p_n = roots of Eq. 8
P = total pressure in system
q = adsorbed-phase concentration expressed on an intracrystalline basis (mol sorbate/g crystal)
q^* = equilibrium value of q
q_o, q_∞ = initial and final steady values of q
q_m = saturation value of q in Langmuir equation
q_s = value of q at crystal surface
$\bar{q}$ = average value of q through the adsorbent bed
Q = defined in Eq. 6
r = equivalent radius of zeolite crystal (cm)
T = sample temperature (°K)
T_o = initial value of T
t = time (s)
y = distance from surface of adsorbent bed (cm)
$-\Delta H$ = heat of sorption (J/mol)
ρ = density of zeolite crystal (g/mL)
ϵ = voidage of adsorbent sample
τ = dimensionless time variable, $D_e t/l^2$
α = $(ha/\rho C_p)\,(D_e/l^2)^{-1}$
β = $\dfrac{\Delta H}{C_p} \cdot \dfrac{\partial q^*}{\partial T}$
χ = tortuosity factor
θ = fractional coverage ($\equiv q/q_m$)

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Hydrogenolysis and Hydrogenation of Dibenzothiophene Catalyzed by Sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$: The Reaction Kinetics

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SCOPE

Upgrading of heavy petroleum fractions and synthetic fuels requires high-pressure catalytic hydroprocessing, whereby sulfur-containing organic molecules react with H_2 at (10-20) × 10^6 Pa to produce H_2S and desulfurized organic products. Thiophenic compounds such as the three-ring dibenzothiophene and the four-ring benzo(*b*)naphtho(2,3-*d*)thiophene represent the least reactive sulfur-containing constituents of heavy feedstocks and are, therefore, the key components in determining process kinetics.

The reaction network involving hydrodesulfurization and hydrogenation of dibenzothiophene has been determined under conditions similar to those of commercial processes (573°K and 10^7 Pa) (Houalla et al., 1978). The results presented here include the kinetics of dibenzothiophene hydrodesulfurization and hydrogenation under similar conditions [548-598°K and 1.8 × 10^7 Pa]. Data were obtained for fresh, stable, sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ (American Cyanamid HDS 16A) with an isothermal piston-flow reactor operating at steady state.

Rates were determined from differential conversion data for hydrodesulfurization and hydrogenation of dibenzothiophene, with the concentrations of the following compounds (in units of kg mol/m^3) having been varied systematically over the ranges indicated: dibenzothiophene (0.008-0.13), H_2 (0.076-0.30), biphenyl (0.00-0.08), and H_2S (0.001-0.068). The results represent the first thorough, quantitative determination of the kinetics of high-pressure catalytic hydroprocessing reactions.

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CONCLUSIONS AND SIGNIFICANCE

In hydrodesulfurizaton in the presence of sulfided CoO-MoO_3/γ-Al_2O_3 catalyst at 548-598°K and 1.8×10^7 Pa, dibenzothiophene reacts by two parallel routes: 1) hydrogenolysis of the C—S bonds to give H_2S and biphenyl; and 2) hydrogenation of one of the benzenoid rings followed by rapid hydrogenolysis of the C—S bonds to give cyclohexylbenzene. The rate data for hydrogenolysis and for hydrogenation were fitted to equations of the Langmuir-Hinshelwood type. For hydrogenolysis, Equation 3 is recommended on the basis of goodness of fit and other conventional criteria, although other equations of similar form are nearly as good. Equation 3 shows that H_2 and dibenzothiophene at the highest concentrations each approached saturation of the catalyst surface, and H_2S strongly inhibited the reaction. For hydrogenation, Equation 7 is recommended as the simplest equation giving a good fit to the data and meeting the conventional criteria. The reaction is first order in H_2 concentration, and the Langmuir dependence indicated that saturation of the surface by dibenzothiophene was approached at the highest concentrations. In contrast to hydrogenolysis, hydrogenation was not inhibited by H_2S.

The results imply that the catalytic sites and mechanism for hydrogenolysis and hydrogenation are different, and the lack of adsorption of H_2S on the catalytic sites for hydrogenation is a new and surprising result.

Because of the differences in the kinetics of the two reactions, the selectivity (rate of hydrogenolysis/rate of hydrogenation) is strongly affected by temperature and H_2S concentration. The kinetics results are recommended for preliminary process design estimates of the dependence of selectivity, rates of reaction, and hydrogen consumption on concentrations of H_2S, H_2 aromatic hydrocarbons, and compounds like dibenzothiophene, and temperature.

A renewed interest in hydrodesulfurization has come about largely as a result of the need to process more and heavier feedstocks, including synfuels. It has been recognized that the frequently studied model compound thiophene is not representative of the least-reactive sulfur-containing constituents of these feedstocks. More representative compounds are dibenzothiophene and benzo(*b*)naphtho(2,3-*d*)thiophene, which are present in high concentrations in heavy oils and in coal-derived liquids and are one to two orders of magnitude less reactive than thiophene (Houalla et al., 1980; Nag et al., 1979).

There is a need for quantitative kinetics characterizing hydroprocessing of these relatively unreactive compounds at temperatures and pressures representative of commercial operation. The goal of this research was to determine detailed kinetics of dibenzothiophene hydrodesulfurization using a high-pressure flow microreactor (Eliezer et al., 1977).

Earlier work had established the reaction network in dibenzothiophene hydrodesulfurization in the presence of commercial, presulfided CoO-MoO_3/γ-Al_2O_3 catalyst (Houalla et al., 1978). Early kinetics studies of dibenzothiophene hydrodesulfurization (Obolentsev and Mashkina, 1958, 1959) fail to account for the complete reaction network and are lacking in experimental detail. Recent kinetics studies of dibenzothiophene hydrodesulfurization (Espino et al., 1978; Myers and Robinson, 1978) also fail to account for the reaction network in sufficient detail; further, the range of H_2 partial pressures was low, and not all the parameters in the rate equations could be determined from the data.

In this study, rates of the two primary reactions of dibenzothiophene with H_2 have been measured independently. The full set of data has been analyzed and summarized in the form of Langmuir-Hinshelwood rate equations. The data allowed precise estimation of all the kinetics parameters at three temperatures.

EXPERIMENTAL

Materials

The catalyst was a commercial CoO-MoO_3/γ-Al_2O_3 (American Cyanamid HDS 16A) which was crushed and sieved to 149-178 μm (80-100 mesh) particle size and sulfided *in situ*. Catalyst compositions are given elsewhere (Houalla et al., 1978). Dibenzothiophene (Eastman, reagent grade) was dissolved in *n*-hexadecane (Humphrey Chemical Company, specially distilled Lots No. 2270375 and No. 4090577), and the solution was filtered through an 0.5-μm filter element (Milipore). Biphenyl (Eastman, reagent grade) was used as supplied. H_2 was obtained from Linde as 3500 psi grade and treated as described below to remove traces of moisture and oxygen. H_2S was supplied by Linde in custom mixtures with H_2 in concentrations of 0.5-10 mol % H_2S. Alundum "RR" (Fisher Scientific, Blue Label) (approximately 90 mesh) was used as an inert reactor packing.

A high-pressure, packed-bed flow microreactor, described in detail by Eliezer et al. (1977), was modified to allow for saturation of the feed mixture with a predetermined H_2S partial pressure (Broderick, 1980). The catalyst (6.5×10^{-5} to 1.2×10^{-4} kg) was mixed with alundum [$(2.31$-$4.25) \times 10^{-4}$ kg] to give the range of bed volumes [$(2.0$-$3.6) \times 10^{-7}$ m^3] and bed heights [$(2.5$-$4.5) \times 10^{-2}$ m]. The catalyst was presulfided in the reactor for 7.2×10^3 s, experiencing a $(5$-$8) \times 10^{-7}$ m^3/s flow of 10 vol % H_2S in H_2 at atmospheric pressure and 673°K.

Reactant solutions containing dibenzothiophene or dibenzothiophene and biphenyl in a carrier oil (*n*-hexadecane) were prepared and were loaded into an autoclave. The reactant mixture was stirred and brought to saturation with H_2 or with H_2 plus H_2S at predetermined partial pressures after the solution had been purged with the gas mixture for 7.2×10^3 s. Calculations of H_2 and H_2S concentrations in the reactor were based on low-pressure gas solubility data extrapolated to high saturation pressures, as described elsewhere (Broderick, 1980). Reactant concentrations used to correlate the reaction rate data were calculated for the liquid at the temperature and pressure of the reactor; no gas phase was present.

Immediately after sulfiding of the catalyst, the reactor was cooled to 573°K, and flow of the reactant mixture was started. The pressure was maintained at $(1.8 \pm 0.1) \times 10^7$ Pa to ensure that no gas formed in the reactor. A catalyst break-in period of $(1.8$-$2.6) \times 10^5$ s was allowed, after which the reactor was operated with low (differential) conversions of dibenzothiophene to provide reaction rate data. Over an extended period, H_2 partial pressures were varied from 3.4×10^6 to 1.6×10^7 Pa (corresponding to 0.076-0.30 kg mol of H_2/m^3 at reactor conditions), dibenzothiophene concentrations were varied from 0.008 to 0.13 kg mol/m^3, and three biphenyl concentrations (0.0, 0.016, and 0.08 kg · mol/m^3) were investigated; temperature was controlled at 548, 573, and 598°K for each combination of reactant and product concentrations studied. Throughout each run, the rate of reaction was repeatedly measured under the standard conditions of 573°K, 9.7×10^6 Pa H_2 partial pressure (0.19 kg mol/m^3), 0.032 kg mol of dibenzothiophene/m^3, 1.6×10^4 Pa H_2S partial pressure (0.02 kg mol/m^3); these data demonstrated the lack of significant catalyst deactivation (Figure 1).

At each condition, 4-8 liquid product samples were collected and analyzed by gas chromatography (glc). An Antek 462 gas chromatograph equipped with a flame ionization detector and an electronic integrator was used. The column was a 3.4-m stainless steel column having a 2.3×10^{-3}-m ID and packed with 3% SP-2100 DB (methyl silicon 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} m^3/s. Gaseous products, such as H_2S and any light cracking products, were not collected.

TABLE 1. TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT K_X

Temperature, °K	K_X^a
548	5.76 ± 0.29
573	3.45 ± 0.33
598	2.05 ± 0.17

$K_X = \exp(-\Delta G°/RT)$

$-\Delta G° = -5.6 \times 10^7 + T(°K) \times 4.4 \times 10^4$ J/kg mol

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[a] K_X is defined as $X_{HHDBT}/X_{H_2}X_{THDBT}$ where X_i is the mole fraction of species i. K_X was calculated for various X_{H_2} and averaged. Error bound is standard deviation.

In the routine analysis, dibenzothiophene, biphenyl, cyclohexylbenzene, and 1,2,3,4-tetrahydrodibenzothiophene (THDBT) were determined quantitatively. Another product was formed in equilibrium with THBDT, namely, 1,2,3,4,10,11-hexahydrodibenzothiophene (HHDBT) (Houalla et al., 1978), and it was masked in the glc traces by the solvent peak. Therefore, sufficient samples were reanalyzed to establish the equilibrium constant for the reaction (THDBT + $H_2 \rightleftharpoons$ HHDBT) at the three temperatures studied. A wall-coated open tubular column (Perkin-Elmer OV-101) was used in a Perkin-Elmer 3920 B gas chromatograph for these analyses. The equilibrium constants are given in Table 1. Using these results, the concentration of HHDBT was calculated for each sample.

RESULTS

Preliminary experiments reported earlier (Houalla et al., 1978) showed that the reactor filled with alundum alone had negligible activity for dibenzothiophene hydrodesulfurization, and the reactor operated in virtual piston flow. Experiments described in Broderick's thesis (1980) confirmed the lack of an influence of catalyst particle size on reaction rate, and calculations with standard correlations confirmed the absence of significant intraparticle and interparticle gradients in concentration and temperature (Broderick, 1980).

Early attempts to measure differential conversions of dibenzothiophene were carried out with feed mixtures containing no H_2S. After the break-in period, H_2 and dibenzothiophene concentrations and temperature were changed systematically, and the rate of reaction was determined at each condition. Catalyst activity, measured by the rate of dibenzothiophene disappearance under the standard conditions (except for the absence of H_2S), was observed to fluctuate and to decline with time (Figure 1). Scattered and irreproducible rates were observed throughout the run.

Addition of at least 0.02 kg mol of H_2S/m^3 of reactant solution was found to be necessary to stabilize the catalyst (Broderick et al., 1978). With the resulting constant catalytic activity (as shown in Figure 1), conversions were determined for a wide range of reactant and product concentrations at 548, 573 and 598°K. Concentrations and temperatures were changed randomly throughout with periodic activity checks at the standard conditions. The full set of data is given elsewhere (Broderick, 1980).

At each set of conditions, feed flow rate was set such that the conversion of dibenzothiophene was normally $\leq 14\%$. Conversions in this region were linearly dependent on the inverse of weight hourly space velocity ($WHSV^{-1}$, kg of catalyst h/kg of feed), as shown by typical data in Figure 2. Therefore, the data determined reaction rates directly.

Data were plotted (Figure 2) showing conversion of dibenzothiophene to cyclohexylbenzene, to biphenyl, and to cyclohexylbenzene plus THDBT plus HHDBT. The latter two plots show a linear dependence of conversion on $WHSV^{-1}$, and the first set of data falls near a curve that approaches the origin with near-zero slope. These results are consistent with the reaction network proposed for dibenzothiophene hydrodesulfurization by Houalla et al. (1978). This network (Figure 3) indicates two

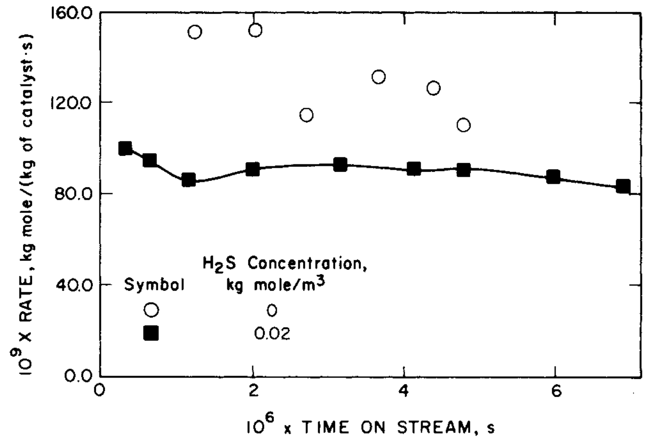

Figure 1. Hydrodesulfurization of dibenzothiophene catalyzed by sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ at 1.8×10^7 Pa and 573°K. The data show the stabilizing effect of H_2S in the feed on catalyst activity. The lower set of data shows reproducibility of rate measurement and constant activity during the kinetics experiments.

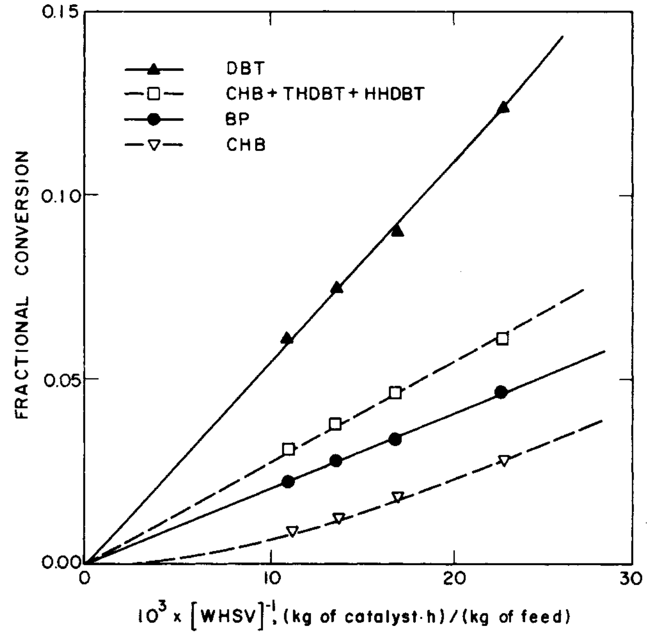

Figure 2. Differential conversion of dibenzothiophene, giving biphenyl as the product of hydrogenolysis and giving a mixture of cyclohexylbenzene, THDBT, and HHDBT as products of hydrogenation. Data were obtained at 573°K and 1.8×10^7 Pa. Feed concentrations were: 0.032 kg mol of dibenzothiophene/m^3, 0.195 kg mol of H_2/m^3, and 0.021 kg mol of H_2S/m^3 in n-hexadecane.

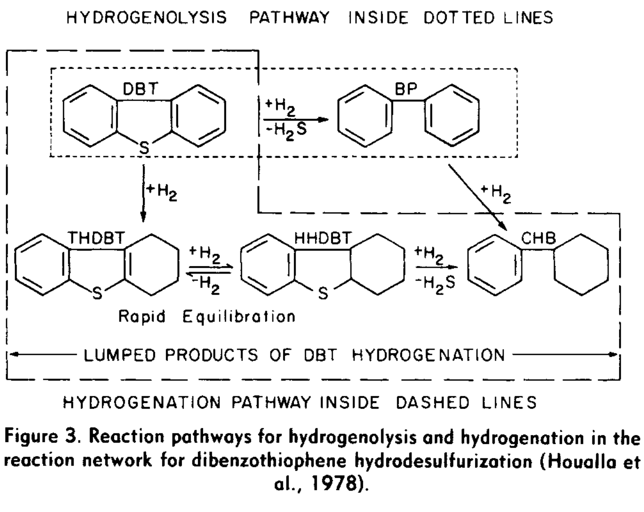

Figure 3. Reaction pathways for hydrogenolysis and hydrogenation in the reaction network for dibenzothiophene hydrodesulfurization (Houalla et al., 1978).

TABLE 2. SUMMARY OF THE MEASURED RATES OF HYDROGENOLYSIS, HYDROGENATION, AND TOTAL DISAPPEARANCE OF DIBENZOTHIOPHENE AT 548°K[a]

Dibenzothiophene Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	Biphenyl Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	H_2 Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	H_2S Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	10^9 × Rate of Hydrogenolysis, $\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot \text{s}}$	10^9 × Rate of Hydrogenation, $\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot \text{s}}$	10^9 × Rate of Dibenzothiophene Disappearance, $\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot \text{s}}$
0.0338	—	0.079	0.0210	3.39 ± 0.10	5.78 ± 0.069	12.1 ± 0.47
0.0333	—	0.107	0.0218	5.14 ± 0.22	8.22 ± 0.17	17.2 ± 0.72
0.0334	—	0.136	0.0210	5.61 ± 0.36	10.1 ± 0.19	20.8 ± 1.2
0.0331	—	0.147	0.0218	6.33 ± 0.17	10.4 ± 0.31	19.6 ± 0.89
0.0331	—	0.200	0.0206	7.25 ± 0.28	14.6 ± 0.19	28.1 ± 1.3
0.0329	—	0.236	0.0211	9.11 ± 0.33	17.1 ± 0.28	30.3 ± 0.83
0.0329	—	0.272	0.0217	9.39 ± 0.31	19.4 ± 1.1	36.4 ± 0.97
0.0326	—	0.299	0.0211	10.4 ± 0.31	21.4 ± 0.47	40.3 ± 2.1
0.0082	—	0.204	0.0205	3.72 ± 0.44	5.42 ± 0.13	12.9 ± 0.61
0.0163	—	0.203	0.0207	4.94 ± 0.5	9.36 ± 0.20	19.5 ± 0.61
0.0654	—	0.193	0.0220	10.1 ± 0.08	21.6 ± 0.67	43.6 ± 3.75
0.100	—	0.193	0.0220	15.8 ± 0.39	31.9 ± 1.2	55.8 ± 2.78
0.134	—	0.188	0.0221	15.0 ± 1.03	35.3 ± 1.0	65.3 ± 7.5
0.0331	—	0.200	0.0013	36.1 ± 1.9	16.7 ± 0.92	59.2 ± 4.2
0.0333	—	0.200	0.0118	11.2 ± 0.36	15.1 ± 0.5	29.7 ± 2.8
0.0329	—	0.197	0.0421	6.06 ± 0.21	14.5 ± 0.39	23.0 ± 0.61
0.0330	—	0.195	0.0701	4.67 ± 0.16	14.9 ± 0.17	21.9 ± 1.0
0.0334	0.0835	0.197	0.0206	—	—	25.7 ± 0.72

[a] Error bonds are 95% confidence limits on the slopes of the differential conversion plots.
[b] Concentrations calculated for the reactor conditions.

primary reactions: Hydrogenation of one aromatic ring gives an equilibrium mixture of THDBT and HHDBT; hydrodesulfurization of these two intermediates occurs rapidly to give cyclohexylbenzene. This combination of reactions is designated as the hydrogenation route (Figure 3), and this combination of products determined rates of hydrogenation of dibenzothiophene. The second reaction, direct hydrodesulfurization of dibenzothiophene to give biphenyl, is referred to as the hydrogenolysis reaction. Biphenyl reacted further with H_2 to give cyclohexylbenzene, but this reaction was typically two orders of magnitude slower than the rate of dibenzothiophene hydrogenolysis (Sapre and Gates, 1980).

In summary, the reactant and product concentration data give the overall rate of dibenzothiophene disappearance and also the rates of the two primary reactions of dibenzothiophene, namely, aromatic ring hydrogenation and hydrogenolysis. The rate data are collected in Tables 2, 3, and 4 for the hydrogenolysis, hydrogenation, and overall dibenzothiophene disappearance.

Data from two experiments with two different catalyst charges are included in these tables; they indicate that the rate data were reproducible with a precision of ±5-10%. The excellent reproducibility and constancy of activity of the catalyst during the experiments are shown by the set of data in the lower part of Figure 1.

TABLE 3. SUMMARY OF THE MEASURED RATES OF HYDROGENOLYSIS, HYDROGENATION, AND TOTAL DISAPPEARANCE OF DIBENZOTHIOPHENE AT 573°K[a]

Dibenzothiophene Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	Biphenyl Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	H_2 Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	H_2S Concentration,[b] $\frac{\text{kg mol}}{\text{m}^3}$	10^9 × Rate of Hydrogenolysis, $\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot \text{s}}$	10^9 × Rate of Hydrogenation, $\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot \text{s}}$	10^9 × Rate of Dibenzothiophene Disappearance, $\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot \text{s}}$
0.0326	—	0.0756	0.0207	14.4 ± 0.28	14.5 ± 0.20	38.6 ± 1.8
0.0324	—	0.104	0.0216	23.3 ± 0.64	23.0 ± 0.4	57.8 ± 2.3
0.0322	—	0.131	0.0207	24.4 ± 0.6	27.1 ± 0.36	68.1 ± 3.3
0.0321	—	0.144	0.0209	27.3 ± 0.3	29.4 ± 0.42	70.0 ± 4.4
0.0322	—	0.195	0.0206	32.2 ± 0.94	38.6 ± 0.61	90.3 ± 4.2
0.0320	—	0.229	0.0212	38.9 ± 2.2	45.0 ± 0.89	107.2 ± 2.67
0.0320	—	0.263	0.0204	38.1 ± 0.6	51.9 ± 0.75	114.7 ± 4.7
0.0318	—	0.296	0.0207	41.9 ± 1.1	61.1 ± 0.44	131 ± 6.1
0.0079	—	0.198	0.0199	16.2 ± 1.4	13.7 ± 0.56	43.3 ± 2.2
0.0158	—	0.198	0.0201	18.9 ± 0.50	24.1 ± 0.47	60.6 ± 3.1
0.0631	—	0.187	0.0217	46.7 ± 1.0	61.1 ± 2.1	136.4 ± 3.3
0.0960	—	0.183	0.0222	68.9 ± 1.3	82.8 ± 1.7	180 ± 11.9
0.129	—	0.181	0.0224	69.7 ± 1.7	95.6 ± 4.2	198.6 ± 16.1
0.0320	—	0.196	0.0013	143.9 ± 4.7	44.4 ± 1.8	199.4 ± 9.2
0.0321	—	0.194	0.0118	48.9 ± 0.56	43.3 ± 0.56	102.5 ± 4.2
0.0320	—	0.191	0.0408	26.0 ± 0.28	42.2 ± 1.0	78.6 ± 2.8
0.0320	—	0.189	0.0682	20.3 ± 0.69	40.8 ± 1.25	67.8 ± 2.2
0.0323	0.0159	0.192	0.0204	—	—	89.2 ± 4.7
0.0323	0.0808	0.190	0.0201	—	—	86.4 ± 2.3

[a] Error bounds are 95% confidence limits on the slopes of the differential conversion plots.
[b] Concentrations calculated for the reactor conditions.

TABLE 4. SUMMARY OF THE MEASURED RATES OF HYDROGENOLYSIS, HYDROGENATION, AND TOTAL DISAPPEARANCE OF DIBENZOTHIOPHENE AT 598°K[a]

Dibenzothiophene Concentration,[b] kg mol / m^3	Biphenyl Concentration,[b] kg mol / m^3	H_2 Concentration,[b] kg mol / m^3	H_2S Concentration,[b] kg mol / m^3	10^9 × Rate of Hydrogenolysis, kg mol / kg of Catalyst · s	10^9 × Rate of Hydrogenation, kg mol / kg of Catalyst · s	10^9 × Rate of Dibenzothiophene Disappearance, kg mol / kg of Catalyst · s
0.0315	—	0.0744	0.0201	57.5 ± 0.56	36.1 ± 1.7	119 ± 5.3
0.0316	—	0.101	0.0207	87.8 ± 2.5	55.6 ± 0.72	178 ± 4.4
0.0312	—	0.139	0.0206	110.8 ± 1.9	72.5 ± 1.4	208 ± 7.2
0.0311	—	0.189	0.0192	137 ± 3.1	100.8 ± 2.0	283 ± 11
0.0311	—	0.223	0.0206	160 ± 6.1	117.8 ± 4.4	337 ± 6.7
0.0311	—	0.254	0.0202	166.4 ± 3.9	134 ± 2.0	363 ± 20
0.0308	—	0.287	0.0202	164 ± 7.2	151.9 ± 2.2	402 ± 25
0.0077	—	0.193	0.0194	54.7 ± 3.9	31.1 ± 2.1	132 ± 3.3
0.153	—	0.190	0.0197	87.2 ± 3.1	62.8 ± 1.4	191 ± 6.7
0.617	—	0.184	0.0211	198.3 ± 3.3	162.5 ± 4.4	458 ± 13.1
0.0938	—	0.180	0.0215	277 ± 3.1	217 ± 4.2	608 ± 44
0.126	—	0.177	0.0218	286 ± 7.5	258 ± 6.4	667 ± 86
0.0310	—	0.190	0.0015	461 ± 14	103.9 ± 4.7	628 ± 21
0.0312	—	0.190	0.0115	192 ± 3.6	106.7 ± 1.6	324 ± 13
0.0311	—	0.187	0.0399	101.4 ± 1.9	105.6 ± 2.1	241 ± 9.2
0.0310	—	0.182	0.0664	83.3 ± 1.8	104.7 ± 4.7	215 ± 5.3
0.0315	0.0789	0.188	0.0198	—	—	246 ± 17

[a] Error bounds are 95% confidence limits on the slopes of the differential conversion plots.
[b] Concentrations calculated for the reactor conditions.

The sum of the hydrogenation and hydrogenolysis rates was consistently about 10-20% less than the rate of dibenzothiophene disappearance; this discrepancy corresponds to a lack of closure of the mass balance on carbon; 1-2% of the total dibenzothiophene was unaccounted for in the product mixture. The difference was random and virtually independent of reaction conditions. The cause of the lack of closure of the mass balance was not determined, but we infer that it is most likely an indication that some cracking occurred to form volatile products lost in sample collection. It is possible that some heavier products were formed, but the lack of catalyst deactivation suggests that the former possibility is more likely.

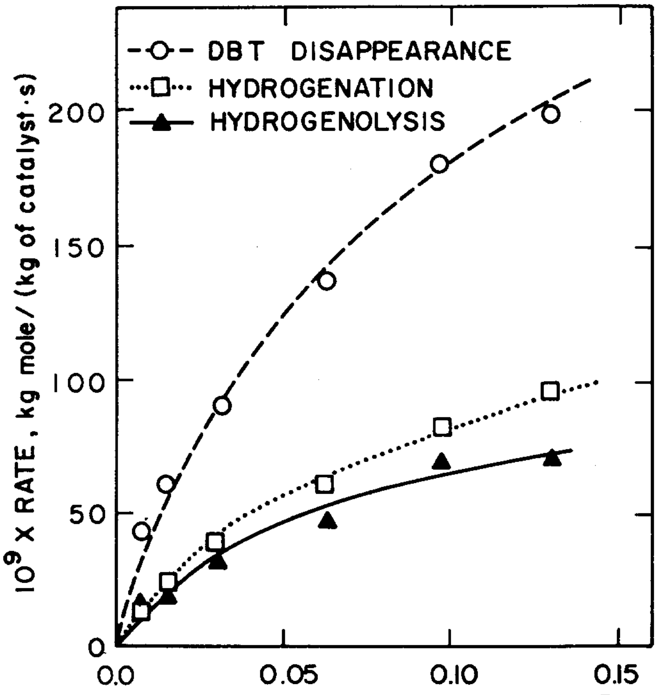

Figure 4. Dependence of reaction rates in dibenzothiophene hydrodesulfurization and dibenzothiophene concentration at 573°K and 1.8 × 10^7 Pa. The average concentrations of H_2 and H_2S were 0.19 and 0.021 kg mol/m^3, respectively. The curves were generated by calculating rates from Eqs. 3 and 7 and a sum of the two for the concentrations associated with each measured rate. A cubic curve was fitted to the calculated points.

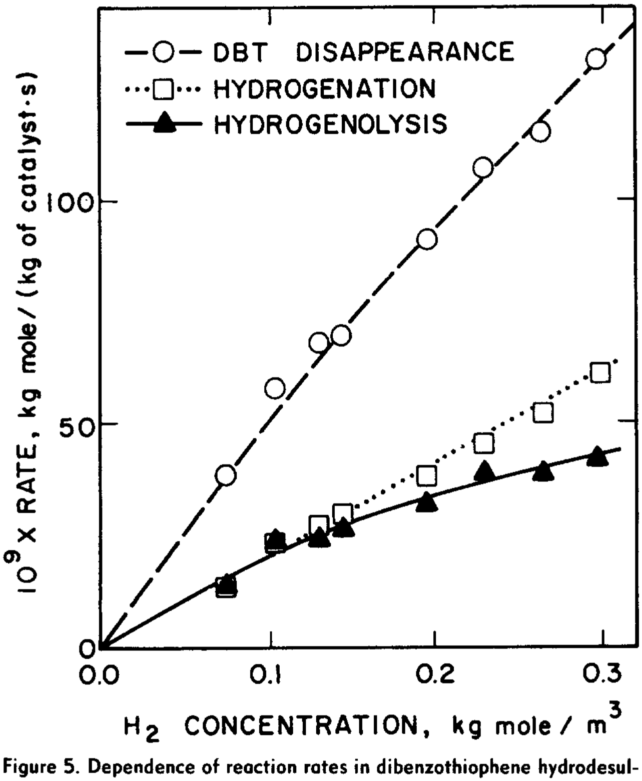

Figure 5. Dependence of reaction rates in dibenzothiophene hydrodesulfurization on H_2 concentration of 573°K and 1.8 × 10^7 Pa. The average concentrations of dibenzothiophene and H_2S were 0.032 and 0.021 kg mol/m^3, respectively. The curve representing the hydrogenation rate data was generated by calculating rates from Eq. 7 for the concentrations associated with each measured rate and by fitting a cubic curve through the calculated points. The curves representing hydrogenolysis and dibenzothiophene disappearance were generated by calculating rates from Eq. 3 and from a sum of Eqs. 3 and 7, respectively, for average concentrations of dibenzothiophene and H_2S (0.032 and 0.021 kg mol/m^3, respectively) and various H_2 concentrations. A cubic curve was fitted through the calculated points for each of the two reactions.

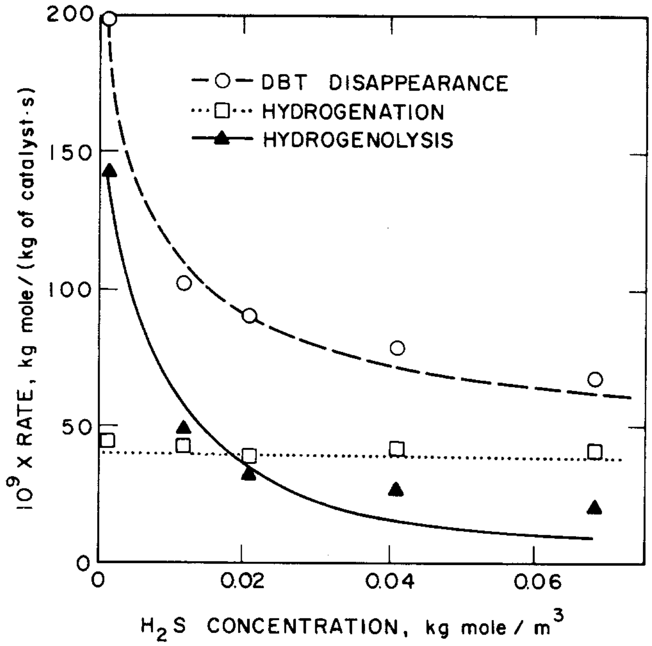

Figure 6. Dependence of reaction rates in dibenzothiophene hydrodesulfurization on H_2S concentration at 573°K and 1.8 × 10^7 Pa. The average concentrations of dibenzothiophene and H_2 were 0.032 and 0.19 kg mol/m^3, respectively. The curves were generated by calculating rates from Eqs. 3 and 7 and a sum of the two for the concentrations associated with each measured rate and by fitting a cubic curve through the calculated points for each reaction.

Representative plots showing the dependence of rates on reactant and product concentrations are given in Figures 4-6. A decreasing slope with increasing dibenzothiophene concentration was observed for each reaction, exemplified by Figure 4. This result implies a Langmuir dependence of rate on dibenzothiophene concentration, indicating that the catalytic sites approached saturation in dibenzothiophene. The rate of hydrogenation was linearly dependent on H_2 concentration (Figure 5), and the hydrogenolysis data showed a Langmuir dependence on H_2 concentration (Figure 5). H_2S inhibited the hydrogenolysis, but, surprisingly, it did not inhibit hydrogenation (Figure 6). The effect of biphenyl concentration on the overall rate of dibenzothiophene conversion was negligible at the lower temperatures; a small inhibition was observed at 598°K.

When biphenyl was included in the reaction mixture to allow study of its effect on the rates, the separate rates of hydrogenolysis and hydrogenation of dibenzothiophene could not be determined accurately, since detailed kinetics of biphenyl hydrogenation were lacking. The effect of biphenyl (or aromatic hydrocarbons in general) on these rates at temperatures near 573°K can be inferred from data reported by Sapre (1980). He observed that at temperatures <598°K, the rate of biphenyl hydrogenation was nearly independent of the concentration of other aromatics. If we assume the same independence for dibenzothiophene hydrogenation, then it follows from the results that the dibenzothiophene hydrogenolysis is not inhibited by aromatics in this temperature range.

DISCUSSION

Determination of Rate Equations

The data were fitted to a number of rate equations, some purely empirical and some corresponding to Langmuir-Hinshelwood models. The data for dibenzothiophene hydrogenation and hydrogenolysis were fitted separately. A list of the equations tested is presented elsewhere (Broderick, 1980); here we consider only the several equations giving the best fits to the data.

A nonlinear least-squares (NLLS) regression analysis (Marquardt, 1963) was used with each equation in Tables 5 and 6 to determine the parameters best representing the data. The output of the NLLS program (University of Delaware Computing Center, 1977) included the parameter values giving the best fit and several statistical measures of the goodness of fit. The statistical data were: (1) ϕ_{min}, the minimized sum of the squares of the differences between the observed and predicted rates; (2) a correlation matrix representing the degree of independence of the parameters; and (3) 95% confidence limits given as an upper and lower bound on the value of each of the parameters. The results are summarized in Tables 5 and 6.

Several other criteria were applied measuring the physical meaningfulness of the parameters:

(1) The estimated rate constants and the parameters which could be identified in terms of Langmuir-Hinshelwood models

TABLE 5. RATE EQUATIONS BEST FITTING DIBENZOTHIOPHENE HYDROGENOLYSIS KINETICS DATA[a]

Rate Equation	Temp., °K	$10^6 \times k$, $\frac{m^6}{\text{kg mol} \cdot \text{kg of Catalyst} \cdot s}$	K_{DBT}, $\frac{m^3}{\text{kg mol}}$	K_{H_2}, $\frac{m^3}{\text{kg mol}}$	K_{H_2S}, $\frac{m^3}{\text{kg mol}}$	$10^{16} \times \phi_{min}$, $\left(\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot s}\right)^2$
1. $\frac{k\, C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2S}C_{H_2S})^2}$	548	11.4 ± 1.3	10.3 ± 3.0	—	86 ± 16	0.366
	573	39.9 ± 4.3	7.2 ± 2.5	—	74 ± 12	6.81
	598	130 ± 15	6.8 ± 2.6	—	59 ± 11	82.3
2. $\frac{k\, C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2S}C_{H_2S} + K_{H_2}C_{H_2})^2}$	548	30.1 ± 3.9	18.1 ± 5.8	2.9 ± 1.3	137 ± 31	0.342
	573	200 ± 22	18.5 ± 6.1	6.0 ± 1.4	161 ± 27	5.39
	598	439 ± 53	14.5 ± 5.0	4.1 ± 1.2	103 ± 21	63.3
3. $\frac{k\, C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2S}C_{H_2S})^2 (1 + K_{H_2}C_{H_2})}$	548	15.7 ± 2.0	11.5 ± 3.5	1.6 ± 1.0	86 ± 19	0.341
	573	69.3 ± 7.5	8.7 ± 2.7	3.2 ± 1.1	75 ± 12	5.36
	598	215 ± 26	8.2 ± 2.8	2.9 ± 1.2	58 ± 12	63.4
4. $\frac{k\, C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2S}C_{H_2S})^2 [1 + (K_{H_2}C_{H_2})^{1/2}]^2}$	548	20.3	11.4	0.46	86.5	0.341
	573	106.3	8.5	1.72	74.9	5.41
	598	315	8.1	1.40	58.1	64.6
5. $\frac{k\, C_{DBT}C_{H_2}}{[1 + K_{DBT}C_{DBT} + (K_{H_2S}C_{H_2S})^{1/2}]^2 (1 + K_{H_2}C_{H_2})}$	548	59.9 ± 4.7	23.9 ± 3.8	1.77 ± 0.59	868 ± 144	0.122
	573	205 ± 14	16.4 ± 2.7	3.20 ± 0.61	518 ± 72	1.99
	598	503 ± 33	13.3 ± 2.2	2.96 ± 0.60	256 ± 38	18.7
6. $\frac{k\, C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2}C_{H_2})^2 [1 + (K_{H_2S}C_{H_2S})^{1/2}]^2}$	548	25.1 ± 1.9	5.2 ± 1.2	0.89 ± 0.28	270 ± 42	0.122
	573	111.0 ± 7.4	4.7 ± 1.0	1.44 ± 0.27	221 ± 29	1.98
	598	323 ± 21	5.0 ± 0.9	1.38 ± 0.27	127 ± 17	18.3

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[a] Error bounds are 95% confidence limits on the fitted parameters. The NLLS program failed to compute confidence limits for Eq. 4.

TABLE 6. RATE EQUATIONS BEST FITTING DIBENZOTHIOPHENE HYDROGENATION KINETICS DATA[a]

Rate Equation	Temp., °K	$10^6 \times k$, $\frac{m^6}{\text{kg mol} \cdot \text{kg of Catalyst} \cdot s}$	K_{DBT}, $\frac{m^3}{\text{kg mol}}$	K_{H_2}, $\frac{m^3}{\text{kg mol}}$	$10^{17} \times \phi_{min}$, $\left(\frac{\text{kg mol}}{\text{kg of Catalyst} \cdot s}\right)^2$
7. $\frac{k C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT})}$	548	2.78 ± 0.11	7.39 ± 0.89	—	1.30
	573	8.11 ± 0.24	7.70 ± 0.72	—	7.14
	598	20.9 ± 0.57	6.61 ± 0.55	—	24.3
8. $\frac{k C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT})(1 + K_{H_2}C_{H_2})}$	548	2.95 ± 0.14	7.6 ± 1.07	0.25 ± 0.25	1.26
	573	8.60 ± 0.30	7.92 ± 0.85	0.28 ± 0.19	6.78
	598	21.6 ± 0.7	6.73 ± 0.67	0.14 ± 0.16	23.7
9. $\frac{k C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2}C_{H_2})}$	548	2.98 ± 0.14	8.0 ± 1.1	0.31 ± 0.35	1.26
	573	8.69 ± 0.30	8.4 ± 0.9	0.32 ± 0.26	6.80
	598	21.7 ± 0.66	6.9 ± 0.7	0.16 ± 0.22	23.7
10. $\frac{k C_{DBT}C_{H_2}}{[1 \times (K_{DBT}C_{DBT})^{1/2}]^2 (1 + K_{H_2}C_{H_2})}$	548	4.34 ± 0.18	3.78 ± 0.50	0.27 ± 0.22	0.987
	573	12.6 ± 0.4	3.91 ± 0.41	0.27 ± 0.17	5.73
	598	30.2 ± 0.74	2.81 ± 0.25	0.16 ± 0.13	16.0

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[a] Error bounds are 95% confidence limits on the fitted parameters.

as adsorption equilibrium constants should be positive or include positive values within their error bounds.

(2) A plot of the logarithm of the rate constant versus reciprocal absolute temperature (Arrhenius plot) should be linear with a negative slope.

(3) A plot of the logarithm of each adsorption equilibrium constant versus reciprocal absolute temperature (van't Hoff plot) should be linear with a positive slope, except when chemisorption is endothermic.

The six best equations for the hydrogenolysis reaction data are given in Table 5. Of these, the first four can be derived from Langmuir-Hinshelwood models assuming various forms of competitive and noncompetitive adsorption (dissociative or undissociative). The last two equations are similar to these in form but do not correspond to any simple Langmuir-Hinshelwood model.

Equations 3, 5 and 6 in Table 5 were found to satisfy all the physical and statistical criteria enumerated above. If, in addition, an equation of Langmuir-Hinshelwood formulation is preferred, Eq. 3 is the only acceptable choice. Equation 1 gives a poorer fit, judging by the magnitude of ϕ_{min}. Equations 2 and 4 show strong parameter correlation and relatively large deviations from linearity of the Arrhenius plot.

Equation 5 differs from Eq. 3 only in the half power on the term $K_{H_2S}C_{H_2S}$ in the denominator. This same power on $K_{H_2S}C_{H_2S}$ in Eq. 6 is largely responsible for the good fit observed for this equation as well. The half power on $K_{H_2S}C_{H_2S}$ in Eq. 5 might be interpreted as the basis for suggesting that adsorption of H_2S occurs dissociatively. In the Langmuir-Hinshelwood model, dissociative adsorption of a molecule such as A_2 to give two atomically adsorbed species $A(s)$ [where (s) is a single surface site] results in a half power on the denominator term K_AC_A. Evidence exists for dissociative adsorption of H_2S on γ-alumina and on MoS_2/γ-Al_2O_3 (Slager and Amberg, 1972; Lunsford et al., 1975). H_2S, however, is not a simple diatomic molecule, and we suggest that at least two types of catalytic sites would be involved in its dissociative adsorption. As a result, a Langmuir-Hinshelwood expression of much greater complexity than Eq. 5 would be necessary to describe dissociative adsorption of H_2S. We infer, however, from the improved fit of Eq. 5 over Eq. 3 that chemisorption of H_2S is more complex than simple nondissociative adsorption.

For simplicity, the half power is omitted, and Eq. 3 is recommended as the best equation resting on a Langmuir-Hinshelwood model for representing the data for hydrogenolysis under all the conditions studied. From the Arrhenius plot for this equation (Figure 7), the activation energy, determined from the temperature dependence of $k/K_{DBT}K_{H_2}$, is $(1.26 \pm 0.62) \times 10^8$ J/kg mol. In the context of the Langmuir-Hinshelwood model, the heats of adsorption $(-\Delta H)$ for dibenzothiophene, H_2S, and H_2 (evaluated from the van't Hoff plots in Figure 7) are $(1.9 \pm 4.2) \times 10^7$, $(2.2 \pm 2.6) \times 10^7$, and $-(3.5 \pm 15) \times 10^7$ J/kg mol, respectively. The negative value for $-\Delta H_{H_2}$ was observed for all of the equations tested; it is suggested to be an anomaly associated with the imprecision in the data, since the 90% confidence limits on the slope of the van't Hoff plot for K_{H_2} include positive values.

For hydrogenation of dibenzothiophene, the rate data were best represented by the four equations in Table 6. Differences in goodness of fit among these equations are relatively small. Equation 7 is recommended for its goodness of fit, its simple form, and its low parameter correlation and error bounds relative to the other equations. Equations 8 and 9 have high error bounds on K_{H_2}, and Eqs. 8 and 10 show large deviations from linear Arrhenius plots. Differences in ϕ_{min} are not significant when compared with the standard deviations of the data. The temperature dependences of k' (defined as k/K_{DBT}) and K_{DBT} were calculated from Arrhenius and van't Hoff plots (Figure 8). The values for E_{act} and $-\Delta H_{DBT}$ were $(1.2 \pm 0.34) \times 10^8$ and $(5.9 \pm 39) \times 10^6$ J/kg mol, respectively.

As a first approximation, the total rate of dibenzothiophene hydrodesulfurization was assumed to be the sum of the rates of hydrogenolysis and hydrogenation. A fit of the sum of Eqs. 3 and 7 to the dibenzothiophene disappearance data was accom-

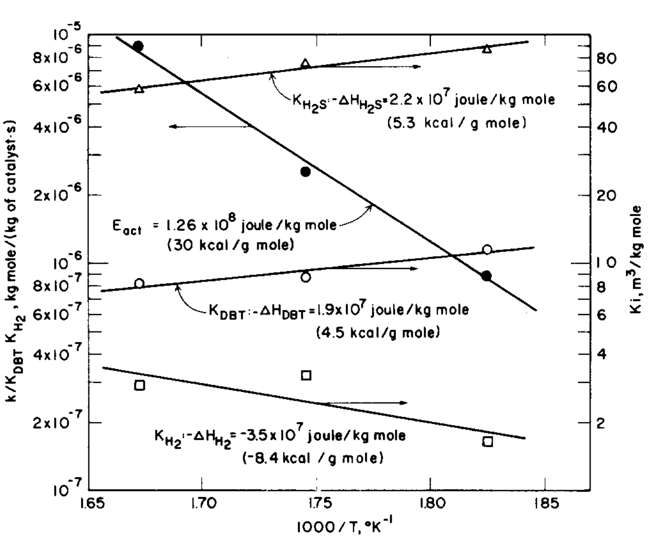

Figure 7. Arrhenius and van't Hoff plots of the parameters in Eq. 3 for dibenzothiophene hydrogenolysis.

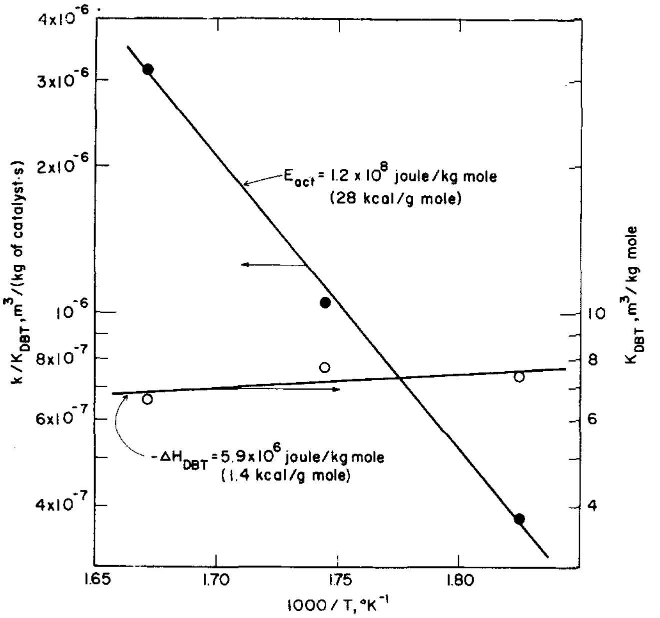

Figure 8. Arrhenius and van't Hoff plots of the parameters in Eq. 7 for dibenzothiophene hydrogenation.

plished by allowing the regression program to select a value for *k* in each term, while the *K*'s were held constant at the values given in Tables 5 and 6. The resulting fit, as determined by the value of ϕ_{min} and visual comparison of the data and predicted curves, was excellent; but the *k* values were different from those given in Tables 5 and 6 (by 7 and 33% for hydrogenolysis and hydrogenation, respectively) because of the lack of closure of the mass balance.

To furnish a comparison with the fit provided by this two-term rate equation, several one-term rate equations with four or more adjustable parameters were fitted to the data (Broderick, 1980) for dibenzothiophene disappearance. Even for the equations showing best fit, ϕ_{min} was nearly three times greater than for the sum of Eqs. 3 and 7; large error bounds were observed for the parameters, and the parameters failed to show the appropriate dependence on temperature.

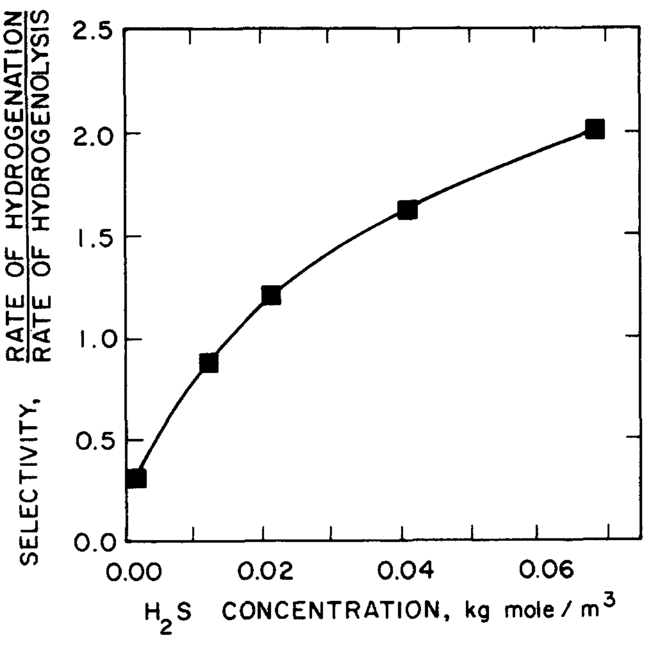

Figure 9. Selectivity for dibenzothiophene hydrogenation with increasing H_2S concentration at 573°K. The average concentrations of dibenzothiophene and H_2 were 0.032 and 0.19 kg mol/m^3, respectively. Points are ratios of measured rate data from Table 3, and the curve is a cubic fit through these points.

Comparison with Literature Kinetics

The literature concerning kinetics of hydrogenolysis reactions in hydrodesulfurization of thiophenic compounds catalyzed by Co-Mo/γ-Al_2O_3 is generally consistent with the results presented here for dibenzothiophene. Much of the work has been done with thiophene (Satterfield and Roberts, 1968; Lee and Butt, 1977; Phillipson, 1971; Morooka and Hamrin, 1977) and benzothiophene (Kilanowski and Gates, 1980) at pressures near atmospheric and for narrow ranges of H_2 partial pressure. There is much evidence that the principal reaction for both thiophene and benzothiophene is hydrogenolysis.

There is strong agreement that the dependence of rate on the concentrations of thiophenic reactant and of H_2S is the same as shown in Eq. 3. The dependence of rate on H_2 partial pressure has typically been represented as first order at low partial pressures (Satterfield and Roberts, 1968; Lee and Butt, 1977; Morooka and Hamrin, 1977), but the data are meager and the representations arbitrary. An important new result of the present kinetics study is, therefore, the firmly established dependence of hydrogenolysis rate on H_2 concentration.

The results of previous kinetics studies of dibenzothiophene hydrodesulfurization differ from the kinetics for hydrogenolysis reported here. For conditions similar to those applied here (but with a maximum H_2 partial pressure of 3.1×10^6 Pa), Espino et al. (1978) and Myers and Robinson (1978) reported rate equations similar to Eq. 3 but with a power of 1 on the denominator term for adsorption of H_2S and dibenzothiophene. Myers and Robinson observed a simple first-order dependence of rate on H_2 partial pressure. In neither study were the hydrogenation and hydrogenolysis reactions resolved; and we infer from our results that under the reported conditions, both reactions contributed significantly to the rates of dibenzothiophene conversion. We infer that the reported kinetics represent only the rate of disappearance of dibenzothiophene and are in qualitative agreement with the rates observed in this work. The rate equations for dibenzothiophene conversion given by Espino et al. and Myers and Robinson are similar to the single-term rate equations found to give the best fit to the data for dibenzothiophene disappearance reported here.

Other differences exist between the kinetics presented here and results reported in the literature. Specifically, the points of disagreement concern the effects of temperature and H_2S concentration on the product distribution (or the relative rates of hydrogenolysis and hydrogenation) reported by Espino et al. (1978) and Rollmann (1977). Espino et al. found that with the addition of H_2S, the ratio of biphenyl concentration to cyclohexylbenzene concentration remained constant (and did not decrease, as was observed in this work). This observation, among others, led them to the conclusion that there was one key intermediate (dihydrodibenzothiophene) in the network, both for hydrogenolysis and hydrogenation of dibenzothiophene (Espino et al., 1978).

The conclusion is not in accord with the results presented here. From the data in Table 3, a ratio of the rate of dibenzothiophene hydrogenation to the rate of hydrogenolysis as a function of H_2S concentration (Figure 9) shows that the ratio approaches a constant maximum value of high H_2S concentrations. In the work of Espino et al., dibenzothiophene concentrations and conversions were sufficiently high to give product H_2S concentrations in the range of 0.2 kg mol/m^3. Extrapolating Figure 9, we would predict that the ratio of biphenyl to cyclohexylbenzene concentration in the products would be insensitive to H_2S concentrations >0.2 kg mol/m^3, consistent with the observations of Espino et al.

Espino et al. (1978) and Rollmann (1977) observed an increase in cyclohexylbenzene concentration relative to biphenyl concentration in the product as the temperature increased, and Espino et al. reported that the activation energy for hydrogenation was greater than that for hydrogenolysis (by 8.2×10^7 J/kg mol); the reverse was observed here, i.e., the activation energy for hydrogenation was less than that for hydrogenolysis (by 1.1 ×

10^7 J/kg mol); and the concentration of cyclohexylbenzene relative to biphenyl was found to decrease as temperature increased.

The only obvious difference in operating conditions between this work and the studies of Espino et al. and Rollmann was that Espino et al. used tetralin as a reactant carrier instead of the *n*-hexadecane used in this work; and tetralin was present as a reaction product in the work of Rollmann. It is unclear how the presence of tetralin could result in such a large increase in the activation energy for hydrogenation relative to hydrogenolysis, but data characterizing the hydrogenation of biphenyl at similar temperatures and pressures in tetralin (Espino et al., 1978) and in *n*-hexadecane (Sapre and Gates, 1980) demonstrate that the activation energy for hydrogenation is greater by 7.7×10^7 J/kg mol when tetralin is used instead of *n*-hexadecane as the solvent. More work is needed to test and explain this apparent solvent effect.

Hydrogenation Reaction

Literature concerning the hydrogenation reaction of dibenzothiophene consists of the work by Houalla et al. (1978) and Bhinde (1979), who used large excesses of H_2 and accurately approximated the rate of dibenzothiophene hydrogenation as pseudo-first-order in dibenzothiophene. Hydrogenations of other heteroaromatics, such as quinoline and pyridine, and of aromatics such as biphenyl, naphthalene, and benzene, catalyzed by sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ have been studied, and limited kinetics data have been reported. For biphenyl, Espino et al. (1978) represented rate data with a Langmuir-Hinshelwood equation indicating competitive adsorption of biphenyl and cyclohexylbenzene on one kind of site and of H_2 on another. No measure of inhibition by H_2S was determined. Few details were given concerning the data and the criteria for selection of the rate equations.

For pyridine (Goudriaan, 1974) and quinoline (Bhinde, 1979; Shih et al., 1977), the rate of ring hydrogenation was approximated as first order in the heteroaromatic; but the rate constant decreased with increasing reactant concentration, suggesting self-inhibition of reaction. The order of reaction in H_2 partial pressure ranged from 1 to 1.5 for pyridine and from 0.5 to 1 for quinoline. The effect of H_2S on the rate of hydrogenation of quinoline was negligible. For pyridine, H_2S was an inhibitor when <2 mole % H_2S was present; otherwise, the rate was independent of H_2S concentrations. These kinetics results for hydrogenation reactions of nitrogen-containing aromatics are, therefore, generally in agreement with the dibenzothiophene hydrogenation kinetics represented by Eq. 7.

Catalytic Sites

Prominent differences in the kinetics of dibenzothiophene hydrogenation and hydrogenolysis highlighted in Figures 5 and 6 and Eqs. 3 and 7 suggest that for sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$ catalyst, the reaction mechanism and catalytic sites differ for the two reactions. The literature supports the proposal of two different kinds of sites for hydrogenation and C-S bond hydrogenolysis. The evidence is provided by the results of poisoning (Lee and Butt, 1977; Desikan and Amberg, 1964; Urimoto and Sakikawa, 1972) and kinetics (Satterfield and Roberts, 1968; Lee and Butt, 1977; Bhinde, 1979; Kilanowski and Gates, 1980) studies, among others.

One kind of site is strongly poisoned by bases such as pyridine and quinoline, and the other is less acidic and less sensitive to such poisons. The former sites are associated with hydrogenation activity and the latter with hydrogenolysis activity. A widely accepted model (Lipsch and Schuit, 1969) suggests that hydrogenolysis activity is associated with sulfur anion vacancies which expose Mo cations. From Eq. 7, it is inferred that the hydrogenation sites bond strongly to dibenzothiophene, but not to H_2 or H_2S. In contrast, H_2S does compete strongly with dibenzothiophene for hydrogenolysis sites, as follows from Eq. 3. The form of this equation suggests that H_2 adsorbs on still another type of site, as is expected from the known formation of $-SH$ groups on the surface.

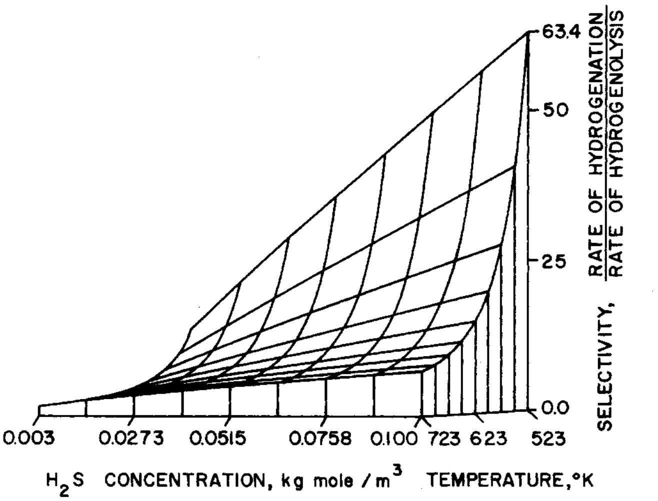

Figure 10. Selectivity surface in dibenzothiophene hydrodesulfurization showing dependence upon temperature and H_2S concentration. The average H_2 concentration was 0.70 kg mol/m^3. The surface was predicted by rate equations fitted to the hydrogenolysis and hydrogenation rate data. Temperature dependence of the equation parameters was determined from Arrhenius and van't Hoff plots.

The nature of the dibenzothiophene chemisorption on the catalyst surface is unknown, but the extensive hydrogenation of the benzenoid rings suggests strong ring interaction with the surface. Dibenzothiophene, being a planar molecule, is believed to adsorb in a plane parallel to the catalyst surface, favoring interactions of the aromatic π-electrons with catalyst cations exposed at anion vacancies. The results presented here support the proposals for adsorption via π-complex formation (Cowley, 1975; Singhal and Espino, 1978) or multipoint bonding (Kwart et al., 1980), and they contradict the one-point adsorption model first suggested for thiophene (Lipsch and Schuit, 1969).

Product Distribution

A well-recognized concern in hydroprocessing is the consumption of expensive H_2. Considering the marked differences in the kinetics reported here for hydrogenation and hydrogenolysis of dibenzothiophene, we recognize two important processing variables for minimizing the H_2 consumption in hydrodesulfurization. As shown in Figure 9, decreased H_2S concentrations (obtainable by recycle gas scrubbing) favor hydrogenolysis. The change in selectivity is dramatic for H_2S concentrations between about 0 and 0.1 kg mol/m^3. Temperature also strongly influences the relative rates of hydrogenation and hydrogenolysis. As the temperature is raised, the relative rate of hydrogenolysis increases sharply. The response of the selectivity in dibenzothiophene hydrodesulfurization (rate of hydrogenation/rate of hydrogenolysis) to changes in temperature and H_2S concentration is shown in Figure 10. The changes in selectivity that result from variations in H_2 partial pressure are relatively small in comparison with the changes shown in Figure 10.

The observation that heavy feedstocks generally consume more H_2 than light feedstocks in hydrodesulfurization is clarified by the results showing relative rates of dibenzothiophene hydrogenation and hydrogenolysis. For lighter feeds and mild processing conditions, many hydrogenation reactions are negligibly slow in comparison with hydrodesulfurization of light, highly reactive sulfur-containing compounds. As feedstocks become heavier and thiophenic sulfur is present in greater concentrations, the rate of hydrodesulfurization decreases. For the heaviest feed materials, for which dibenzothiophene, benzo(*b*)naphtho(2,3-*d*)thiophene, and similar compounds predominate, the rates of hydrogenation and hydrodesulfurization are nearly equal; and H_2 consumption is well in excess of the stoichiometric amount required for sulfur removal.

We recognize that competition between the sulfur-containing reactants and other feed components which were not tested in this work may alter the kinetics and selectivity. Quinoline, a basic nitrogen-containing heteroaromatic found in many heavy feeds, is a good example of such a component. Bhinde (1979) reported markedly increasing rates of dibenzothiophene hydrogenolysis relative to hydrogenation in the presence of increasing quinoline concentrations. Notwithstanding the complications imposed by competitive adsorption and reaction of other feed components, we recommend the pure-compound kinetics presented here for guidance in process design; we suggest that the forms of the rate equations (modified to account for the presence of various inhibitors) may be the most appropriate in the open literature for use in reaction engineering models for process simulation.

SUMMARY

In high-pressure hydrodesulfurization of dibenzothiophene catalyzed by sulfided $CoO\text{-}MoO_3/\gamma\text{-}Al_2O_3$, the kinetics of the two primary reactions are summarized with the following recommended rate equations determined from differential conversion data. For dibenzothiophene hydrogenolysis, giving biphenyl as a primary product, the equation is:

$$r_{\text{Hydrogenolysis}} = \frac{k'\, K_{DBT}\, K_{H2}\, C_{DBT}\, C_{H2}}{(1 + K_{DBT}C_{DBT} + K_{H2S}\, C_{H2S})^2\,(1 + K_{H2}\, C_{H2})} \tag{3}$$

The equation parameters are the following:

$k' = 7.87 \times 10^5 \exp(-1.26 \times 10^8/RT)$ kg mol/(kg of catalyst · s)
$K_{DBT} = 1.8 \times 10^{-1} \exp(1.9 \times 10^7/RT)$ m^3/kg mol
$K_{H2} = 4.0 \times 10^3 \exp(-3.5 \times 10^7/RT)$ m^3/kg mol
$K_{H2S} = 7.0 \times 10^{-1} \exp(2.2 \times 10^7/RT)$ m^3/kg mol
T is in °K and R is in J/kg mol · °K).

For dibenzothiophene hydrogenation, giving a combination of products, i.e., cyclohexylbenzene, THDBT, and HHDBT, the recommended rate equation is:

$$r_{\text{Hydrogenation}} = \frac{k'\, K_{DBT}\, K_{H2}\, C_{DBT}\, C_{H2}}{(1 + K_{DBT}C_{DBT})} \tag{7}$$

The parameters are the following:
$k'K_{H2} = 4.22 \times 10^4 \exp(-1.16 \times 10^8/RT)$ kg mol/(kg of catalyst · s)
$K_{DBT} = 2.0 \exp(6.0 \times 10^6/RT)$ m^3/kg mol
where T is in °K and R is in J/(kg mol · °K)

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NOTATION

C_i = concentration of species i, kg mol/m^3
E_{act} = activation energy, J/kg mol
$-\Delta H$ = heat of adsorption on catalyst, J/kg mol
k = apparent rate constant, m^6/kg mol · kg of catalyst · s)
k' = $k/(K_{DBT}K_{H2})$, kg mol/(kg of catalyst · s)
K_i = adsorption constant for species i, m^3/kg mol
r = reaction rate, kg mol/(kg of catalyst · s)
ϕ_{min} = minimized sum of the squares of the differences between measured and predicted rates [kg mol/(kg of catalysts · s)]^2

Subscripts and Abbreviations

BP = biphenyl
CHB = cyclohexylbenzene
DBT = dibenzothiophene
HHDBT = 1,2,3,4,10,11-hexahydrodibenzothiophene
THDBT = 1,2,3,4-tetrahydrodibenzothiophene

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Employment of Vapor Pressure Data in the Description of Vapor-Liquid Equilibrium with Direct Method

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A procedure for inserting vapor pressure data in the equations of state is presented. It provides a straightforward scheme for the extension of direct methods to the study of phase equilibria of polar mixtures and of solutions containing nonvolatile electrolytes. Some examples of application are also given.

SCOPE

Equations of state are always more often employed to estimate thermodynamic properties of fluids. Specifically this paper will focus on their use to describe vapor-liquid equilibria in multicomponent systems, where equations of state represent an alternative method to the so-called "indirect methods." The accuracy of the prediction of the multicomponent equilibrium data depends on the ability of the equation of state to represent the vapor pressure of the pure components present in the mixture. For this reason, parameters of the cubic equations of state (Soave, 1972; Peng and Robinson, 1976) are given as functions of the temperature, obtained through a regression procedure in order to fit the vapor pressure data of a set of compounds in a specific range of temperature.

A general procedure will be developed to introduce the vapor pressure of pure component in the van der Waals-type equations of state, so that, at any given temperature, the equality of the liquid and vapor fugacity occurs at a pressure value exactly equal to the vapor pressure. This procedure will improve the multicomponent vapor-liquid equilibria prediction and allow use of the equation of state in all compounds and in the whole temperature range.

Furthermore, such a procedure can also be regarded as a useful tool to study the intrinsic ability of equations of state with different structure to describe the vapor-liquid equilibrium of multicomponent system, once they all exactly describe the vapor pressure of the pure components, without any previous regression analysis.

CONCLUSIONS AND SIGNIFICANCE

A general procedure is introduced for the vapor pressure data of pure components in the equations of state derived from the van der Waals theory.

The procedure has been applied to the PR (Peng and Robinson, 1976) and RSRK (Carnahan and Starling, 1972) equations of state. We have thus overcome lack of accuracy in the prediction of the vapor pressure of pure components at temperatures below the boiling points. Besides, in this region, the proposed procedure improves the vapor liquid equilibria prediction of multicomponent mixtures, obtained by using the two equations of state in the common way.

Further, this procedure is expected to be of some use in the approximate prediction of the effect of electrolytes on vapor-liquid equilibrium of multicomponent mixtures, once you know only the effect of the electrolytes themselves on the pure components vapor pressure.

Finally, we deem it worthwhile to point out that the present analysis does not consider any adjustable parameter. However, such parameters can be easily introduced, as it is usually done in the application of the equations of state, to improve the agreement between the experimental and the predicted values.

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