Hydrodesulfurization of Thiophene, Benzothiophene, Dibenzothiophene, and Related Compounds Catalyzed by Sulfided CoO–MoO₃/γ-Al₂O₃: Low-Pressure Reactivity Studies

D. R. Kilanowski,[1] H. Teeuwen,[2] V. H. J. de Beer,[3] B. C. Gates,[4]
G. C. A. Schuit, and H. Kwart

*Center for Catalytic Science and Technology, Departments of Chemical Engineering and Chemistry,
University of Delaware, Newark, Delaware 19711*

Hydrodesulfurization experiments were carried out with a sulfided CoO–MoO₃/γ-Al₂O₃ catalyst in a pulse microreactor operated at atmospheric pressure and temperatures of 350 to 450°C. The reactants were hydrogen and pure sulfur-containing compounds (or pairs of compounds), including thiophene, benzothiophene, dibenzothiophene, several of their hydrogenated derivatives, and various methyl-substituted benzothiophenes and dibenzothiophenes. The aromatic compounds appeared to react with hydrogen by simple sulfur extrusion; for example, dibenzothiophene gave H₂S + biphenyl in the absence of side products. The reactivities of thiophene, benzothiophene, and dibenzothiophene were roughly the same. Each hydrogenated compound (e.g., tetrahydrothiophene) was more reactive than the corresponding aromatic compound (e.g., thiophene). Methyl substituents on benzothiophene had almost no effect on reactivity, whereas methyl substituents on dibenzothiophene located at a distance from the S atom slightly increased the reactivity, and those in the 4-position or in the 4- and 6-positions significantly decreased the reactivity. In contrast to the observation of a near lack of dependence of low-pressure reactivity on the number of rings in the reactant, the literature shows that at high pressures the reactivity decreases with an increased number of rings. The pressure dependence of the structure–reactivity pattern is suggested to be an indication of relatively less surface coverage by the intrinsically more reactive compounds (e.g., thiophene) at low pressures but not at high pressures. The relative reactivities are also suggested to be influenced by differences in the structures of the catalyst at low and high hydrogen partial pressures, which may be related to the concentrations of surface anion vacancies and the nature of the adsorbed intermediates.

INTRODUCTION

Hydrodesulfurization of petroleum distillates has been practiced for many years,

but basic questions about the catalyst structure and the reaction mechanism remain unanswered. The current technological emphasis on hydrodesulfurization of petroleum residua and of coal-derived liquids points to the need for understanding the chemistry of hydrodesulfurization of the heterocyclic compounds, which are expected to be among the least reactive compounds in these feedstocks. Thiophene, the simplest compound in this class, has

[1] Present address: American Cyanamid Co., Stamford, Connecticut.
[2] Present address: Wiener & Co., Amsterdam, The Netherlands.
[3] Present address: Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands.
[4] To whom all correspondence should be addressed, Department of Chemical Engineering.

often been chosen for kinetics studies, and thiophene has often been assumed to be representative of the whole class of sulfur-containing aromatic compounds. Even though thiophene hydrodesulfurization has received much attention, the reaction mechanism remains to be clarified. Owens and Amberg (*1*) concluded that hydrogenolysis of the C–S bond in thiophene, which leads to the formation of 1,3-butadiene, precedes hydrogenation of the aromatic ring. Kolboe (*2*) alternatively proposed an intramolecular dehydrosulfurization, whereby the hydrogen in the product H_2S comes from positions β to the sulfur of the thiophene; Kolboe's suggestion is supported by product distributions of the D_2-thiophene reaction (*3*).

The literature of reaction studies of hydrodesulfurization of benzothiophene, dibenzothiophene, and related compounds (*4–11*) is fragmentary, failing to establish structure–reactivity patterns that might shed light on the reaction mechanisms. The results of this literature were obtained with various catalyst compositions and various reaction temperatures and hydrogen partial pressures, and the lack of a pattern points to the need for systematic experiments with a series of reactants and a single catalyst. The experiments reported here were performed with a variety of reactants and a commercial Co–Mo/γ-Al_2O_3 catalyst operating at atmospheric pressure.[5] The objective was to provide qualitative results for a range of important reactant structures at comparable reaction conditions. The pulse microreactor method (*12*) was chosen since it has the advantage of allowing rapid generation of data from only small amounts of reactants (many of which had to be synthesized for this work) and since it readily allows vapor-phase reactant flow with the relatively non-

[5] A complementary set of experiments at pressures of the order of 100 atm is to be reported elsewhere (*11*).

TABLE 1

References Giving the Methods of Synthesis of Reactants

Compound	Reference
3-Methylbenzothiophene	*13*
3,7-Dimethylbenzothiophene	*14*
2-Methylbenzothiophene	*15*
7-Methylbenzothiophene	*16*
2,3-Dihydrobenzothiophene	*5*
4-Methyldibenzothiophene	*17*
2,8-Dimethyldibenzothiophene	*18*
4,6-Dimethyldibenzothiophene	*18*

volatile dibenzothiophene and methyl-substituted dibenzothiophenes.

EXPERIMENTAL METHODS

Reactants

The following compounds were obtained commercially and used without further purification: *n*-heptane (J. T. Baker, 98%, Baker Grade), *n*-dodecane (Aldrich, 99%), thiophene (Aldrich, 99+%, Gold Label), tetrahydrothiophene (Eastman), benzothiophene (Aldrich, 99%), ethylbenzene (Aldrich, 99%), styrene (Aldrich, 99%), *m*-ethyltoluene (Aldrich, 99%), cumene (Eastman), *n*-propylbenzene (Aldrich, 98%), dibenzothiophene (Aldrich, 95%), biphenyl (Eastman), and cyclohexylbenzene (Aldrich, 96%).

The synthesis techniques for the substituted benzothiophenes and dibenzothiophenes are cited in Table 1. The 1,2,-3,4,10,11-hexahydrodibenzothiophene was prepared from 1,2,3,4-tetrahydrodibenzothiophene, which was obtained by a procedure similar to that of Campaigne *et al.* (*17*).

Pulse Microreactor Experiments

Hydrodesulfurization experiments were carried out with a pulse microreactor operating at atmospheric pressure and temperatures of 350 to 450°C. Purified

Catalyst	CoO content (wt%)	MoO₃ content (wt%)	Pore volume (cm³/g)	Surface area (m²/g)
American Cyanamid (HDS-16A)	5.6	11.2	0.50	176
Ketjen (124–1.5E HD)	4.0	11.8	0.53	256

[a] Properties of the original oxidic catalysts as specified by the manufacturers.

hydrogen served both as the reactant and carrier gas.

The microreactor was a 0.085-in.-i.d. stainless-steel tube. It was heated externally with Briskeat flexible heating tape, and it was surrounded by Cerafelt insulation. The reactor temperature was measured with a sheathed XACTPAK chromel–alumel thermocouple positioned at the external tube wall.

The reactor was packed with 28- to 48-mesh CoO–MoO₃/γ-Al₂O₃ catalyst particles (American Cyanamid AERO HDS-16A, MTG-S-0731), received as $\frac{1}{16}$-in.-diameter extrudates. In some preliminary experiments, the catalyst was a similar Ketjen product (type 124-1.5E HD, test number 18043). The catalyst properties are summarized in Table 2.

Reactant solutions were prepared with a 50 wt% n-heptane in n-dodecane solvent and a single sulfur-containing compound (or occasionally a pair of them) added to give a solution containing 0.3 wt% sulfur. The maximum standard sulfur concentration was limited by the solubilities of dibenzothiophenes in the paraffinic solvent; aromatic solvents were avoided since aromatic compounds are reaction inhibitors. Liquid samples (0.5 μl) were injected by syringe into the hydrogen stream, which flowed at 40 cm³ (STP)/min. Alternatively, in some experiments the pure sulfur-containing compound was injected as a pulse in the absence of solvent. This method was applicable only to the more volatile reactants, including thiophene, benzothio-

phene, and their methyl-substituted derivatives. A four-port, two-position valve allowed for bypassing of the reactor and analysis of the feed stream (including the pulse) with an on-line gas chromatograph equipped with a flame ionization detector. Alternatively, the pulse flowed to the catalyst bed, where it was partially converted; it then flowed directly into the gas chromatograph for product analysis.

Separation of the major products was achieved with a 9 ft × 0.085-in.-i.d. stainless-steel glc column packed with 3% SP-2100 DB on 100–120-mesh Supelcoport (Supelco). The glc column was temperature-programmed at three different rates, dependent upon the products (19).

A standard series of hydrodesulfurization experiments with a given reactant solution was carried out with a catalyst charge of 5 mg in the microreactor. Immediately after charging the catalyst to the reactor, it was heated from ambient temperature to 400°C with hydrogen flow and then presulfided by contacting with 10 mol% H₂S in H₂ at 400°C flowing at a rate of 40 cm³ (STP)/min for 2 hr. In each standard experiment, the following procedure was followed: First, two or three injections of reactant (e.g., benzothiophene) were made through the bypass loop to obtain a glc analysis of the unreacted sample; next, hydrogen was allowed to pass through the reactant feed line for a few minutes at the desired reaction temperature, and the catalyst was conditioned by injection of five sequential 1.0-μl pulses of pure CS₂ into the hydrogen stream. Four to ten 0.5-μl pulses of the reactant solution were then injected in sequence at 35-min intervals (or 1-hr intervals in the case of two-component reactant mixtures) until a repeatable conversion was observed. Finally, two or three pulses were injected through the bypass loop to confirm that there was no change in the detector response for the unconverted reactant. This procedure was found by

trial and error to be the one best suited to determination of repeatable data.

RESULTS

Preliminary Experiments

A series of preliminary experiments was performed to provide qualitative confirmation of a variety of results expected from the literature (*20, 21*). When the reactor was packed with 5 mg of particles of η-Al$_2$O$_3$ (crushed from Harshaw pellets—AL-0104T $\frac{1}{8}$-in.; lot 30; surface area, 140 m^2/g), neither dibenzothiophene nor biphenyl pulses in hydrogen underwent detectable conversion at 450°C (confirming the lack of catalytic activity of the support), and neither of these compounds experienced a detectable holdup in the packed bed (confirming the lack of significant adsorption on the support). Under comparable conditions with 5 mg of hydrodesulfurization catalyst, thiophene, benzothiophene, and dibenzothiophene each experienced measurable conversions into H$_2$S and hydrocarbon products. When 525 ppm of H$_2$S were included in the hydrogen stream, the conversion of dibenzothiophene decreased considerably (confirming that H$_2$S is a reaction inhibitor), and when CS$_2$ was included in the dibenzothiophene pulses, the conversion similarly decreased (again confirming the inhibition by H$_2$S, which formed rapidly from CS$_2$ under these conditions). When benzene was added to pulses containing benzothiophene, the conversion was also reduced (confirming that benzene is a reaction inhibitor).

A series of experiments was performed with a range of pulse volumes using pure compounds in the absence of solvent. The representative results shown in Fig. 1 demonstrate that the conversion decreased markedly with increasing pulse size,[6] and

[6] The decrease in conversion with increasing pulse size is consistent with the increasing depletion of hydrogen in the catalyst bed as the carrier stream was displaced by larger and larger pulses of reactant.
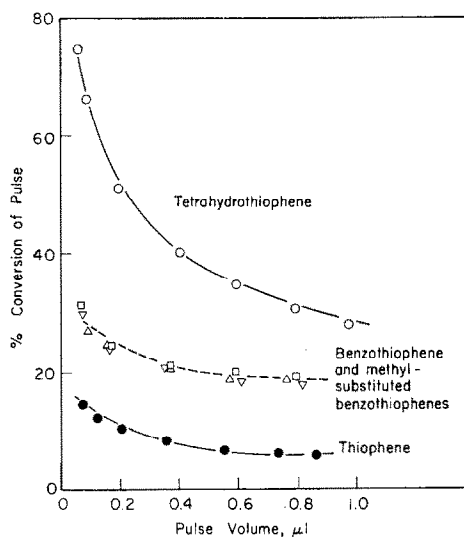

FIG. 1. Effect of pulse size on conversion in the microreactor. Conditions: catalyst, 3 mg of Ketjen CoO–MoO/γ-Al$_2$O$_3$; temperature, 375°C; pressure, 1 atm; H$_2$ flow rate, 40 cm^3 (STP)/min.

the ratio of conversions was approximately independent of pulse size. These results confirm that the pulse method gives a self-consistent set of reactivity data.

Thiophene conversion experiments with the Ketjen catalyst showed the lack of intraparticle mass transfer effects, since conversions with 28- to 48-mesh particles were the same as those with 270- to 400-mesh particles at 375 and 400°C. Similarly, there was no diffusion influence observed for conversion of dibenzothiophene at 450°C; the performance of 100- to 140-mesh particles of the American Cyanamid catalyst was indistinguishable from that of 28- to 48-mesh particles.

Most experiments were performed with reactant pulses including paraffinic solvents. Results of a series of experiments are summarized in Table 3. The conversion of dibenzothiophene decreased as temperature was increased from 350 to 400°C. A somewhat smaller conversion was observed for dibenzothiophene than for the substituted compound having methyl groups in the 2- and 8-positions. The

TABLE 3

Hydrodesulfurization of Reactant Pulses in the Presence of 5 mg of Sulfided American Cyanamid HDS-16A (CoO–MoO_3/γ–Al_2O_3): Comparison of Fresh and Broken-in Catalysts. Conditions—Pressure, 1 atm; H_2 Flow Rate, 40 cm³ (STP)/min; Pulse Size, 0.5 μl

Reactant	Reaction temperature (°C)	Fractional conversion with fresh catalyst	Fractional conversion with broken-in catalyst
Dibenzothiophene	350	0.31	0.064
	400	0.23	0.10
	450	0.25	0.12
2,8-Dimethyldibenzothiophene	450	0.70	0.24
4-Methyldibenzothiophene	450	0.13	0.047
4,6-Dimethyldibenzothiophene	450	0.09	0.023

compound with methyl groups in the 4- and 6-positions gave the lowest conversion.

After the experiments summarized in Table 3 were performed (during a period of 2 weeks), a decrease in catalytic activity was observed. Reduction of the catalyst in hydrogen at 350 to 450°C for 1 to 12 hr failed to restore the catalyst to its initial state. The results indicated, however, that the catalyst had assumed a stable "broken-in" condition, for which reproducibility of ±2% was observed for dibenzothiophene conversion at 450°C. In experiments with all the reactants that followed with this catalyst charge, periodic checks confirmed the stability of the broken-in catalyst. The following results, therefore, provide the desired self-consistent and repeatable data for hydrodesulfurization in the presence of a sulfided catalyst and a basis for comparing reactivities of the various compounds.

Reaction Networks and Relative Reactivities

Single-reactant pulses. The full series of available sulfur-containing compounds was studied with the broken-in catalyst. The group of substituted benzothiophenes is listed in Table 4 with the hydrocarbon products of the reaction of each. The results are consistent with the suggestion that direct sulfur extrusion was the primary reaction for these compounds, although

trace amounts of unidentified products were occasionally observed, and the reaction networks are still not fully characterized. One compound in this class, benzothiophene itself, was exceptional, giving not one, but two major hydrocarbon products, ethylbenzene and styrene.

The product analyses showed that dibenzothiophene and related compounds, like the benzothiophenes, can be considered to react by simple sulfur extrusion, since biphenyl and the corresponding methyl-substituted biphenyls were the major hydrocarbon products.

A summary of conversion data is given in Table 5; all the experiments were carried out with the broken-in catalyst at 450°C. Benzothiophene and dibenzothiophene had nearly the same reactivity, which was greater than that of thiophene. Hydrodesulfurization conversion was found to be almost identical for all the methylbenzothiophenes. When a second methyl group was added, the reactivity was reduced.

The result for 2,8-dimethyldibenzothiophene shows that methyl groups situated at a distance from the sulfur atom in the three-ring compound increase the reactivity. Methyl substituents in the β-position, however, reduce the reactivity, as shown by the results for 4-methyldibenzothiophene. The results for 4,6-dimethyl-

dibenzothiophene indicate that incorporation of the second methyl group in the β position reduces the reactivity only little.

The data of Table 5 show a rough parallel between the reactivity and the strength of adsorption of compounds in the dibenzothiophene family (determined from the holdup on the catalyst as calculated from mass balances). The amount held up on the catalyst decreased with incorporation of methyl groups in the 4-position or in the 4- and 6-positions (and the reactivity correspondingly decreased), and the amount held up increased with incorporation of methyl groups in the 2- and 8-positions (and the reactivity correspondingly increased).

Data for hydrogenated sulfur-containing compounds are collected in Table 6. These were found to be significantly more reactive than the corresponding aromatic compounds. Specifically, conversion of tetrahydrothiophene was 96%, and that of thiophene was 7%; conversion of 2,3-dihydrobenzothiophene was 71%, and that of benzothiophene was 14%; conversion of 1,2,3,4,10,11-hexahydrodibenzothiophene was 19%, and that of dibenzothiophene was 12%. These data show that the effect of prehydrogenation in increasing the reactivity decreases with an increase in the number of rings.

Besides hydrodesulfurization, dehydrogenation was also observed for both dihydrobenzothiophene and hexahydrodibenzothiophene. (Dehydrogenation products were not observed for tetrahydrothiophene.) Reaction of 2,3-dihydrobenzothiophene in hydrogen gave a substantial amount of benzothiophene in addition to ethylbenzene and styrene; the total conversion was about 97% compared with the hydrodesulfurization conversion of 71% reported in Table 6. For 1,2,3,4,10,11-hexahydrodibenzothiophene, the products included

TABLE 4

Structures of Benzothiophene and Related Reactants and Their Hydrodesulfurization Products
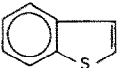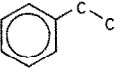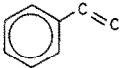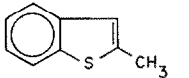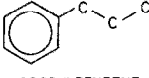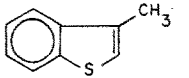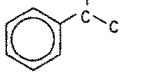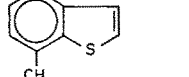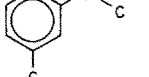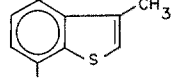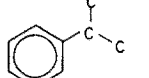

Reactant	Products
BENZOTHIOPHENE	ETHYLBENZENE STYRENE
2-METHYLBENZOTHIOPHENE	n-PROPYLBENZENE
3-METHYLBENZOTHIOPHENE	ISOPROPYLBENZENE
7-METHYLBENZOTHIOPHENE	m-ETHYLTOLUENE
3,7-DIMETHYLBENZOTHIOPHENE	3-ISOPROPYLTOLUENE

Hydrodesulfurization of Reactant Pulses in the Presence of Broken-in Catalyst: Conditions— Catalyst, 5 mg of Sulfided American Cyanamid HDS-16A (CoO–MoO$_3$/γ-Al$_2$O$_3$); Temperature, 450°C; Pressure, 1 atm; H$_2$ Flow Rate, 40 cm^3 (STP)/min; Pulse Size, 0.5 μl

Reactant	Fractional conversion	Holdup[a]
Dibenzothiophene	0.12	340
2,8-Dimethyldibenzothiophene	0.24	690
4-Methyldibenzothiophene	0.047	70
4,6-Dimethyldibenzothiophene	0.023	0
Benzothiophene	0.14	
2-Methylbenzothiophene	0.10	
3-Methylbenzothiophene	0.093	
7-Methylbenzothiophene	0.10	
3,7-Dimethylbenzothiophene	0.033	
Thiophene	0.070	

[a] Holdup is defined as the average of the glc peak areas of the sulfur-containing reactant obtained for a series of bypass injections less the sum of the desulfurized product and remaining reactant areas, averaged over a set of reactor injections.

dibenzothiophene and cyclohexylbenzene[7] as well as biphenyl, and the total conversion was about 58%. There were also trace amounts of another product which has not been identified.

Two-reactant pulses. To test the possibility that competitive adsorption phenomena might make the aforementioned results unrepresentative of more complex reactant mixtures, experiments were performed with a series of solutions containing two reactants. Solutions were prepared of each of the compounds listed in Table 7, with benzothiophene added to each to such an extent that half the sulfur was contained in benzothiophene. The data allowed calculation of the reactivity (conversion) of each of these components relative to that of benzothiophene. The results are listed

[7] Cyclohexylbenzene has previously been reported as a product of dibenzothiophene hydrodesulfurization in batch reactor experiments with MoS$_2$ (10, 22) and in flow reactor experiments with CoO–MoO$_3$/γ-Al$_2$O$_3$ (9).

in the right-hand column of Table 7. A comparison of these data with the relative reactivity data determined from the single-compound pulse experiments (shown in the center column of Table 7) indicates that the expected competition for surface catalytic sites between the sulfur-containing compounds does not significantly affect their relative reactivities as determined in the pulse experiment.

DISCUSSION

The results demonstrate that the reaction networks in hydrodesulfurization of benzothiophenes and of dibenzothiophenes at low pressure can be approximated as simple sulfur extrusions. The product distribution data are in agreement with those of other authors who performed experiments at atmospheric pressure (6, 23), and the apparent discrepancy between the present results and those of Givens and Venuto (5), who observed dealkylation and alkyl migration reactions, is suggested to be an indication of differences in reaction temperature and/or differences in structure between sulfided and unsulfided catalysts; the CoO–MoO$_3$/γ-Al$_2$O$_3$ catalyst used by Givens and Venuto was reduced in hydrogen but not sulfided before use.

The lack of observed aromatic ring saturation is in accord with the suggestion that ring hydrogenation is not a prerequisite to C–S bond scission and sulfur removal from benzothiophenes and dibenzothiophenes (6, 24). The presence of styrene in the product spectrum of benzo-
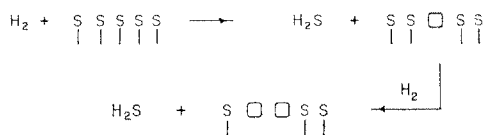
Hydrodesulfurization of Pulses of Hydrogenated Compounds at 450°C and 1 atm: Conditions—Same as for Table 5

Reactant	Fractional conversion
1,2,3,4,10,11-Hexahydrodibenzothiophene	0.19
2,3-Dihydrobenzothiophene	0.71
Tetrahydrothiophene	0.96

thiophene and of dihydrobenzothiophene is consistent with this suggestion (*23*), and the absence of sulfides and mercaptans in the products is in accord with the identification of the initial C–S bond breaking as a slow reaction step (*9*).

The near lack of dependence of reactivity on the number of rings in the reactant compound is supported by results of several authors, but it appears to contradict the results of some others (*19*). Bartsch and Tanielian (*6*) found that at 375°C and 1 atm, dibenzothiophene required about three times as much catalyst as benzothiophene for equal degrees of hydrodesulfurization, but their results were obscured by the influence of pore diffusion, which could account for the discrepancy. Obolentsev and Mashkina (*8*) reported that in high-pressure experiments, the ratio of rate constants for benzothiophene relative to dibenzothiophene was 2.8, and Frye and Mosby (*7*) and Nag *et al.* (*11*) found that in compounds of this group the reactivity at high pressure decreased even more significantly with an increased number of rings in the reactant. We suggest that the structure–reactivity patterns in hydrodesulfurization are different at low and high pressures, in part because surface coverages may be different, with the intrinsically

more reactive compounds (such as thiophene) present in lower surface concentrations than compounds like dibenzothiophene at low pressures, but possibly present in similar surface concentrations at high pressures. Further, the surface structure of a hydrodesulfurization catalyst [the sulfided form may be promoted MoS_2 on an alumina support (*25*)] may depend strongly on the hydrogen partial pressure, which, for example, may determine the number of surface anion vacancies by a reaction such as

$$H_2 + \underset{|}{S}\ \underset{|}{S}\ \underset{|}{S}\ \underset{|}{S}\ \longrightarrow\ H_2S + \underset{|}{S}\ \underset{|}{S}\ \square\ \underset{|}{S}\ \underset{|}{S}$$

$$H_2S + \underset{|}{S}\ \square\ \square\ \underset{|}{S}\ \underset{|}{S}\ \overset{\displaystyle \underset{|}{H_2}}{\longleftarrow}$$

This suggestion is speculative and in need of critical evaluation, but it provides a basis for interpretation of structure–reactivity data, and it is consistent with the suggestion of a number of authors of the existence of more than one kind of surface site (*21, 25, 26*). Perhaps one kind of site (such as an adjacent pair of anion vacancies) might allow one kind of adsorption (such as a flat adsorption involving the π electrons of the aromatic system and perhaps also the sulfur atom), consistent with the observed inhibition by benzene; another kind of site (such as a single anion vacancy) might allow another kind of adsorption (such as an end-on adsorption with the sulfur atom at the anion vacancy), which might explain the high reactivities observed for the hydrogenated compounds which lack π electrons required for the flat adsorption.

The small enhancement in dibenzothiophene reactivity upon incorporation of methyl groups in the 2- and 8-positions may be explained by electronic effects, i.e., a combination of induction and hyperconjugation of the methyl groups at positions *para* to the two α-carbon atoms of the reactant could enrich their respective electron densities and increase the

TABLE 7

Hydrodesulfurization of Pulses Having Two Sulfur-Containing Compounds at 450°C and 1 atm: Conditions—Same as for Table 5[a]

Reactant	Relative reactivity[b]	Relative reactivity[c]
Dibenzothiophene	0.84	0.50
2,8-Dimethyldibenzothiophene	1.8	1.3
4-Methyldibenzothiophene	0.34	0.16
4,6-Dimethyldibenzothiophene	0.17	0.06
1,2,3,4,10,11-Hexahydrodibenzothiophene	1.3	0.54
7-Methylbenzothiophene	0.70	0.55
Thiophene	0.51	0.62
Tetrahydrothiophene	6.7	3.3

[a] Note: Relative reactivity is defined as fractional conversion of the reactant/fractional conversion of benzothiophene.

[b] Relative reactivity for one-reactant pulses.

[c] Relative reactivity for two-reactant pulses.

reactivity with an acidic catalytic surface site. The decrease in conversion caused by methyl substituents in the β-position can be explained by a small steric hindrance, i.e., a shielding of the lone pair electrons on sulfur by the hydrogens of either of the two methyl groups, which would reduce the bonding of the sulfur atom at a surface catalytic site.

Little literature is available for comparison with the results of Table 6 for the hydrogenated compounds. Desikan and Amberg (28) and Kolboe (2) compared the reactivities of thiophene and tetrahydrothiophene. The former authors showed tetrahydrothiophene to be more reactive than thiophene over the range 270 to 372°C. Kolboe found, however, that a 288°C, thiophene and tetrahydrothiophene were desulfurized at almost equal rates. Givens and Venuto (5) reported a rapid equilibrium between benzothiophene and 2,3-dihydrobenzothiophene, and Furimsky and Amberg (23) reported dihydrobenzo-thiophene:benzothiophene conversion ratios of 3 to 7, depending on catalyst loading and temperature; the latter result is consistent with results of this work. Again, we suggest that the apparent inconsistencies may be explained by differences in catalyst structure influenced by the nature of sulfiding, and perhaps the hydrogen partial pressure may be important in determining reactivity patterns.

REFERENCES

1. Owens, P. J., and Amberg, C. H., *Advan. Chem. Ser.* 33, 182 (1961).
2. Kolboe, S., *Canad. J. Chem.* 47, 2623 (1969).
3. Mikovksy, R. J., Silvestri, A. J., and Heinemann, H., *J. Catal.* 34, 324 (1974).
4. Papadopoulos, R., and Wilson, M. J. G., *Chem. Ind.* 6, 427 (1965).
5. Givens, E. W., and Venuto, P. B., *Amer. Chem. Soc. Prepr., Div. Petrol. Chem.* 15 (4), A183 (1970).
6. Bartsch, R., and Tanielian, C., *J. Catal.* 35, 353 (1974).
7. Frye, C. G., and Mosby, J. F., *Chem. Eng. Progr.* 63 (9), 66 (1967).
8. Obolentsev, R. D., and Mashkina, A. V., *Dokl. Akad. Nauk SSR* 131, 1092 (1960).
9. Rollmann, L. D., *Amer. Chem. Soc. Prepr., Div. Fuel Chem.* 21 (7), 59 (1976); *J. Catal.* 46, 243 (1977).
10. Landa, S., and Mrnkova, A., *Collect. Czech. Chem. Commun.* 31, 2202 (1966).
11. Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., to appear.
12. Kokes, R. J., Tobin, H., and Emmett, P. H., *J. Amer. Chem. Soc.* 77, 5860 (1955).
13. Werner, E. G. G., *Rec. Trav. Chim.* 68, 509 (1949).
14. Banfield, J. E., Davies, W., Gamble, N. W., and Middleton, S. J., *J. Chem. Soc.*, 4791 (1956).
15. Hansch, C., and Lindwall, H. G., *J. Org. Chem.* 10, 383 (1945).
16. Suthankar, A. V., and Tilak, B. D., *Proc. Ind. Acad. Sci.* 324, 396 (1950).
17. Campaigne, E., Hewitt, L., and Ashby, J., *J. Heterocyclic Chem.* 6, 553 (1969).
18. Gerdil, R. and Lucken, E. A. C., *J. Amer. Chem. Soc.* 87, 213 (1965).
19. Kilanowski, D. R., Ph.D. thesis, University of Delaware, Newark, 1979.
20. de Beer, V. H. J., Ph.D. thesis, University of Technology, Eindhoven, The Netherlands, 1975.
21. Schuit, G. C. A., and Gates, B. C., *Amer. Inst. Chem. Eng. J.* 19, 417 (1973).
22. Urimoto, H., and Sakikawa, N., *Sekiyu Gakkaishi* 15, 926 (1972).
23. Furimsky, E., and Amberg, C. H., *Canad. J. Chem.* 54, 1507 (1976).
24. de Beer, V. H. J., Dahlmans, J. G. J., and Smeets, J. G. M., *J. Catal.* 42, 467 (1976).
25. Farragher, A. L., and Cossee, P., *in* "Proceedings of the Fifth International Congress on Catalysis" (J. W. Hightower, Ed.), p. 1301. North Holland, Amsterdam, 1973.
26. Tanaka, K., Okuhara, T., Sato, S., and Miyahara, K., *J. Catal.* 43, 360 (1976).
27. Desikan, P., and Amberg, C. H., *Canad. J. Chem.* 42, 843 (1964).