dibenzothiophene, the primary hydrogenation reaction is approximately as fast as the primary hydrodesulfurization reaction. Nickel and molybdenum or nickel and tungsten used instead of cobalt and molybdenum in the catalyst, or hydrogen sulfide in the reactant mixture, also favor hydrogenation relative to hydrodesulfurization.

Correspondence concerning this paper should be addressed to B. C. Gates. M. Houalla is at the Universite Catholique de Louvain, Louvain La-Neuve, Belgium.

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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., 1978). Many authors have found biphenyl, cyclohexylbenzene, and bicyclohexyl among the reaction products, which indicates that hydrogenation reactions are important, and some authors (for example, Obolentsev and Mashkina, 1958, 1959) have found that biphenyl was the only product besides hydrogen sulfide, which indicates that under certain conditions (598 to 698°K and 10 to 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 Company 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 3.25×10^{-7} m^3 and a length of 4.1×10^{-2} m. The catalyst (2.5×10^{-5} kg) was mixed with 6.25×10^{-4} kg of alundum, an inert reactor packing material. The catalyst particle size was usually 149 to 178 μm.

The catalyst was presulfided in the reactor for 2 hr with a flowing mixture of 10 vol % hydrogen sulfide in hydrogen at atmospheric pressure and 673°K. The reactant solution usually contained about 0.15 mole % dibenzothiophene in *n*-hexadecane. Before operation, the solution (2.6×10^{-4} m^3) was saturated with hydrogen (or occasionally with hydrogen + hydrogen sulfide) in a stirred autoclave by first purging with hydrogen for 2 hr at atmospheric pressure to remove air and then saturating with hydrogen at room temperature and 69 atm for 3 hr. It was estimated from hydrogen solubility data that under these conditions the mole fraction of hydrogen in the solution was 0.055. 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 $(2 \text{ to } 20) \times 10^{-10}$ m^3/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 ±1°K.

The first product samples were collected after about 3×10^{-5} 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

TABLE 1. CATALYST PROPERTIES*

Catalyst	$NiO-MoO_3/\gamma-Al_2O_3$ (HDS-9A)	$CoO-MoO_3/\gamma-Al_2O_3$ (HDS-16A)	$NiO-WO_3/\gamma-Al_2O_3$ (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_2O	0.05	0.03	—
Fe	—	0.04	—
$10^{-5} \times$ surface area, m^2/kg	1.49	1.76	2.50
$10^{10} \times$ pore volume, m^3/kg	5.1	5.0	5

* The reported values were determined by the catalyst suppliers.

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 mole %. The mass of catalyst was 2.21×10^{-4} kg and the volume of liquid reactant was 3.5×10^{-4} m^3. The reaction temperature was 573 ± 1°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 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 to 200 mesh Supelcoport (Supelco) at 423°K with a helium carrier gas flow rate of about 5×10^{-7} m^3/s. The hydrogen sulfide 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 0V-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 (Figure 1) gave predominantly biphenyl; yields as high as 87 mole % 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 to 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.

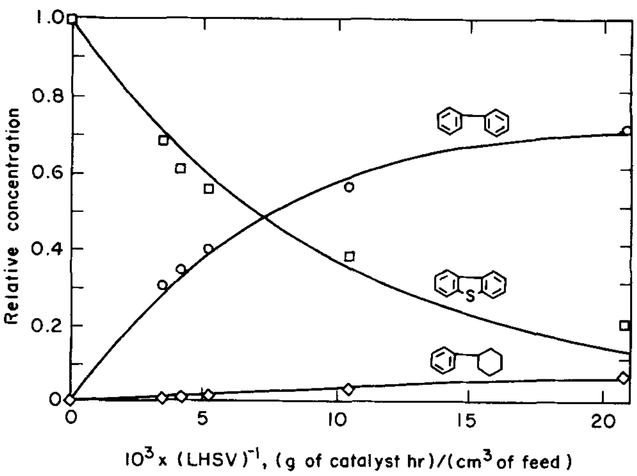


Fig. 1. Product distribution in the reaction of dibenzothiophene with hydrogen catalyzed by sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ at 573°K and 102 atm. The reactor feed was 0.15 mole % dibenzothiophene dissolved in *n*-hexadecane, which was saturated with hydrogen at room temperature and 69 atm. The lines correspond to the network of pseudo first-order reactions summarized in Figure 5.

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

The product distribution also depended on the concentration of hydrogen sulfide in the reactant solution. Results summarized in Table 2 show that hydrogen sulfide suppressed the dibenzothiophene hydrodesulfurization (hydrogenolysis) reaction relative to the hydrogenation reaction forming cyclohexylbenzene. At high feed hydrogen sulfide concentrations ($C_{H_2S}/C_{H_2} = 0.13$), 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 hydro-

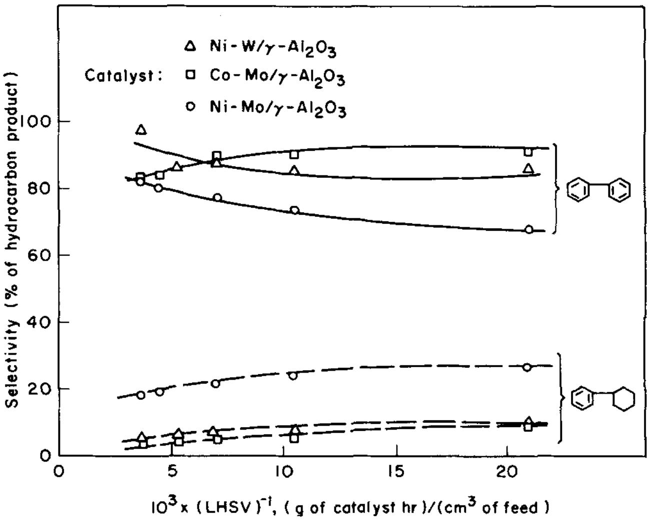


Fig. 2. Effect of catalyst composition on the product distribution in the conversion of dibenzothiophene + hydrogen. The reaction conditions are specified in the text.

Table 2. Effect of Hydrogen Sulfide on the Selectivity for Hydrogenation vs. Hydrodesulfurization of Dibenzothiophene*

C_{H_2S}/C_{H_2} in feed	Space velocity m³ of feed/kg of catalyst · s	Yield of cyclohexylbenzene, mole % of hydrocarbon product
0.00	3.52×10^{-5}	7.4
0.00	2.02×10^{-4}	1.9
0.01	3.34×10^{-5}	9.0
0.01	1.92×10^{-4}	2.0
0.13	3.47×10^{-5}	13.3
0.13	1.99×10^{-4}	3.8

* The catalyst was 1.0×10^{-5} kg of sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ diluted with 2.8×10^{-4} kg of alundum. The feed contained 0.15 mole % dibenzothiophene in *n*-hexadecane, which was subsequently saturated with hydrogen at 69 atm. The temperature was 573 ± 1°K, and the pressure was 102 atm.

genation 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 Figure 3, and the data are therefore summarized as pseudo first-order rate constants having dimensions of cubic meters per kilogram of catalyst per second; the rate equation is

$$r = k_i C_i \tag{1}$$

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 mole % 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.

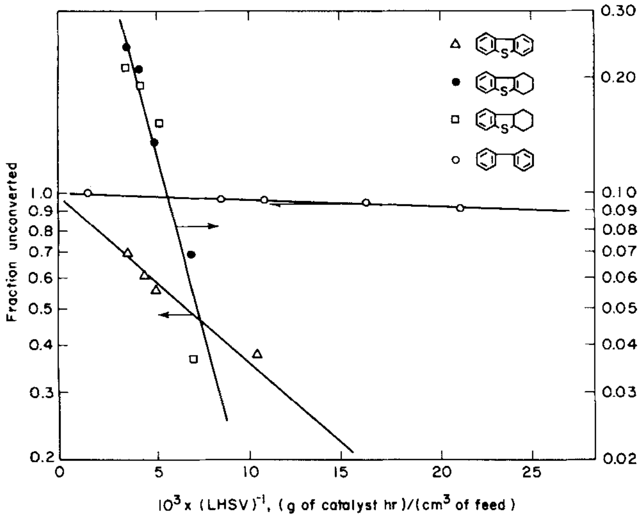
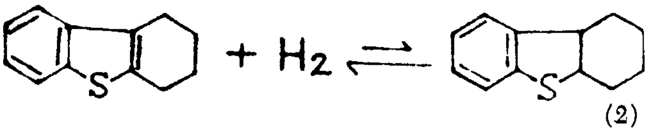


Fig. 3. Pseudo first-order kinetics of the disappearance of each of the reactants shown in the presence of hydrogen and sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ catalyst under the conditions described in the text. Each reactant was fed separately (with hydrogen) into the flow reactor.

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 1.2×10^{-6} m³/kg of catalyst·s (the underlying assumption is that *o*-phenylthiophenol was converted instantaneously into biphenyl and hydrogen sulfide).

Two experiments were done with biphenyl as the reactant. In the first, biphenyl (0.12 mole %) 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, hydrogen sulfide was generated during the hydrodesulfurization reaction, and since it had been found (Broderick et al., 1978) that some hydrogen sulfide 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 hydrogen sulfide to prevent the catalyst from slowly deactivating. The first-order rate constant for the conversion of biphenyl under these conditions was 1.1×10^{-6} m³/kg of catalyst·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:



(2)

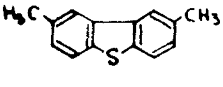
In all the experiments, the hydrogen was present in stoichiometric excess, and its concentration was virtually constant. Therefore, the concentration equilibrium constant

$$K = \frac{C_{1,2,3,4,10,11\text{-hexahydrodibenzothiophene}}}{C_{H_2} \cdot C_{1,2,3,4\text{-tetrahydrodibenzothiophene}}} \tag{3}$$

was estimated to be about 1.5×10^{-3} m³/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 1.12×10^{-4} m³/kg 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



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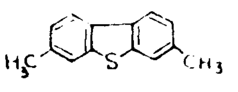
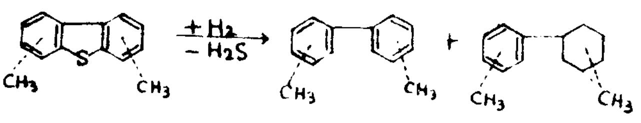
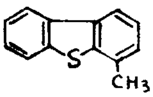


were studied under conditions cited earlier; their concentrations in the reactant solution were about 0.06 mole %. These compounds were found to have nearly the same reactivity as dibenzothiophene (Houalla et al., 1977). The product distribution with each was similar to that expected from the results with dibenzothiophene (Figure 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



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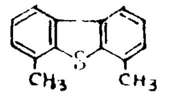

These compounds were less reactive than dibenzothiophene (Houalla et al., 1977), and the yields of the substituted cyclohexylbenzene products formed from them were greater than the yield of cyclohexylbenzene formed from dibenzothiophene under comparable conditions. These results suggest that 4-methyldibenzothiophene 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 networks.

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 (Figure 1), the simplest reaction network consistent with the data of Figure 1 was postulated, as shown in Figure 4. The individual rate constants k_i were estimated in the following way:

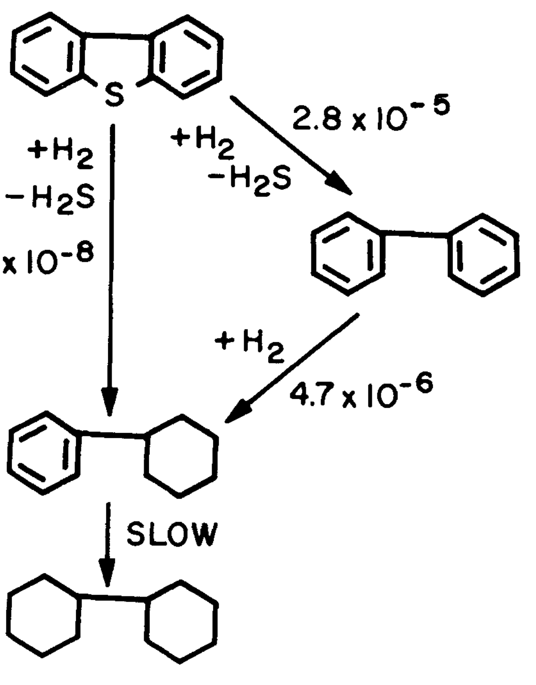

Fig. 4. Approximate reaction network for conversion of dibenzothiophene and hydrogen in the presence of sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ at 573°K and 102 atm. Each reaction is assumed to be first order in the organic reactant; the numbers next to the arrows are the pseudo first-order rate constants in cubic meters per kilogram of catalyst per second.

1. Each reaction in the network of Figure 4 was assumed to be first order in the organic reactant.
2. The data of Figure 1 were smoothed by fitting to the following simple functions:

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

$$C_{\text{biphenyl}} = A_3\{\exp[\underline{A}_4 (SV)^{-1}] - \exp[\underline{A}_5 (SV)^{-1}]\} \tag{5}$$

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

The coefficients A_i and $\underline{A}_i$ were determined with a nonlinear least-squares program. [We note that the smoothing functions (4) and (5) are the actual solutions of the

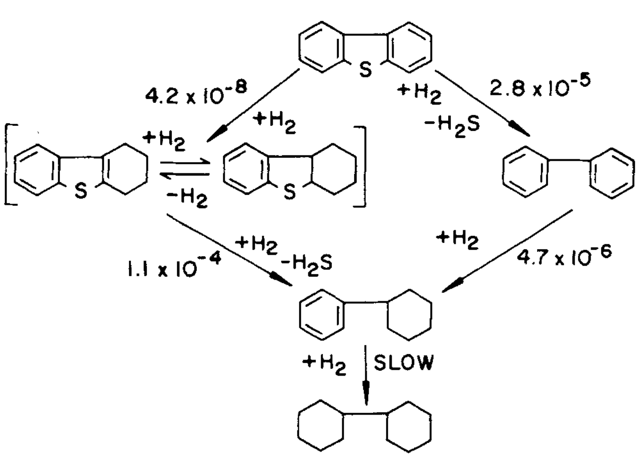

Fig. 5. Conversion of dibenzothiophene and hydrogen in the presence of sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ at 573°K and 102 atm: the reaction network. Each reaction is first order in the organic reactant; the numbers next to the arrows are the pseudo first-order rate constants in cubic meters per kilogram of catalyst per second.

differential equations for the network of Figure 4, provided that each reaction is indeed first order. The exact solution for cyclohexylbenzene could not be fitted, since there were too few data.]

3. Points were taken at equal intervals of $(SV)^{-1}$ from the smoothed curves predicted by Equations (4) to (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 reactions in the network of Figure 4 were obtained:

$$k_1 = 2.8 \times 10^{-5}\ \text{m}^3/\text{kg of catalyst}\cdot\text{s}$$

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

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

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 1.1×10^{-4} m^3/kg of catalyst·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 Figure 1. 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 Figure 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 Figure 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 fourfold 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 hydrogen sulfide. There are too few data to allow determination of full rate equations indicative of these effects.

The lines in Figure 1 show the good fit to the dibenzothiophene conversion data obtained with the rate constants of Figure 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 Figure 5 emphasizes the high selectivity of the cobalt-molybdenum/aluminum oxide 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 nickel-molybdenum and nickel-tungsten 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. 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 hydrogen sulfide is added to the reactant mixture, as nickel replaces cobalt 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, various pressures, and various hydrogen sulfide concentrations, which explains the variety of their product distributions.

The influence of hydrogen sulfide and of methyl substitution on the reactant provides the basis for some suggestions about the surface chemistry of the catalytic reactions. The effect of hydrogen sulfide in increasing the rate of hydrogenation relative to hydrodesulfurization indicates differing degrees of inhibition of the two reactions by hydrogen sulfide, 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 elsewhere (Kwart et al., to be published).

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NOTATION

A_i = empirical constant, mole/m^3

$\underline{A}_i$ = empirical constant, kg of catalyst·s/m^3 of reactant solution

C = concentration, mole/m^3

k = pseudo first-order reaction rate constant, m^3 of reactant solution/kg of catalyst·s

K = concentration equilibrium constant, m^3/mole

r = reaction rate, moles of organic reactant converted/kg of catalyst·s

SV = space velocity, m^3 of reactant solution/kg of catalyst·s

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Optimum Design of Chemical Plants with Uncertain Parameters

A new strategy is proposed for the optimum design of chemical plants whose uncertain parameters are expressed as bounded variables. The design is such that the plant specifications will be met for any feasible values of the parameters while optimizing a weighted cost function which reflects the costs over the expected range of operation. The strategy is formulated as a nonlinear programme, and an efficient method of solution is derived for constraints which are monotonic with the parameters, a case which arises frequently in practice. The designs of a pipeline with a pump, of a reactor-separator system, and of a heat exchanger network, all with uncertain technical parameters, illustrate the effectiveness of the strategy for rational overdesign of a chemical plant.

I. E. GROSSMANN
and
R. W. H. SARGENT
Department of Chemical Engineering
and Chemical Technology
Imperial College
London S.W.7, England

SCOPE

In the design of chemical plants, it is very often the case that some of the technical or commercial parameters are subject to significant uncertainty. In order to overcome this difficulty, the procedure which is normally used is to apply empirical overdesign factors to the sizes of the units. Other methods which predict more rational overdesign factors have been proposed, but their use in practice has been very limited. The main reasons for this is because the computational requirements of these methods are expensive and/or because the objectives in the basic strategy are not very realistic for design purposes. In this paper, a strategy is proposed which attempts to circumvent these difficulties. The objective of the proposed strategy is to design chemical plants which are able to meet the specifications for a bounded range of values of the parameters and which, at the same time, are optimum with respect to a weighted cost function. When probability distribution functions of the parameters are available, the expected value of the cost can be approximated by choosing appropriate weights. The mathematical formulation of the strategy leads to a large nonlinear program, where the inequality constraints must be maximized with respect to the uncertain parameters. The purpose of the paper is to derive a reasonable method of solution for the problem and to apply the strategy to typical design examples in chemical engineering, where uncertainty is present in parameters such as pump efficiencies, friction factors, reaction rate constants, and heat transfer coefficients.
