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Kinetics of Hydrodesulfurization of Benzothiophene Catalyzed by Sulfided Co–Mo/Al_2O_3

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Kinetics of the hydrodesulfurization of benzothiophene (BT) to give ethylbenzene was measured with a steady-state differential flow microreactor containing particles of sulfided Co–Mo/Al_2O_3 catalyst at 252–332°C. Partial pressures of reactant species were varied in the following ranges: BT, 0.015–0.23; H_2, 0.20–2.0; and H_2S, 0.02–0.14 atm. Catalyst deactivation was negligible over hundreds of hours of operation. Rate equations of the Langmuir–Hinshelwood type were compared with the rate data using a nonlinear least-squares regression technique. No single equation with a prudent number of parameters gave a good fit at all three temperatures. The kinetics results demonstrate the competitive adsorption of BT and H_2S on one kind of catalytic site and of hydrogen on another. The literature indicates that thiophene is about half as reactive as BT under these conditions, and a comparison of the kinetics results for the two reactants suggests a similarity in the mechanisms of their reactions.

INTRODUCTION

Hydrodesulfurization of petroleum is the catalytic process with the highest throughput of all, but there is still only a meager quantitative basis for characterization of the individual catalytic reactions. Most of the few reported kinetics studies involved the reaction of thiophene with hydrogen at atmospheric pressure in the presence of Co–Mo/Al_2O_3 catalyst (*1–4*); there is one reported study of dibenzothiophene hydrodesulfurization kinetics at high pressure (*5*). The remaining kinetics literature, summarized in detail elsewhere (*6*), gives fragmentary information, failing to establish the dependence of reaction rate on all the pertinent reactant and product concentrations or failing to specify fully the nature of the experiments and analysis of the data (e.g., *7*).

There is only one reported set of kinetics data for a hydrodesulfurization reaction which is clearly not influenced by transport disguises and which is based on directly measured reaction rates for several temperatures and for fairly wide ranges in concentration of each pertinent component in the reaction mixture. This is the study of thiophene hydrodesulfurization reported by Lee (*3*) [and summarized in the paper by Lee and Butt (*8*)]. There is need for further data of this kind, and the objective of the work reported here was to extend the base of hydrodesulfurization kinetics to include benzo[*b*]thiophene (referred to as benzothiophene), a reactant more representative than thiophene of the heavier petroleum feedstocks like gas oils (*9, 10*). The experiments were carried out with vapor-phase reactants in a conventional steady-state flow microreactor containing sulfided Co–Mo/Al_2O_3 catalyst; differential conversion data were obtained to determine reaction rates directly.

EXPERIMENTAL

Materials. Benzothiophene (99%) and ethylbenzene (99%) (Aldrich) were used without purification. Air (dry grade), nitro-

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gen (high-purity dry grade, 99.995% min), helium (high purity), and hydrogen (prepurified, 99.99% min) were obtained from Linde; the helium was purified in the flow reactor system to remove traces of water, and the hydrogen was purified to remove traces of oxygen and water. A mixture of 10 mole% H_2S in H_2 was obtained from Matheson (custom mixture grade) and was also treated to remove traces of water.

The catalyst was the same commercial $CoO–MoO_3/\gamma-Al_2O_3$ used in pulse microreactor studies reported earlier (*11*) (American Cyanamid AERO HDS-16A, MTG-S-0731). It was supplied as $\frac{1}{16}$-in. extrudates which were crushed and sieved before use. The catalyst physical properties and analysis are given in Ref. (*11*).

Flow microreactor. The pulse-reactor apparatus described earlier (*11*) was modified to allow steady introduction of vapor-phase reactant mixtures at accurately measured and easily varied temperatures and compositions. The reactant feeds consisted of benzothiophene and cylinder gases including hydrogen, hydrogen sulfide, and helium. Liquid benzothiophene was fed from a 5-ml Hamilton "gas/liquid tight" syringe (Model 1005) by a syringe pump (Harvard Apparatus Co. Model 975). A heating lamp was used to prevent crystallization of the benzothiophene in the syringe and in an accompanying reservoir. The benzothiophene flowed through a length of 0.08-cm-i.d. stainless-teel capillary tubing (thermostated at 50°C) to a vaporizer in a separately thermostated oven. The design of the vaporizer [described in detail elsewhere (*6*)] and the temperature of its operation (230°C) were critical in establishing steady (nonpulsing) flow of the reactants.

The vaporized benzothiophene was mixed with the metered cylinder gases in the vaporizer and flowed to a 50-cm length of capillary tubing in a thermostated oven to ensure adequate mixing and preheating of the feed before it entered the reactor. The mixture flowed through a Carle Model 2017 valve and either flowed to the reactor, which was situated external to the oven, or bypassed the reactor and flowed to an on-line gas chromatograph.

The reactor was constructed from a 6.4-cm-o.d. × 10.7-cm cylindrical block of 304 stainless steel. A 0.32-cm hole was drilled vertically through the center of the block, serving as the reactor volume. Two 0.32-cm holes were drilled at 90° angles to the reactor axis at the top and bottom to provide the reactor inlet and outlet, respectively. Reactor heating was provided by four 1.3-cm-o.d. × 10.2-cm long Superwatt cylindrical cartridge heaters (J. C. Whidett Co.) inserted in holes parallel to the axis of the reactor, one in each quadrant of the block. Temperature was monitored and controlled via a 0.32-cm-o.d. platinum resistance element (Yellow Springs, Inc.), positioned perpendicular and adjacent to the reactor cavity at the midpoint, and connected to a control panel. Temperature along the reactor cavity was measured by three equally spaced ceramic-insulated chromel-alumel thermocouples placed adjacent to the cavity and opposite the resistance thermometer. The reactor block was surrounded by pellets of vermiculite, and temperature could be controlled within ±0.3°C over the range 150–450°C. The reactor cavity was packed by filling the lower section with 60-mesh particles of alundum (Fisher, "RR" Blue Label) and the upper section with a mixture of alundum and 28–48 mesh catalyst particles. Glass wool plugs were placed at the top and bottom of the reactor and between the upper and lower sections.

The product vapors flowed from the reactor to the previously mentioned Carle valve in the oven and then to a six-port, two-position gas sampling valve (Carle Model 2014) equipped with two matched 0.22-cm^3 sample loops. One loop contained product vapors, while the other was continuously flushed with hydrogen flowing to the gas chromatograph. The hydrogen served both as the carrier stream for the sampling valve and as the reference stream for the gas chromatograph.

Measurement of kinetics. Benzothiophene hydrodesulfurization kinetics studies were performed at 252.5, 302.0, and 332.5°C with a catalyst charge of 100 mg. The catalyst bed was heated to 400°C with helium flow at a rate of 50 cm^3 (STP)/min, then presulfided with 10% in H_2S in H_2 flowing at 50 cm^3 (STP)/min for 2 hr. The reactor was then cooled to the desired temperature under helium flow.

Reactant flow was started at the desired rate, and the system was allowed to reach steady state, as demonstrated by the near equality of conversions measured in successive samples. A sufficient number of samples (3 to 10) were analyzed by glc at each set of reactant partial pressures to ensure that steady state had been reached. At benzothiophene flow rates of 1.5×10^{-6} and 2.1×10^{-6} mole/sec, 6 to 8 hr were typically required to attain steady state after a change in flow rates; with a benzothiophene flow rate of 4.1×10^{-6} mole/sec, steady state was usually achieved in 3 hr.

Product analysis was performed with the on-line glc, using the same column as that previously reported for the pulse-reactor experiments (*11*). In contrast to these earlier experiments, the steady-state kinetics experiments were carried out without a solvent for the benzothiophene feed, and the simpler product mixtures allowed good component separation without temperature programming; the column was operated isothermally at 110°C.

Details of the equipment and procedures are given by Kilanowski (*6*).

RESULTS

Experiments carried out using the reactor packed with alundum demonstrated the absence of conversion of benzothiophene and hydrogen in the absence of the Co–Mo/Al_2O_3 catalyst. With this catalyst, the only hydrocarbon product formed in more than trace amounts was ethylbenzene, and conversions were therefore determined from the ethylbenzene analysis. Experiments with different catalyst loadings gave reproducible conversions, and changing the catalyst particle size from 28–48 mesh to 100–140 mesh led to no change in conversion, demonstrating the absence of an intraparticle diffusion influence on the rate. Calculations using standard correlations confirmed that the rates were not influenced by mixing or transport processes (*6*).

When benzothiophene and hydrogen in the absence of added H_2S were fed to the reactor and experienced low conversions (typically ≤2% of the benzothiophene), the catalyst lost activity, as evidenced by a decreasing conversion with increasing on-stream time; data are presented elsewhere (*6*). This decreasing activity of the catalyst was attributed to structure changes associated with sulfur depletion (*12*); therefore, for determination of quantitative kinetics, H_2S was included in all feeds to prevent the deactivation. When approximately 2 mole% of the feed was H_2S, the catalyst after 40 hr on stream achieved a steady-state activity which was about half the initial activity.

Kinetics

Kinetics experiments were performed at 252.5, 302.0, and 332.5°C with a single 100.2-mg sample of 28–48 mesh sulfided $CoO–MoO_3/\gamma\text{-}Al_2O_3$ catalyst. Partial pressures of benzothiophene, hydrogen, hydrogen sulfide, and helium were varied in the following ranges: benzothiphene, 0.015–0.232; H_2, 0.215–2.04; H_2S, 0.020–0.142; He, 0.819–1.24 atm. Repeat experiments demonstrated that the conversion under standard conditions remained constant within ±5%.

Typical data are shown in Fig. 1, plotted to demonstrate that conversions were differential, determining reaction rates directly. Each experiment produced a value of the rate, and the data set consists of 47 rate values, summarized in Table 1. Repre-

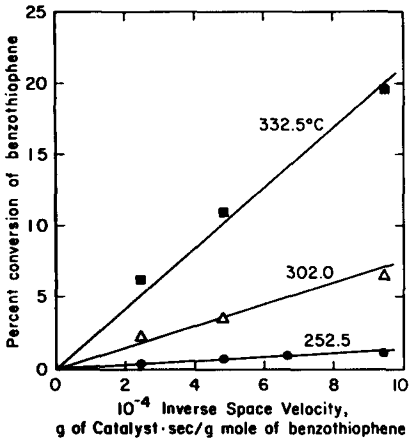

FIG. 1. Hydrodesulfurization of benzothiophene catalyzed by sulfided Co–Mo/Al_2O_3 in a flow microreactor: demonstration of differential conversions. The data were adjusted slightly to $P_{BT} = 0.065$, $P_{H_2} = 1.14$, and $P_{H_2S} = 0.023$ atm.

sentative plots of some of the data are shown in Fig. 2 to indicate trends and comparisons with the equations. The data obtained at 302.0 and 332.5°C (Fig. 2) fall near smooth curves, suggesting saturation kinetics in benzothiophene, but the data obtained at 252.5°C (Fig. 2) show a sharp maximum, indicating complicated kinetics. Inhibition of reaction by H_2S is clearly indicated (Table 1).

DISCUSSION

A number of plausible rate equations of the Langmuir–Hinshelwood type were considered in attempting to correlate the data of Table 1. The equations are listed elsewhere (*6*), and only the several found to be most successful in representing the data are considered here; they are listed in Table 2. All the equations have been identified with Langmuir–Hinshelwood (Hougen–Watson) models (*6*). We proceed empirically, selecting equations on the basis of goodness of fit to the data and deferring the discussion of mechanistic implications until the final paragraphs.

A nonlinear least-squares regression analysis was used with the equations of Table 2 to determine the best equations to describe the data of Table 1. The Univer-

TABLE 1

Summary of Results of Benzothiophene Hydrodesulfurization Kinetics

T (°C)	P_{BT} (atm)	P_{H_2} (atm)	P_{H_2S} (atm)	P_{He} (atm)	$10^7 \times$ Rate of benzothiophene conversion (g mole/g of catalyst sec)
252.5	0.105	0.215	0.022	0.819	0.272
252.5	0.068	0.234	0.026	1.04	0.309
252.5	0.197	0.842	0.020	—	1.04
252.5	0.063	1.14	0.124	—	1.10
252.5	0.063	1.14	0.094	—	1.19
252.5	0.114	0.985	0.021	—	1.25
252.5	0.063	1.11	0.045	—	1.29
252.5	0.082	1.07	0.022	—	1.37
252.5	0.064	1.14	0.023	—	1.42
252.5	0.053	1.20	0.025	—	1.46
252.5	0.046	1.26	0.025	—	1.51
252.5	0.015	1.86	0.038	—	1.77
252.5	0.018	1.94	0.040	—	2.29
252.5	0.022	2.04	0.041	—	2.55
252.5	0.024	1.82	0.037	—	2.62
252.5	0.036	1.39	0.028	—	2.70
252.5	0.030	1.54	0.032	—	3.03
252.5	0.026	1.67	0.034	—	3.15
302.0	0.118	0.238	0.025	0.920	1.84
302.0	0.080	0.272	0.030	1.24	2.00
302.0	0.071	1.28	0.142	—	4.71
302.0	0.070	1.26	0.101	—	5.48
302.0	0.015	1.86	0.038	—	5.51
302.0	0.026	1.67	0.034	—	6.54
302.0	0.073	1.33	0.054	—	7.41
302.0	0.231	0.836	0.023	—	7.85
302.0	0.212	0.866	0.022	—	8.10
302.0	0.155	0.971	0.024	—	8.22
302.0	0.125	1.05	0.024	—	8.43
302.0	0.043	1.79	0.036	—	8.78
302.0	0.106	1.11	0.025	—	8.84
302.0	0.074	1.35	0.027	—	9.16
302.0	0.091	1.17	0.025	—	9.33
332.5	0.127	0.268	0.024	0.980	5.35
332.5	0.014	1.86	0.038	—	12.0
332.5	0.070	1.28	0.143	—	12.2
332.5	0.069	1.26	0.102	—	14.8
332.5	0.025	1.67	0.035	—	17.0
332.5	0.072	1.33	0.055	—	20.1
332.5	0.229	0.834	0.027	—	21.6
332.5	0.210	0.863	0.026	—	22.0
332.5	0.153	0.970	0.027	—	23.0
332.5	0.043	1.79	0.037	—	23.6
332.5	0.123	1.05	0.027	—	24.6
332.5	0.073	1.35	0.029	—	25.6
332.5	0.090	1.17	0.027	—	26.1
332.5	0.104	1.11	0.027	—	26.5

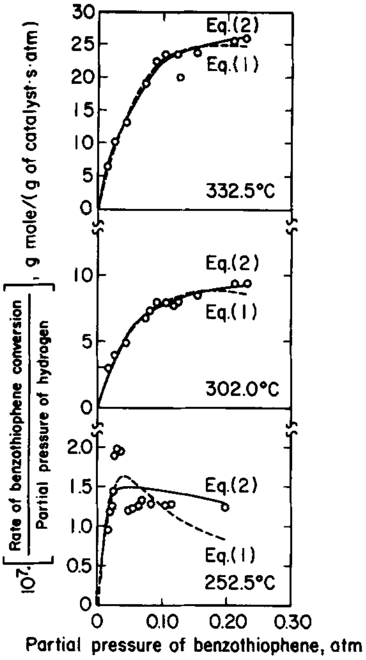

FIG. 2. Benzothiophene hydrodesulfurization kinetics at three temperatures: comparison of data with the predictions of Eqs. (1) and (2) (Table 2). The lines correspond to the reactant mixtures with $P_{H_2S} = 0.025$ atm; the data are for feeds with various P_{H_2S} values, which are only approximately equal to 0.025 atm (Table 1).

sity of Delaware Computing Center's program NLLS (1977) was used, which is based on the technique of Marquardt (*13*). The output of the program includes the best values of the parameters and criteria with which to judge the goodness of fit with the particular equation: (1) $\phi_{\min}$, the minimized sum of the squares of the differences between the observed and predicted rates for each of the observations and (2) nonlinear confidence limits—95% confidence limits are set and the upper and lower bounds on each of the rate equation parameters are listed.

The overall goodness of fit of a prospective rate equation to the data was assessed by these criteria, and the appropriateness of each was also judged by the physical meaningfulness of the calculated parameter values. Meaningful parameter values should comply with the following criteria (*14*): (1) the estimated rate and adsorption constants should be positive; (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, indicating exothermic adsorption.

The values of the parameters giving the best fit accompany each of the equations in Table 2, with the values obtained for $\phi_{\min}$ also included. The data for the full set of equations tested are summarized in Ref. (*6*).

Equation (1) (Table 2) is the only one which fits at all well at all three temperatures (Table 2 and Fig. 2). Equation (3) gave a better fit than Eq. (1) at 302.0 and 332.5°C, as evidenced by the lower values of $\phi_{\min}$, but a poorer fit at 252.5°C, as indicated by the higher $\phi_{\min}$ values and even more so by the high error bounds on the adsorption constants K_{H_2S} and (especially) K_{BT}. Equation (2), (4), and (5) each gave a better fit to the data at 302.0 and 332.5°C than Eqs. (1) and (3) [note the $\phi_{\min}$ values]. The fit with Eq. (2) is illustrated in Fig. 2; the lines representing the predictions of Eq. (2) at 302.0 and 332.5°C are indistinguishable from those given by Eq. (5) at these temperatures. None of these three equations [(2), (4), and (5)], however, gave an acceptable fit of the data at 252.5°C; Eqs. (2) and (4) gave negative values of K_{H_2}; Eq. (5) gave relatively large error bounds for all of the parameters; and the error bounds for K_{BT} are high for all three equations.

Since Eq. (1) is the only one which even roughly fit the data at all three temperatures, it is the only one for which it was meaningful to calculate an apparent activation energy and heats of adsorption. According to the Langmuir–Hinshelwood formulation, the apparent rate constant, k, of Eq. (1) is a lumped parameter which incorporates K_{BT}. Therefore, the apparent activation energy was found from the slope of a

TABLE 2
Summary of Kinetics

Rate equation	Temperature (°C)	k^a (g mole/g of catalyst sec atm²)	K_{BT} (atm⁻¹)	K_{H_2S} (atm⁻¹)	K_{H_2} (atm⁻¹)	$10^{14} \times \phi_{min}$ (g mole/g of catalyst sec)²
(1) $r = \frac{kP_{BT}P_{H_2}}{(1 + K_{BT}P_{BT} + K_{H_2S}P_{H_2S})^2}$	252.5	$(3.40 \pm 0.56) \times 10^{-5}$	$(3.95 \pm 0.60) \times 10^{1}$	$(1.20 \pm 0.55) \times 10^{1}$	—	2.10
	302.0	$(2.58 \pm 0.18) \times 10^{-5}$	6.50 ± 0.61	5.64 ± 1.56	—	3.71
	332.5	$(7.07 \pm 0.33) \times 10^{-5}$	6.06 ± 0.40	6.24 ± 1.04	—	11.7
(2) $r = \frac{kP_{BT}P_{H_2}}{(1 + K_{BT}P_{BT} + K_{H_2S}P_{H_2S})(1 + K_{H_2}P_{H_2})}$	252.5	$(1.41 \pm 0.32) \times 10^{-3}$	$(1.10 \pm 1.14) \times 10^{4}$	$(2.86 \pm 0.22) \times 10^{3}$	$(-1.87 \pm 1.06) \times 10^{-1}$	2.76
	302.0	$(2.36 \pm 0.10) \times 10^{-4}$	$(2.03 \pm 0.08) \times 10^{2}$	$(1.57 \pm 0.17) \times 10^{2}$	$(1.79 \pm 0.41) \times 10^{-1}$	0.985
	332.5	$(2.83 \pm 0.13) \times 10^{-4}$	$(8.71 \pm 0.44) \times 10^{1}$	$(8.73 \pm 1.16) \times 10^{1}$	$(6.54 \pm 3.89) \times 10^{-2}$	8.38
(3) $r = \frac{kP_{BT}P_{H_2}}{(1 + K_{BT}P_{BT} + K_{H_2S}P_{H_2S})}$	252.5	$(1.70 \pm 0.35) \times 10^{1}$	$(1.10 \pm 22.59) \times 10^{8}$	$(1.17 \pm 1.64) \times 10^{7}$	—	3.19
	302.0	$(7.61 \pm 0.31) \times 10^{-5}$	$(7.25 \pm 0.38) \times 10^{1}$	$(6.21 \pm 0.88) \times 10^{1}$	—	1.31
	332.5	$(1.98 \pm 0.08) \times 10^{-4}$	$(6.30 \pm 0.34) \times 10^{1}$	$(6.63 \pm 0.82) \times 10^{1}$	—	8.76
(4) $r = \frac{kP_{BT}P_{H_2}}{(1 + K_{BT}P_{BT} + K_{H_2S}P_{H_2S})(1 + K_{H_2}P_{H_2})^2}$	252.5	$(1.41 \pm 0.32) \times 10^{-3}$	$(1.10 \pm 4.51) \times 10^{4}$	$(2.86 \pm 2.21) \times 10^{3}$	$(-1.88 \pm 1.06) \times 10^{-1}$	2.76
	302.0	$(2.58 \pm 0.11) \times 10^{-4}$	$(2.23 \pm 0.08) \times 10^{2}$	$(1.71 \pm 0.18) \times 10^{2}$	$(8.47 \pm 1.83) \times 10^{-2}$	0.977
	332.5	$(2.95 \pm 0.14) \times 10^{-4}$	$(9.05 \pm 0.44) \times 10^{2}$	$(9.03 \pm 0.12) \times 10^{2}$	$(3.47 \pm 1.91) \times 10^{-2}$	8.34
(5) $r = \frac{kP_{BT}P_{H_2}^2}{(1 + K_{BT}P_{BT} + K_{H_2S}P_{H_2S})(1 + K_{H_2}P_{H_2})^2}$	252.5	7.55 ± 1.58	$(3.65 \pm 5.90) \times 10^{7}$	$(1.28 \pm 0.68) \times 10^{7}$	$(1.68 \pm 0.54) \times 10^{-1}$	2.36
	302.0	1.79 ± 0.07	$(2.43 \pm 0.08) \times 10^{5}$	$(1.64 \pm 0.20) \times 10^{5}$	1.78 ± 0.04	0.804
	332.5	$(4.63 \pm 0.16) \times 10^{-3}$	$(2.99 \pm 0.08) \times 10^{2}$	$(2.78 \pm 0.19) \times 10^{2}$	1.31 ± 0.03	4.24

[a] For Eq. (5) the units of k are g mole/g of catalyst · sec · atm³.

plot of log k/K_{BT} vs $1/T$, the value being 20 ±3 kcal/mole. The heats of adsorption for benzothiophene and hydrogen sulfide were calculated to be -15 ± 10 and -6 ± 6 kcal/mole, respectively. The uncertainty in these latter values reflects the poorness of fit of the data to Eq. (1) at 252.5°C (Fig. 2).

The three equations fitting the data best at the two higher temperatures [Eqs. (2), (4), and (5)] were compared on the basis of just the data obtained at these temperatures. Equation (2) was the only one giving meaningful values of the heats of adsorption; the values for BT and H_2S, respectively, are -19 and -13 kcal/mole.

In summary, the best of the equations of Table 2 in representing all the data is Eq. (1), but Eq. (2) is recommended for the two higher temperatures.

The kinetics results presented here are compared in detail elsewhere (*6*) with kinetics results in the literature. A brief comparison of rates of thiophene hydrodesulfurization measured by several authors and rates of benzothiophene hydrodesulfurization is given in Fig. 3; benzothiphene is about twice as reactive as thiophene under these conditions, whereas at high pressure (70 atm), it is about half as reactive (*15*). In the following paragraphs, we emphasize the comparison with Lee and Butt's (*8*) data for thiophene hydrodesulfurization, since theirs are the most thorough of the literature results and the ones providing the best basis for interpretation.

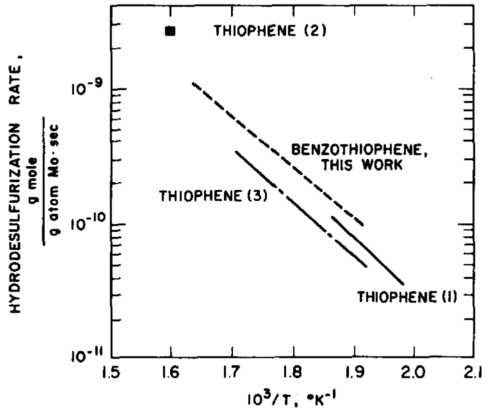

FIG. 3. Rates of hydrodesulfurization of thiophene and of benzothiophene catalyzed by sulfided Co–Mo/Al_2O_3 at 1 atm. The lines are interpolated from the data of the cited authors for the following reactant partial pressures: P_{BT} (or P_T) = 0.04; P_{H_2} 0.94, and P_{H_2S} = 0.02 atm. Rates were calculated from the equations of the respective authors, and values were smoothed to give the lines shown. Similar comparisons for other reactant compositions are given elsewhere (*6*).

Lee and Butt compared their rate data to a set of equations, each of which was compared with the benzothiophene data in this work (*6*). Lee and Butt used a Marquardt (*13*) nonlinear least-squares fitting technique (similar to that used in this work) to determine the parameters and the most appropriate rate equations.

Lee and Butt (*8*) represented their thiophene hydrodesulfurization data with an equation of the form

$$r = \frac{kP_TP_{H_2}}{(1 + K_TP_T + K_{H_2S}P_{H_2S})} \left[\frac{1}{(1 + K_{H_2}P_{H_2})} + k'\right]. \quad (6)$$

With the parameter values they recommended, Eq. (6) predicted rates at 249°C equal within a few percent to those of a limiting case having the form of Eq. (3) [with P_{BT} replaced by P_T]; and Eq. (6) predicted rates at 313°C equal within a few percent to those of a limiting case of the form of Eq. (2) [with P_{BT} replaced by P_T], which is equivalent to the form of equation determined by Espino *et al.* (*5*) for dibenzothiophene hydrodesulfurization.

Comparison of the benzothiophene rate data with an equation of the form of Eq. (6) according to the Marquardt (*13*) technique did not lead to a successful fit. We infer that the development of Eq. (6) for the thiophene rate data was not as straightforward as implied by Lee (*3*) and Lee and Butt (*8*). Application of the Marquardt technique to Lee's data (*6*) failed to generate the parameter values reported by Lee (*3*) and Lee and Butt (*8*), and we infer [having carried out substantiating calculations[3] (*6*)] that the values of K_{H_2} reported by Lee and Butt for Eq. (6) were determined not by the standard Marquardt method, but by an unspecified method, perhaps chosen to ensure reduction of Eq. (6) to the aforementioned limiting cases at the low and high temperatures, for which the parameter values were determined by the standard Marquardt regression technique (*6, 8*).

In summary, we conclude that Eq. (6) is not a good representation of the benzothiophene kinetics data reported here and does not rest on as firm a foundation as other equations (e.g., the aforementioned limiting cases) in representing the thiophene kinetics data of Lee and Butt. We conclude that, both for thiophene and benzothiophene, a single equation with a prudent number of parameters may fail to represent kinetics of hydrodesulfurization over a wide range of temperatures. We suggest that the observed kinetics and changes in kinetics with temperature, which are *roughly* similar for thiophene and benzothiophene, may indicate similar reaction mechanisms for the two and also perhaps similar changes in catalytic activity resulting from changes in surface structure as temperature is changed with mixtures of similar composition.

We also suggest that the repeated recognition of rate equations similar in form to Eq. (2) adds strength to the often recognized (e.g., *8*) conclusion that there is competitive adsorption of H_2S and the sulfur-containing reactant on one kind of catalytic site and noncompetitive adsorption of hydrogen on another kind of site.

NOTATION

BT	Benzothiophene
F_i	Molar flow rate of *i*
k,k'	Reaction rate constant, variable dimensions
K_i	Adsorption equilibrium constant for species *i* in Langmuir–Hinshelwood rate equation, atm^{-1}
P_i	Partial pressure of *i*, atm
r	Rate of catalytic hydrodesulfurization, moles/g of catalyst · sec
T	Temperature, °K; thiophene
W	Mass of catalyst, g

Greek

$\phi_{\min}$	Minimized sum of squares of deviations between observed and predicted rates, [moles/g of catalyst · sec]^2

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[3] The Lee–Butt values of K_{H_2} could not be generated by application of the Marquardt technique, but when the value of K_{H_2} at each temperature was fixed (and equal to the Lee–Butt value), the other parameter values were generated in agreement with those of Lee and Butt (*6*). The singular absence of upper and lower bounds for K_{H_2} in this equation in Lee's thesis (*3*) confirms the inference that values of K_{H_2} were determined arbitrarily. It is not surprising that Lee and Butt's data did not allow a clear determination of the dependence of thiophene hydrodesulfurization rate on P_{H_2}, since this partial pressure was varied in only narrow range (0.72–0.99 atm) (*3*).

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