Kinetics of Thiophene Hydrogenolysis on a Cobalt Molybdate Catalyst

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The intrinsic kinetics of the hydrogenolysis of thiophene on a cobalt molybdate catalyst were studied in a differential reactor with recirculation, at a total pressure of about 1 atm. and temperatures of 235° to 265°C. Retardation of the reaction by both thiophene and hydrogen sulfide was significant and the rate of thiophene disappearance was correlated by a Langmuir-Hinshelwood type of kinetic equation. Hydrogenation of the butene intermediate was inhibited by both butene and hydrogen sulfide and the rate of this reaction was also described with a Langmuir-Hinshelwood rate equation. The forms of the kinetic expressions obtained imply that the butene is not hydrogenated at the original desulfurization site.

The hydrogenolysis of thiophene has received substantial attention in the past, in part because this reaction is a simple analog of the reactions that take place when sulfur-containing petroleum fractions are catalytically desulfurized. Previous investigators (*1* to 7), working at a total pressure of about 1 atm. and in the temperature range 200° to 500°C., have determined the main products of the reaction, and have speculated about the reaction mechanism. There is general agreement that the reaction proceeds on a number of catalysts as shown below.

$$C_4H_4S + 3H_2 \rightarrow C_4H_8 + H_2S \qquad (1)$$

$$C_4H_8 + H_2 \rightarrow C_4H_{10} \qquad (2)$$

The consensus is that the first step of the overall reaction, Reaction 1, proceeds through a butadiene intermediate; butadiene has actually been isolated in small quantities in several studies (2 to 5). The second step of the overall reaction, Reaction 2, is not rapid compared with the first step, so that the C_4 product obtained consists of butane and a mixture of the *n*-butene isomers.

A variety of catalysts has been employed for the reaction, including oxides of vanadium (*3*), oxides of chromium (*2, 4, 5, 7*), oxides or sulfides of molybdenum (*1, 2*), and the so-called cobalt molybdate catalyst (*2, 4, 6*). Cobalt molybdate is an important commercial catalyst for hydrodesulfurization.

Despite the commercial relevance of thiophene hydrogenolysis, studies of the kinetics of this reaction have been limited. The above studies have provided some information, but the only detailed kinetic investigation performed to date is by van Looy and Limido (*7*) on 15% chromium oxide supported on carbon. They studied partial pressures of thiophene and hydrogen in the ranges of 0.5 to 5.0 cm. Hg and 5 to 50 cm. Hg, respectively, at temperatures of 319° to 448°C. At low temperatures the initial rate went through a maximum as the hydrogen partial pressure was increased, at constant thiophene partial pressure. They therefore postulated that the two reactants were competing for the same sites and fitted their data to a Langmuir-Hinshelwood type rate equation of the form

$$r_T = kp_Tp_H/(1 + K_Tp_T + K_Hp_H)^2 \qquad (3)$$

They used a batch reactor and unfortunately the rates were calculated from the initial rate of pressure increase, with the assumption that the products consisted only of butane and hydrogen sulfide. The recent studies of Kolboe and Amberg (*2*) on the reaction over molybdenum sulfide, cobalt molybdate, or chromia gel in a flow system revealed a very marked dependence of reaction rate on degree of conversion on all three catalysts at conversions of a fraction of 1%. On chromia gel, the reaction rate dropped by a factor of about 4 as the percent conversion was increased from 0.2 to about 1.5%. This strong dependence on conversion seems to be caused by adsorption of hydrogen sulfide formed in the reaction (*2, 4*) which van Looy and Limido neglected to consider. The validity of their expressions, even for so-called initial rate conditions, is therefore highly uncertain.

No detailed study of the kinetics of thiophene hydrogenolysis over a cobalt molybdate catalyst has previously been made, although Pease and Keighton (*6*) earlier had studied a cobalt molybdate catalyst at 200°C. and 1 atm. pressure, using thiophene feed concentrations of 0.1 to 0.7%, and mixtures of benzene and hydrogen. They reported that variation of hydrogen concentration between about 0.3 and 0.6 atm. had little effect on the rate and speculated that reaction was retarded by some product. There has been no detailed kinetic study of butene hydrogenation on any catalyst under the conditions that exist when thiophene hydrogenolysis takes place, that is, on a catalyst surface that is fully sulfided.

EXPERIMENTAL APPARATUS AND PROCEDURE

Studies were made with a differential recirculation flow reactor which was operated at steady state. Recent evidence suggests that it may take an appreciable time for concentrations of adsorbed species to reach a steady state (*4, 8*) and for the catalyst surface to become fully sulfided, so a steady state technique was preferred to an unsteady state method. In addition, since it was desired to measure the kinetics of both steps of the reaction, differential rather than integral operation was desired. By use of a recirculation rate which is rapid relative to the rate of reaction, the system becomes a true differential reactor in which rates of reaction can be determined without the necessity of analyzing for very small concentration differences. The recirculation also minimizes temperature and concentration gradients in the reaction zone. The principal disadvantage is that it is not easy to control the composition of the material entering the catalyst bed. Here it was judged to be prohibitively difficult to vary the composition of one component while holding all other concentrations constant. With a recirculation reactor, reaction products are always present in the material entering the catalyst bed. Only by introducing some product in the feed to the loop (or by selectively removing one component) can the concentration of that product be varied independently of the reactant concentration. In the present study, provision was made for feeding hydrogen sulfide to the reaction loop.

Figure 1 is a schematic diagram of the experimental apparatus. Airco prepurified grade hydrogen was fed through

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a Deoxo purifier which converted trace amounts of oxygen to water; the water was then adsorbed by a column of Linde 13X molecular sieve. The hydrogen flow rate was measured with a capillary flowmeter and was accurately controlled by a needle valve and an auxiliary regulator. The hydrogen sulfide feed rate (Matheson technical grade) was also measured with a capillary flowmeter. In this case, the capillary tubing also served to stabilize the hydrogen sulfide flow by introducing a large pressure drop. The flow was adjusted with a pressure regulator above the capillary tubing. Thiophene (Pennsalt Chemicals, minimum purity of 98%) was fed as a liquid by a calibrated hypodermic pump.

Feed streams entered the reaction loop just below the reactor and mixed with the hot gases leaving the reaction zone. The mixture was then passed through a coil which was immersed in a water bath. Gas left the coil at approximately room temperature and passed into a cross, which had a pressure gauge and a 1 lb./sq. in. gauge check valve connected to two of its ports. The check valve maintained a constant pressure in the reaction loop by allowing a small amount of gas to bleed out of the loop. The bleed passed through the sampling valve of the chromatograph and then to vent. The remainder of the gas leaving the coils stayed in the loop and entered a Model 7062 Bantam Dyna-Vac diaphragm pump from which it was pumped through a preheater and then through the reactor. All lines in the feed system and reaction loop were of ¼-in. stainless steel tubing.

In all runs, the feed rate was very small compared to the recirculation rate, so that the composition was essentially uniform at all points in the reaction loop. The composition of the purge from the loop was therefore the same as the composition of the gas entering the reactor. Since the reactor was differential, the kinetic behavior of the present reactor is the same as that of a continuous-flow, stirred-tank reactor (CSTR).

The reactor was a six-in. long, ½-in. diameter, Schedule 40 nipple made of 304 stainless steel. The reactor was positioned vertically for all runs, and the catalyst was supported on a stainless steel screen which was silver-soldered into the reactor. Fittings were located in the walls of the reactor such that thermocouples could be inserted into the gas stream above and below the catalyst bed.

The catalyst used for all the runs reported here consisted of 8.16 g. (as charged to the reactor) of Girdler T-1209 cobalt molybdate catalyst, an extrudate with an average outside diameter of 0.11 in. and about ½-in. in length. The manufacturer reported the following catalyst properties: composition, approximately 3.5% cobalt oxide and 10% molybdenum oxide on activated alumina; surface area, 343 sq. m./g. The apparent density was about 1.2 g./cc. The catalyst was activated prior to the first run by passing hydrogen sulfide, at 662° F. and 1 atm. pressure, through the reactor for 3 hr., at a rate of about 1 liter/hr.

The preheater consisted of a section of tubing, wrapped with a heating tape and insulated over its whole length. The heating tape leads were connected to the output of a control system consisting of a Stepless Controls Corporation PP-14-115 silicon diode rectifier, the signal for which was supplied by a Wheelco 407D proportional controller. The leads from the thermocouple located just above the catalyst bed (No. 2 on Figure 1) were connected to the proportional controller, on which the desired temperature was set. The reading of the thermocouple No. 2 varied by less than ± 0.50°F during the steady state portion of any run.

A second heating tape was wrapped around the reactor, which also was heavily insulated. The tape was connected in series with a variable resistor and an ammeter, and the combined load was plugged into a Variac. The temperature at the thermocouple below the catalyst bed (No. 3 on Figure 1) was controlled by adjusting the Variac and the variable resistor. Temperature control was such that the difference between the temperatures above and below the catalyst bed was typically less than 1°C. The thermocouples in the reactor were made of 20 gauge chromel-alumel wire, and each was connected to a reference thermocouple immersed in an ice bath. Voltages were measured on a potentiometer.

The purge from the reaction loop was analyzed with a Chronofrac VP-1 chromatograph, using the thermal conductivity cell detector. The column was a 7.5 ft. section of 25% dibutyl phthalate on 50-60 mesh Chromosorb, plus a 4.5 ft. section of Burell standard-concentration dimethyl sulfolane packing. The whole column was immersed in an ice bath. Under normal operating conditions, this column effectively separated hydrogen, hydrogen sulfide, butane, 2-butene, and thiophene, but 1-butene was not completely separated from butane. However, by varying conditions such that butane and 1-butene were well separated, it was found that the amount of 1-butene present was within experimental error of the amount that would be predicted by assuming that the double-bond and cis-trans isomerization reactions between the three normal butenes were at equilibrium at the reaction temperature. This assumption was therefore used throughout the study to calculate the amounts of butane and 1-butene present. Negligible error was involved, since the amount of 1-butene was always small compared with the amounts of both butane and 2-butene. The column performed some separation of the cis and trans isomers of 2-butene, but this separation was not complete. The time taken for thiophene to emerge from the column was too long to permit accurate measurement and for convenient experimentation. Therefore, the thiophene concentration was calculated from a sulfur balance. The good closure of the remaining material balances (an average of less than 3%) allows one to place confidence in the calculated thiophene concentration.

Additional details concerning the experimental apparatus and procedure may be found in the thesis of Roberts (*8*).

RESULTS

Twenty-five usable runs were made at one of three reaction temperatures and at a total pressure which varied from 780 to 840 mm. Hg. In twenty of the runs the fresh feed to the reactor loop consisted of hydrogen and thiophene only, in molar ratios varying between about 10 and 30. In 5 of the runs hydrogen sulfide was also included in the fresh feed, in a molar ratio to the thiophene which varied from about ½ to 1. The gas composition in the reactor loop, which is essentially uniform, is determined by the rate of reaction relative to the rate of introduction of fresh feed. The range of partial pressures of reactants and products in the reaction loop (mm. Hg) in the twenty-five runs is shown in Table 1.

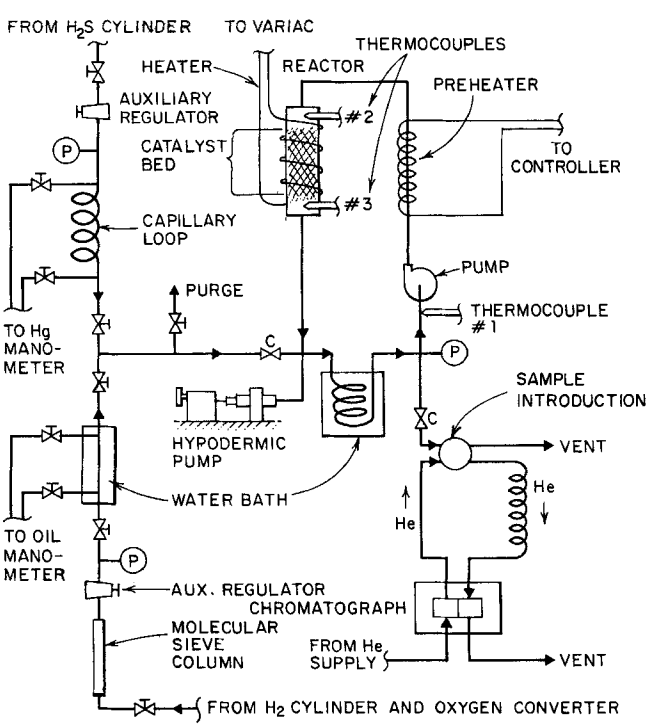

Fig. 1. Diagram of apparatus.

TABLE 1.

	Range of partial pressures studied, mm. Hg				
	C_4H_4S	H_2	H_2S	C_4H_8	C_4H_{10}
No hydrogen sulfide added to the feed	1.7 to 56	605 to 780	6 to 80	0.5 to 15	5.5 to 68
Hydrogen sulfide added to the feed	14 to 51	654 to 734	41 to 95	4 to 11.5	3.5 to 39

Rate of Thiophene Disappearance

Figure 2 is a graph of the rate of thiophene disappearance, that is, the rate of Reaction 1, as a function of the thiophene partial pressure, at each of three reactor temperatures, 235°, 251°, and 265°C. The solid lines on this figure do not describe the best fit of the points, but merely serve to connect the points representing the runs in which no hydrogen sulfide was supplied in the fresh feed, at each of the three reactor temperatures. The number in parentheses beside each point is the partial pressure of hydrogen sulfide in mm. Hg, rounded off to two significant figures. The seeming scatter of the data in Figure 2 is caused mainly by variations in the partial pressure of hydrogen sulfide in the gas in the reaction loop from run to run which affects the reaction rate, and is not primarily the result of experimental error or lack of reproducibility from run to run.

Rate of Butane Formation

Figure 3 is a graph of the rate of butane formation vs. the total partial pressure of the butene isomers, at each of the three reactor temperatures. Once again, the solid lines on the figure do not describe the best fit of the points, but are only meant to connect the points representing the runs in which no hydrogen sulfide was supplied in the feed, at each of the three reactor temperatures. As with Figure 2, the apparent scatter in Figure 3 is caused primarily by the variation in partial pressure of hydrogen sulfide in the reaction loop from run to run.

Reproducibility

Table 2 shows the results of a standard run made periodically during the course of the study to check the activity of the catalyst. In between these standard runs the catalyst was taken through repeated temperature cycles from a minimum temperature of 0°C. to a maximum temperature of over 300°C. The composition of the gas in the reactor ranged from about 100% hydrogen sulfide to 100% hydrogen. Furthermore, although prolonged exposure of the catalyst to air was avoided, some air undoubtedly was introduced into the bed during the connecting and disconnecting of the thiophene pump. The first and last runs in Table 2 encompass in time all twenty-five runs made in this study. It is seen that the reproducibility of experimental data was quite good and no significant drift in catalytic activity took place.

DATA REDUCTION

Calculations (*8*) based on the experimental data showed that temperature and concentration differences between the bulk stream and the catalyst surface were negligible and that the effectiveness factor of the catalyst, which was estimated via the modulus Φ_L (*9*), was greater than 0.95 in all cases.

Since the rate is a complex function of the partial pressures of products and reactants, various forms of Langmuir-Hinshelwood type of rate equations were used to describe the kinetics of the reactions. For the first step, Reaction 1, of the overall reaction, terms for the adsorption of thiophene and hydrogen sulfide were included in the denominator of the rate equation, but no terms were included for the adsorption of butane or hydrogen. Previous work (*4*) suggests that butane and butene have a negligible effect on the reaction rate. Hydrogen was not included because, in the present study, the variation of the hydrogen partial pressure from run to run was too small to allow a meaningful hydrogen adsorption coefficient to be calculated. For Reaction 1, the general form of the rate equation was thus taken to be

$$r_T = \frac{k p_T^{n_T} p_H^{n_H}}{(1 + K_T p_T + K_S p_S)^{n_D}} \tag{4}$$

Taking, for example, $n_D = 2$, if one introduces the term $K_H p_H$ into the denominator, our numerical value for k would represent the term $k''/(1 + K_H p_H)^2$, that for K_T would represent $K_T''/(1 + K_H p_H)$ and that for K_S would represent $K_S''/(1 + K_H p_H)$. Calculations of the best values of the constants k, K_T, and K_S were made at each of the three experimental temperatures by multiple linear regression, for a number of different combinations of n_T, n_H, and n_D. In order to apply this technique, Equation (1) was linearized as

$$\left(\frac{p_T^{n_T} p_H^{n_H}}{r_T}\right)^{(1/n_D)} = \frac{1}{k^{(1/n_D)}} (1 + K_T p_T + K_S p_S) \tag{5}$$

The sum of the squares of the differences between the experimental and the calculated reaction rates was computed for each rate equation, that is, for each combination of n_T, n_H, and n_D using the values of k, K_T, and K_S calculated by regression. The rate equation with the lowest sum of squares was chosen as the final rate equation.

Once the final form of the rate equation had been chosen by the method described above, k, K_T, and K_S were put into the Arrhenius form, $k = Ae^{-E/RT}$, providing six adjustable parameters in Equation (5). The exponentials were expanded in a Taylor series to linearize the resulting equation and an iterative solution to the least-square equations was then obtained. Full details may be found in reference *8*.

Linear multiple regression analyses such as those described above, when applied to Langmuir-Hinshelwood rate equations, have the drawback that deviations in the quantity

$$\left(\frac{p_T^{n_T} \cdot p_H^{n_H}}{r_T}\right)^{1/n_D}$$

are minimized, rather than the deviations in r_T. The errors inherent in this procedure have been discussed (*10* to *12*) and it would be interesting to compare the present results with those that might be derived from the application of a nonlinear, least-squares technique.

The same method was also used for the second step of the overall reaction, Reaction 2. The rate equation was taken to be

TABLE 2. RESULTS OF STANDARD KINETIC RUNS

Temp., °C.	Thiophene partial pressure, mm. Hg	H_2S partial pressure, mm. Hg	Rates, moles/min. × 10^6 Thiophene disappearance	Butane formation
235.6	50.1	22.7	20.4	10.4
236.0	52.2	21.6	19.1	10.0
236.0	51.9	24.2	20.8	12.2
234.8	50.8	21.2	19.2	10.3

Table 3. Potential Rate Equations for Thiophene Disappearance

Model No.	n_T	n_H	n_D	Sum of squares of deviations $\times 10^{+12}$
1	1	1	1	5.39
2	1	1	2	2.11
3	1	0	2	2.03
4	1	1	3	3.03
5	1	2	3	3.28
6	1	1	4	3.75

$$r_c = k' p_B p_H^{n'_H} / (1 + K'_B p_B + K'_T p_T + K'_S p_S)^{n'_D} \quad (6)$$

To avoid the introduction of too many adjustable constants, either K'_B or K'_T was always taken to be zero. Strictly, one should deal with both constants simultaneously, but K_B and K_T are interrelated because of the way in which the experiments were conducted, and with the modest number of sets of data available, we doubted that any additional significance could be obtained from a more elaborate procedure.

A thermodynamic analysis (8) shows that reverse reaction should be negligible for both thiophene disappearance and butane formation under the conditions studied.

Correlating Equations

Rate of Thiophene Disappearance. The correlating equations considered were of the form of Equation (4) with the combinations of n_T, n_H, and n_D shown in Table 3.

The difference between the sum of the squares for models 2 and 3 is too small to be considered significant. Therefore final calculations, that is, values of A, E, A_T, E_T, A_S, and E_S were made for both models. The final value of the sum of the squares of the deviations for model 2, 0.315 $\times 10^{-11}$ was about 25% lower than that for model 3. The best kinetic equation for thiophene disappearance is thus

$$r_T = \frac{k p_T p_H}{(1 + K_T p_T + K_S p_S)^2} \quad (7)$$

The values of E, E_T, and E_S are +3.7, −24, and −19, respectively. If model 3 were chosen, the corresponding values are +9, −18, and −12.

Rate of Butane Formation. The five rate equations shown in Table 5 were tested using the general form of the rate equation given by Equation (6). The difference between the sums for models 4 and 5 is not significant. Model 4, Equation (8), gives values of K'_S closer to those of K_S.

$$r_c = k' p_B p_H / (1 + K'_B p_B + K'_S p_S) \quad (8)$$

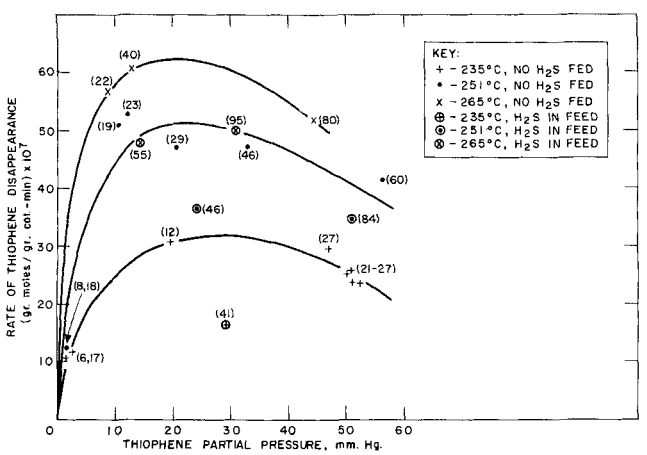

Fig. 2. Summary of experimental results; rate of thiophene disappearance (hydrogen sulfide partial pressure, mm. Hg, given in parentheses).

Table 4. Values of Constants in Equation (7)

T, °C.	k	K_T	K_S
235	0.156×10^{-8}	0.056	0.042
251	0.164×10^{-8}	0.031	0.018
265	0.180×10^{-8}	0.033	0.0074

Tables 4 and 6 present the values of the constants in Equations (7) and (8), respectively, obtained by multiple linear regression of the data at each of the three temperatures. The smoothed values of these constants after being put into the Arrhenius form to calculate activation energies, which are slightly different, are given by Roberts (8).

Rate expressions such as Equation (8) are based on the assumption that all the butene is first desorbed from the site on which it is formed, and subsequently that which is hydrogenated is readsorbed from the gas phase onto the site where hydrogenation takes place. If a fraction f of the butene molecules hydrogenates on the original desulfurization site, without intermediate desorption-adsorption, then under conditions of essentially constant hydrogen partial pressure, the rate expressions should be of the form

$$r_C = f r_T + g(p_B) \quad (9)$$

where $g(p_B)$ denotes some function of the butene partial pressure. Tests of Equation (9) for various forms of $g(p_B)$ were made, both by manual plotting of the data and by computer calculation. However, no equation of the form of Equation (9) that was tested fitted that data as well as Equation (8), including those with $g(p_B)$ in the form of Equation (8). For the form of $g(p_B)$ given by Equation (8) the correlation was poorer the greater the value of f.

DISCUSSION: THIOPHENE REACTION KINETICS

In any series of runs at one temperature without deliberate addition of hydrogen sulfide, the partial pressure of hydrogen sulfide was generally higher in those runs having also a higher partial pressure of thiophene. This was essentially happenstance, from the method used for varying gas composition. For this series of runs the thiophene feed rate was held constant and its partial pressure varied by changing the feed rate of hydrogen. Consequently, the hydrogen sulfide was diluted simultaneously with the thiophene.

Comparison in Figure 2 of runs in which hydrogen sulfide was deliberately added to increase the hydrogen sulfide concentration in the reaction loop with those in which this was not done shows clearly that hydrogen sulfide exerts an inhibiting effect on the reaction rate. The inhibiting effect of thiophene is perhaps less immediately obvious from the figure because of the partial coupling in the experiments between hydrogen sulfide and thiophene concentrations, but is indicated by the necessity to include a term for this effect in order to obtain satisfactory correlation of the data by any of the forms of the Langmuir-Hinshelwood model. Table 4 shows that at all three temperatures K_T exceeds K_S in value, the ratio of the two being greatest at the highest temperature.

The paucity of previous kinetic studies, especially on cobalt molybdate catalysts, limits the comparisons which can be made with past work. In the theory which leads to Langmuir-Hinshelwood models, K_T and K_S are so-called adsorption equilibrium constants for thiophene and hydrogen sulfide, respectively. Therefore, E_T and E_S may be regarded as the apparent heats of chemisorption of these two species. The values, quoted below Equation (7), were derived from data that covered a temperature range of only 30°C. Consequently they are probably somewhat in-

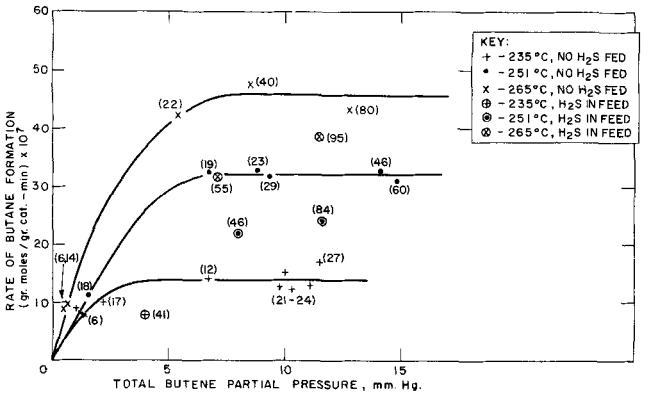

Fig. 3. Summary of experimental results; rate of butane formation (hydrogen sulfide partial pressure, mm. Hg, given in parentheses).

accurate and it is seen that they vary somewhat depending upon which of the two most likely models is chosen. Nevertheless, it is gratifying that both E_T and E_S have negative values as required by theory. The value for thiophene compares fairly well with the value of −17 kcal./mole reported by van Looy and Limido (*7*). Considering the assumptions involved in Langmuir-Hinshelwood type models, it is not surprising that these values are substantially different than the actual heat of adsorption of thiophene on cobalt molybdate of 9.5 kcal./mole which was reported by Owens and Amberg (*4*) from studies using a chromatographic technique. It should also be noted that if a term $K_H p_H$ were significant and were to be included in the denominator of Equation (4), its variation with temperature would result in different values of E, E_T, and E_S than those calculated here.

The value of the apparent activation energy of the reaction rate constant k of 3.7 kcal./mole cannot be directly compared with the value of about 25 kcal./mole reported for the overall thiophene hydrogenolysis reaction on cobalt molybdate catalyst by Owens and Amberg (*4*). The latter was based on an Arrhenius type of plot of log of the percent conversion of thiophene vs. the reciprocal of the temperature, for a series of studies at different temperatures, in a steady state flow reactor using one flow rate and with feed containing 2% thiophene in hydrogen. Conversions varied from about 3.5% at 210°C. to about 50% at 260°C., over which range the data were well represented by a straight line. However, the activation energy dropped off at higher percent conversions. Strictly, this method of plotting is only valid for zero-order reactions and the apparent activation energy reflects the effect of temperature on the adsorption constants as well as on k.

Some Speculations on the Reaction Mechanism

The fallacy of using the form of a kinetic equation to prove that a certain reaction mechanism occurs is well known. In addition to the assumptions underlying Langmuir-Hinshelwood or other models is the fact that especially with complex systems, two or more different postulated mechanisms can lead to the same rate equation. Such is the case with Equation (7), which can be derived from at least two widely different sets of mechanistic assumptions. Granting these valid and powerful criticisms, it is worth noting that Equation (7) is consistent with a reasonably plausible picture of the reaction mechanism. Equation (7) can be derived by assuming that the catalyst surface has two types of sites. Thiophene and hydrogen sulfide compete with each other for one type, but only hydrogen adsorbs on the second type. Thiophene undergoes a two-point adsorption; hydrogen sulfide adsorbs on a single site. The surface coverage of hydrogen is relatively low, and the rate limiting step is the combination of adsorbed thiophene with adsorbed hydrogen. These assumptions seem reasonable on several counts. A two-point thiophene adsorption is generally regarded as necessary (*1*, 3). Furthermore, this picture of a heterogeneous surface has a physical rationale. Thiophene, once it covers the surface in moderate amounts, presents a steric hinderance to the adsorption of other molecules of comparable size. However, a small hydrogen molecule should have access to sites that are inaccessible to larger molecules.

Table 5. Potential Rate Equations for Butane Formation

Model No.	n'_H	n'_D	Restriction	Sum of squares of deviations $\times 10^{+12}$
1	0	1	$K'_B = 0$	1.12
2	0	2	$K'_B = 0$	1.72
3	1	2	$K'_T = 0$	0.76
4	1	1	$K'_T = 0$	0.49
5	0	1	$K'_T = 0$	0.47

Table 6. Values of Constants in Equation (8)

T, °C.	k'	K'_B	K'_S
235	0.319×10^{-8}	1.31	0.123
251	0.153×10^{-8}	0.16	0.026
265	0.130×10^{-8}	0	0.018

The variation in partial pressure of hydrogen in the present studies was so slight that the best functional form of p_H could not be determined with confidence and no mechanistic significance should be inferred from the functional forms presented here.

DISCUSSION: KINETICS OF BUTANE FORMATION

Figure 3 shows that hydrogen sulfide exerts an inhibiting effect on the rate of butene hydrogenation. Furthermore, beyond a certain minimum, the rate of butene hydrogenation appears to be independent of total butene partial pressure. Table 6 shows that the adsorption constant for butene is much larger than that for hydrogen sulfide at 235°C., but they are of about equal value at 265°C. The constants in Equation (8) were fitted to Arrhenius type of expressions, yielding values of E', E'_B, and E'_S of −6, −49, and −32, respectively. However, the accuracy is highly questionable and no fundamental significance should be attributed to them.

An interesting implication of the results on butene hydrogenation is that the best correlation is obtained when f, the fraction of the butene molecules that hydrogenates on the original desulfurization site without undergoing an intermediate desorption, is taken equal to zero. Various pieces of evidence concerning the role of butene in the reaction on different catalysts have been cited, particularly in the papers by Amberg and co-workers (*2*, *4*, *5*), but the matter is far from clear. One might expect thiophene to be adsorbed at least as strongly as butene and therefore to appear in Equation (8) but the mathematical analysis of the potential rate equations in Table 5 indicates that butene has the greater inhibiting effect. The two points of view can be reconciled by the two-site concept if those sites covered with thiophene are assumed to be relatively ineffective for butene hydrogenation.

CONCLUSIONS

The kinetics of both major steps of the reaction between thiophene and hydrogen on a cobalt molybdate catalyst have been studied over a rather narrow range of process conditions. Complex rate equations were found to be necessary to describe adequately the kinetic behavior of both steps. In view of the complex kinetic behavior of the present system, it is unlikely that meaningful results could

have been obtained from anything but a differential reactor operated at steady state, and the present study emphasizes the usefulness of the recirculation type of differential reactor for studies of this type. Even though the kinetics are relatively complex, the stable activity of the sulfided cobalt molybdate catalyst and the fact that the stoichiometry follows a simple series type of reaction sequence without side products suggest that this may be also a useful model reaction.

ACKNOWLEDGMENT

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NOTATION

A = pre-exponential factor in Arrhenius expression for k or K
E = apparent activation energy in Arrhenius expression for k, kcal./mole
E_i = apparent heat of chemisorption of species i
f = fraction of butene molecules which hydrogenate at the original desulfurization site without first desorbing
$g(p_B)$ = function of butene partial pressure, g.-moles/(min.)(g. catalyst)
k = reaction rate constant, g.-moles/[(g. catalyst)(min.)(mm. Hg)]$^{(n_T+n_H)}$
K_i = adsorption constant of species i in Langmuir-Hinshelwood rate equations, mm. Hg^{-1}
n_D = power of denominator in Langmuir-Hinshelwood rate equations
n_i = reaction order with respect to species i in numerator of Langmuir-Hinshelwood rate equations
p_i = partial pressure of component i, mm. Hg
r_i = rate of disappearance or formation of species i, g.-moles/(g. catalyst)(min.)
R = gas constant, cal./(mole)(°K.)
T = absolute temperature, °K.

Subscripts

B = total butenes
C = butane
H = hydrogen
T = thiophene
S = hydrogen sulfide

Superscripts

′ = parameters used in rate equation for butane formation
″ = values of parameters if term $K_H p_H$ were introduced into Equation (4)

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Turbulent Flow in Concentric Annuli

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An eddy diffusivity model was developed and used to predict velocity distributions for turbulent flow of air in annuli. Comparison of distributions calculated by the model with experimental data shows that good agreement between calculated and measured values can be attained for core-to-shell ratios from 0.001 to 0.990. The significant advantage of using a diffusivity model to predict velocity distributions lies in the inherent ability to consider systems with nonlinear stress distributions.

Fully developed turbulent flow of a Newtonian fluid in smooth concentric annuli is of interest to the engineer because of its direct engineering applications and to the scientist because it can provide insight into the problem of developing a complete theory of turbulent flow. The two limiting cases of one-dimensional fully developed turbulent flow in annuli have been studied in detail. They are flow in circular pipes and flow between parallel flat plates. For flows of these types the velocity distributions can be predicted within the accuracy of experimental data with the use of various universal velocity distribution laws (*2, 5, 9, 11*). Although better predictions would be ob-