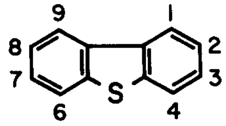
JOURNAL OF CATALYSIS **61**, 523–527 (1980)

Hydrodesulfurization of Methyl-Substituted Dibenzothiophenes Catalyzed by Sulfided Co–Mo/γ-Al_2O_3

Although hydrodesulfurization of petroleum residua is widely practiced and the need for similar technology for coal-derived liquids is well recognized, there is only little literature reporting the relative reactivities of various sulfur-containing compounds found in the heavy feedstocks (*1*). Akhtar *et al.* (*2*) identified a number of the thiophenic compounds liberated from coal during liquefaction/hydroprocessing. These include thiophene, benzo[*b*]-thiophene, dibenzothiophene (DBT), and benzo[*b*]naphtho[2,3-*d*]thiophene. Under typical hydroprocessing conditions (300°C, 71 atm), DBT has been found to be the least reactive of these compounds (*3*). Since methyl groups are the predominant substituent groups on the aromatic molecules of coal-derived liquids, abundant and relatively unreactive methyl-substituted dibenzothiophenes evidently represent the class of thiophenic compounds most in need of study.

Qualitative studies of the reactivities of these compounds with a pulse microreactor operated at low pressures (*4*) with sulfided Co–Mo/γ-Al_2O_3 catalyst have shown that incorporation of methyl groups in the 4 or 4 and 6 positions of DBT reduced the reactivity significantly, consistent with Beuther's (*5*) report (based on experiments for which the catalyst and reaction conditions were not specified) that incorporation of methyl groups in the 4 and 6 positions led to roughly a 100-fold decrease in the rate of hydrodesulfurization. Incorporation of methyl substituents in the 2 and 8 positions of DBT, however, led to slightly increased reactivities, as measured by conversions in the pulse microreactor (*4*).



DBT

The objective of the experiments described here was to provide a quantitative measure of the reactivities of these compounds under high-pressure reaction conditions representative of industrial practice. A flow microreactor (*6*) was used with liquid feeds containing *n*-hexadecane (carrier oil), H_2, and either a single sulfur-containing compound [e.g., 4-methyldibenzothiophene (4-MeDBT)] or a pair of sulfur-containing compounds, one of them being DBT.

The results show that, to a first approximation, each of the compounds reacted by simple sulfur extrusion (with DBT, for example, giving primarily biphenyl + H_2S). Methyl substituents in the 4 and 4 and 6 positions (but not the others) reduced the reactivity significantly. The competitive reaction studies indicate competitive adsorption of the sulfur-containing reactants, with the less reactive compounds being less strongly adsorbed and being less effective as inhibitors.

The catalyst was commercial Co–Mo/γ-Al_2O_3 (American Cyanamid HDS 16A), from the same batch used in related studies (*3, 4, 6, 7*). The physical properties and composition are given elsewhere (*7*). A catalyst charge was 0.025 g diluted with 0.625 g of inert alundum particles; the catalyst particles were 149–178 μm in dimension, demonstrated experimentally to be small enough to ensure the absence of intraparticle mass transfer influence. The

0021-9517/80/020523-05$02.00/0

catalyst bed was 4.4 cm long with a volume of 0.32 cm^3.

The catalyst was sulfided *in situ* prior to the hydrodesulfurization experiments; it experienced a flow of 10 vol% H_2S in H_2 at 400°C for 2 hr. The hydrodesulfurization experiments were carried out with a liquid feed rate ranging from 0.6 to 12 cm^3/hr; the reactor pressure was 102 atm, and the temperature was 300°C. All conversion data were obtained under steady-state operating conditions, as demonstrated by the agreement of several successive product analyses. Catalyst deactivation, measured by the decrease in a pseudo-first-order rate constant, was typically $<10\%$.

The *n*-hexadecane was supplied by Humphrey Chemical Company and was redistilled before use. Each feed solution was purged with H_2 and saturated with H_2 at 68 atm and room temperature. DBT (95%) was obtained from Aldrich Chemical Company. The 4-MeDBT (*8*) and the dimethyl-substituted dibenzothiophenes (*9*) were synthesized according to published methods.

In a typical kinetics run, after the catalyst had been sulfided in the reactor, the reactant mixture was supplied to the feed pump, and the desired flow rate was set. The liquid feed flowed through the catalyst bed to a dead-volume cylinder. In the routine experiments, the product stream was sampled every several hours, and the products (except H_2S) were analyzed with a gas chromatograph (glc) equipped with a flame ionization detector (*7*). Occasionally, more thorough analyses were done to obtain mass spectra of the individual products and to search for side products. Preparative glc was used, with a 5 ft × 0.25 in. o.d. column packed with 10% SP2100 (Supelco) held at 200°C with a He flow rate of 40 cm^3/min. The collected products were identified and analyzed with a glc–mass spectrometer system. Products were also occasionally concentrated by solvent extraction and column chromatography prior to analysis by glc–mass spectrometry.

Integral conversion data were collected individually for each of the five reactant compounds listed in Table 1, and in separate experiments, DBT was mixed with each of the other four compounds. The observed conversions were calculated on the basis of disappearance of the respective sulfur-containing compounds. The H_2 concentrations in the liquid feeds were estimated from the equilibrium solubility of hydrogen in *n*-hexadecane at room temperature (the temperature at which the feed solutions were prepared) (*10*). The lowest H_2 : sulfur-containing reactant ratio was

TABLE 1

Pseudo-First-Order Rate Constants for Hydrodesulfurization Catalyzed by Sulfided Co–Mo/γ-Al_2O_3 at 300°C and 102 atm

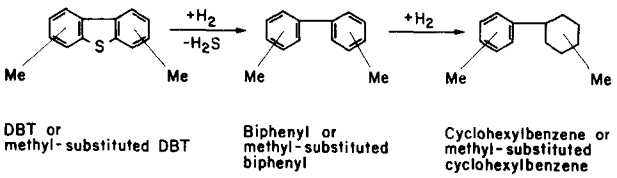
Sulfur-containing reactant	Concentration (mole%)	Pseudo-first-order rate constant[a] [cm^3/(g of catalyst · hr)]	Second sulfur-containing reactant	Concentration (mole%)	Pseudo-first-order rate constant for second sulfur-containing reactant[a] [cm^3/(g of catalyst · hr)]
Dibenzothiophene	0.058	258.4 ± 10.3	None	—	—
Dibenzothiophene	0.130	77.5 ± 11.8	None	—	—
2,8-Dimethyldibenzothiophene	0.075	241.9 ± 23.5	None	—	—
3,7-Dimethyldibenzothiophene	0.072	126.5 ± 10.2	None	—	—
4-Methyldibenzothiophene	0.071	23.9 ± 1.2	None	—	—
4,6-Dimethyldibenzothiophene	0.064	17.7 ± 2.8	None	—	—
2,8-Dimethyldibenzothiophene	0.057	233.3 ± 9.2	Dibenzothiophene	0.065	88.1 ± 8.0
3,7-Dimethyldibenzothiophene	0.070	108.3 ± 11.5	Dibenzothiophene	0.074	66.4 ± 3.5
4-Methyldibenzothiophene	0.073	28.4 ± 1.9	Dibenzothiophene	0.081	100.8 ± 1.4
4,6-Dimethyldibenzothiophene	0.080	21.7 ± 5.0	Dibenzothiophene	0.071	213.8 ± 48.4

[a] Data are reported with 95% confidence limits.

about 35 moles/mole. Assuming a H_2 consumption of two molecules per molecule of sulfur-containing compound, the maximum decrease in the H_2 concentration in the reactant mixture was only 6% at 100% conversion of the sulfur-containing compound; consequently, the H_2 concentration was virtually constant in all the experiments.

Since the reactor operated in nearly piston flow (*6*), the reaction order in the sulfur-containing reactant could be determined straightforwardly. The results in Fig. 1 show that pseudo-first-order kinetics describes the conversion of each of the sulfur-containing reactants used singly; similar linear plots were obtained when pairs of the reactants were fed to the reactor. Table 1 summarizes the pseudo-first-order rate constants calculated from the integral conversion data, with 95% confidence limits on the linear regression parameter (*11*).

The detailed reaction network for hydrodesulfurization of DBT in the presence of low H_2S concentrations has been reported elsewhere (*7*). The results obtained here are consistent with the earlier results and show that, to a first approximation, the following network pertains to the whole group of methyl-substituted dibenzothiophenes:



For DBT, the pseudo-first-order rate constant for the first of these two reactions is about six times greater than that for the second (*7*).

The product distribution data obtained with 2,8-DiMeDBT and 3,7-DiMeDBT conform closely to this network, but the product distribution data obtained with 4-MeDBT and 4,6-DiMeDBT are somewhat different. The yields of the substituted cyclohexylbenzene products formed from the latter two compounds were 5 to 10 times greater than the yield of cyclohexylbenzene formed from DBT under comparable conditions. These results suggest that the reactants with methyl groups in the 4 or in the 4 and 6 positions experienced more hydrogenation prior to sulfur removal than the others.

Increasing the feed concentration of DBT about twofold decreased the pseudo-first-order rate constant more than threefold (Table 1), suggesting self-inhibition of reaction by DBT and qualitatively confirming

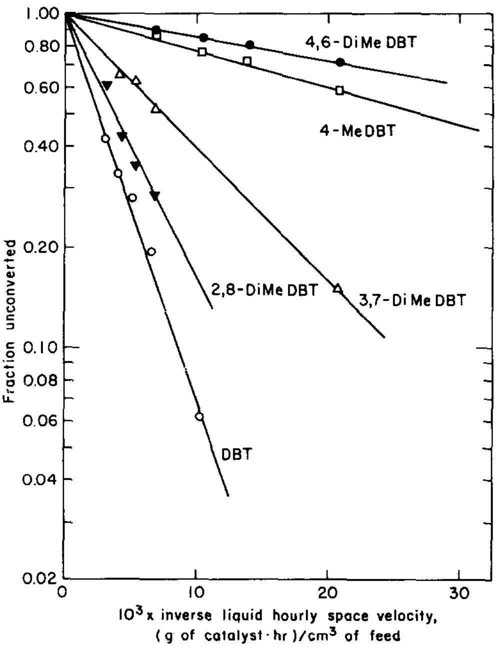


FIG. 1. Pseudo-first-order kinetics of hydrodesulfurization of dibenzothiophene and methyl-substituted dibenzothiophenes. Reaction in a flow microreactor was catalyzed by sulfided Co–Mo/Al_2O_3 at 300°C and 102 atm.

the expectation based on the kinetics results of Espino *et al* (*12*).

The data obtained with reactants used singly (Table 1) show that methyl groups added to the 2 and 8 positions of DBT hardly changed the reactivity, and methyl groups in the 3 and 7 positions also had only a small effect. Methyl groups in the 4 position, however, reduced the reactivity by an order of magnitude, and methyl groups in the 4 and 6 positions reduced it somewhat more. When DBT was added in turn to a solution of each of these methyl-substituted compounds, the order of the reactivities was the same as mentioned previously, with the pseudo-first-order rate constants of the substituted compounds being almost the same as those found in the experiments with these reactants used singly.

When DBT was in the reactant solution with 2,8-DiMeDBT or 3,7-DiMeDBT, the pseudo-first-order rate constant for DBT (in contrast to those for the methyl-substituted compounds) was reduced significantly—about as much as when a corresponding amount of DBT itself was added to the reactant solution (Table 1). This result implies that there was competitive adsorption of DBT and the methyl-substituted DBT, as was expected from the occurrence of the self-inhibition by DBT. The contrasting result that DBT did not strongly inhibit the reaction of 3,7-DiMeDBT or of 2,8-DiMeDBT (Table 1) indicates that these methyl-substituted compounds were more strongly adsorbed than DBT. The effect of 4,6-DiMeDBT on the reactivity of DBT, on the other hand, is almost negligible, demonstrating that it is more weakly adsorbed than DBT. Following this line of reasoning, we interpret the data of Table 1 as suggesting that 4-MeDBT has an adsorption strength between those of DBT and 4,6-DiMeDBT. The strengths of adsorption indicated by holdup in a pulse microreactor (*4*) are in accord with the foregoing interpretation.

Although it is not clear why DBT appears to have almost no influence on the reactivity of the presumably less strongly adsorbed 4-MeDBT and 4,6-DiMeDBT (Table 1), it can be inferred that the reactivity depends on the rate of hydrogen transfer from the catalyst surface, which is apt to be affected by orientation of the reactant on the surface. We emphasize that the patterns of competitive adsorption and intrinsic reactivity of adsorbed reactants are still incompletely resolved; more thorough kinetics and adsorption studies are required. The data presented here are, however, supportive of the idea [presented elsewhere (*3, 7, 13–15*)] that adsorption of the reactants involves bonding to the catalyst surface with the π electrons of the benzenoid rings as well as with the sulfur atom; mild steric effects explain the influence of methyl groups in the 4 and 6 positions.

ACKNOWLEDGMENTS

This research was supported by the Department of Energy. D. H. Broderick was supported by a National Science Foundation energy-related traineeship.

REFERENCES

1. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw-Hill, New York, 1979.

2. Akhtar, S., Sharkey, A. G., Schultz, J. C., and Yavorsky, P. M., Paper Presented at ACS Meeting, Los Angeles, March–April 1974.

3. Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., *J. Catal.* **57**, 509 (1979).

4. Kilanowski, D. R., Teeuwen, H., de Beer, V. H. J., Gates, B. C., Schuit, G. C. A., and Kwart, H., *J. Catal.* **55**, 129 (1978).

5. Beuther, H. Paper Presented at ACS Meeting on Coal Conversion Catalysis, Pittsburgh, April 1975.

6. Eliezer, K. F., Bhinde, M., Houalla, M., Broderick, D., Gates, B. C., Katzer, J. R., and Olson, J. H., *Ind. Eng. Chem. Fundam.* **16**, 380 (1977).

7. Houalla, M., Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., *AIChE J.* **24**, 1015 (1978).

8. Campaigne, E., Hewitt, L., and Ashby, J., *J. Heterocycl. Chem.* **6**, 553 (1969).

9. Gerdil, R., and Lucken, E. A. C., *J. Amer. Chem. Soc.* **87**, 213 (1965).

10. Cukor, P. M., and Prausnitz, J. M., *J. Phys. Chem.* **76**, 598 (1972).

11. Draper, N. R., and Smith, H., "Applied Regression Analysis," Wiley, New York, 1966.

12. Espino, R. L., Sobel, J. E., Singhal, G. H., and Huff, G. A., *Prepr. Amer. Chem. Soc. Div. Petrol. Chem.* **23** (1), 46 (1978).
13. Cowley, S. W., Ph.D. thesis, Southern Illinois University, 1975.
14. Singhal, G. H., and Espino, R. L., *Prepr. Amer. Chem. Soc. Div. Petrol. Chem.* **23** (1), 36 (1978).
15. Kwart, H., Schuit, G. C. A., and Gates, B. C., *J. Catal.*,

M. HOUALLA
D. H. BRODERICK
A. V. SAPRE
N. K. NAG
V. H. J. DE BEER[1]
B. C. GATES[2]
H. KWART

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

Received February 26, 1979; revised July 26, 1979

---

[1] Present address: Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands.

[2] To whom correspondence should be addressed at Department of Chemical Engineering.