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Kinetics of the Desulfurization of Thiophene: Reactions of Thiophene and Butene

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The kinetics of the desulfurization of thiophene on a representative $CoO–MoO_3/Al_2O_3$ were studied in the temperature range of 250–313°C for partial pressures of thiophene from 20 to 160 Torr and for partial pressures of hydrogen from 550–750 Torr. Rates of butene hydrogenation were determined in the same experiments for butene partial pressures from 3 to 31 Torr. In addition, separate experiments were carried out on the direct hydrogenation of 1-butene in the absence of thiophene on the same catalyst. Results are also presented for kinetics of the isomerization of 1-butene. The rate correlations developed for these data are generally consistent with the view that the primary hydrogenolysis of thiophene and the hydrogenation of butene occur on different sites, although there is some parallelism of the response of these reactions to pyridine poisoning. A combined model is presented to represent the contributions of strongly and reversibly chemisorbed hydrogen in the reaction of thiophene.

INTRODUCTION

Catalytic desulfurization is an increasingly important process, yet the simplets model reaction of this class, that of thiophene, remains largely unresolved both as to mechanism and kinetics. The present study is addressed to the latter area for both the primary hydrogenolysis of thiophene and the hydrogenation of butenes on a representative cobalt oxide–molybdenum oxide catalyst.

A variety of mechanistic possibilities has been suggested on the basis of results with many catalysts. These may be summarized as follows (*1*, *2*): (i) What is the nature of thiophene chemisorption: across the ring double bond, the C–S bond ("two-point" adsorption), or via the heteroatom ("one point" adsorption)? (ii) What is the nature of the ring opening: via cleavage of C–S bonds, ring hydrogenation, or intramolecular dehydrogenation? (iii) What is the product distribution: are dienes, diacetylenes, or tetrahydrothiophene reaction intermediates? (iv) Are the active sites for ring opening the same as for hydrogenation of primary products? (v) What is the extent of isomerization of olefinic intermediates? These are all fundamental questions; while we do not presume to resolve mechanistic debates on the basis of kinetic data alone, reaction rate correlations may nonetheless be examined for consistency with such proposals.

The kinetics of thiophene desulfurization have been investigated by Pease and Keighton (*3*), Owens and Amberg (*4*), Ghosal, *et al.* (*5*), Satterfield and Roberts (*6*), and Morooka and Hamrin (*7*); Satterfield and Roberts also report data for the hydrogenation of butene. Pease and Keighton report near zero order in hydrogen and

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less than first order in thiophene, while Owens and Amberg report an activation energy of 25 kcal/mole (270–400°C), based on an assumption of zero order in thiophene. Preadsorbed H_2S selectively retarded butene hydrogenation in comparison to thiophene hydrogenolysis, indicating a difference in sites for the two reactions. Satterfield and Roberts (*6*) have reported the most extensive investigations to date; their experimental results for the hydrogenolysis reaction were correlated by:

$$r_T = \frac{kP_TP_H{}^n}{(1 + K_TP_T + K_SP_S)^2}, \qquad (1)$$

where $n = 0$ or 1. Morooka and Hamrin have recently used this form in correlation of rate data in the range of 250–350°C. The kinetics of butane formation were also correlated by Satterfield and Roberts using the expression:

$$r_B = \frac{k'P_BP_H}{(1 + K_B'P_B + K_S'P_S)}, \qquad (2)$$

although they ascribed no particular significance to this form since the correlation produced a negative apparent activation energy. Comparison of the adsorption parameters of Eqs. (1) and (2) strongly suggested differing sites for the two reactions. The major limitation in that work was the limited range of temperature and hydrogen partial pressure employed in experimentation.

Specific studies of the isomerization occurring simultaneously with the desulfurization have been reported by Owens and Amberg (*4*); such activity may be associated with acidic support materials. These reactions are thought to be at or near equilibrium (*6*) under the conditions employed in desulfurization studies; a triangular reaction network (*8*) is commonly employed for representation of the kinetics of acid-catalyzed butene isomerization.

EXPERIMENTAL

Catalyst. The catalyst was prepared via co-impregnation of γ-alumina with aqueous cobalt nitrate and ammonium paramolybdate to incipient wetness (*9, 10*). The support was a Nalco γ-alumina, $\frac{1}{8}$-in. extrudates; 273 m^2/g; by weight: 96.65% Al_2O_3, 2.3% SiO_2, 0.26% Na, 0.28% Ca (Na and Ca as oxide), and trace Ni, Co, Mo, and Fe. After impregnation, the catalyst was air dried for 16 hr at 110°C and then calcined in oxygen for 6 hr. Final composition was 12.5 ± 0.12% MoO_3 and 3.5 ± 0.04% CuO. Metals distribution across the extrudate cross section was constant within ±10% as determined by electron microprobe analysis.

Reagents and analysis. Prepurified hydrogen (99.99%, 5 ppm of H_2O) was passed through a Deoxo D-10-15 unit and was dried by passage through a 13 molecular sieve trap. Hydrogen sulfide (C.P. grade, 99.5%) was dried over anhydrous $CaSO_4$ and was used without further purification. Thiophene (98%, major impurity: benzene) tetrahydrothiophene, and pyridine (Fisher Highest Purity grade) were used as supplied. A dual column in series gc analysis was developed for product composition measurement. Components resolved were hydrogen, hydrogen sulfide, *n*-butane, *cis*- and *trans*-2-butene, butadiene, 1-butene, thiophene, and tetrahydrothiophene. Full details are given by Lee (2).

Reactor system and operation. A standard flow system with separate feed trains for the gases and thiophene, mixed before passage into the reactor, was employed. The reactor was an internally recycled type after the design of Brown and Bennett (*11*), containing from 25 to 35 g of catalyst in the various experiments. Temperature control within ±2°C was provided via a fluidized sand bath.

Reversibly adsorbed water was removed from the catalyst by treatment in flowing argon at 400°C, then reduction was carried out in flowing hydrogen for 10 hr at 400°C (*10*). This pretreatment was carried out prior to all rate measurements at different conditions. Reduction rather than presulfidation was employed for pretreatment for reasons of experimental convenience; the two procedures were shown to yield identical activity levels (*2*). Since sulfidation of the catalyst occurs under reaction conditions in the former case, several hours were required for the catalyst to attain constant activity. At this point, two or three separate measurements of feed and product compositions were made, and the rate was determined from the average values. Care was taken to ensure the absence of intra- and interphase gradients; the conditions required to maintain perfect mixing behavior were determined in separate experimentation and were employed in all rate measurements.

A standard run was repeated periodically during the experimental program. These reproducibility checks indicated no deactivation and yielded rates within ±4.5% after the standard pretreatment. In addition, one set of runs ($T = 313°C$, $20 \leq P_T \leq 160$ mm) was repeated after a period of 3 months on one catalytic sample; rates were reproduced within ±5%.

RESULTS

Primary products from thiophene were 1-butene, *cis*- and *trans*-2-butene, and hydrogen sulfide. Very small amounts of lighter hydrocarbons were formed at high temperature and low P_H. Tetrahydrothiophene was detected in small amounts in all experiments; no butadiene was found under any condition.

The Reaction of Thiophene

Data on thiophene rates are given in Fig. 1. Solid lines join rates measured with no H_2S in the feed, but, since the reactor operates at finite conversion levels, H_2S is present in all runs. There is a significant inhibition of rate by H_2S, observed elsewhere (*6, 7*), as well as inhibition by thiophene at higher concentrations. However, no maximum in rate with P_T was observed, (*6*).

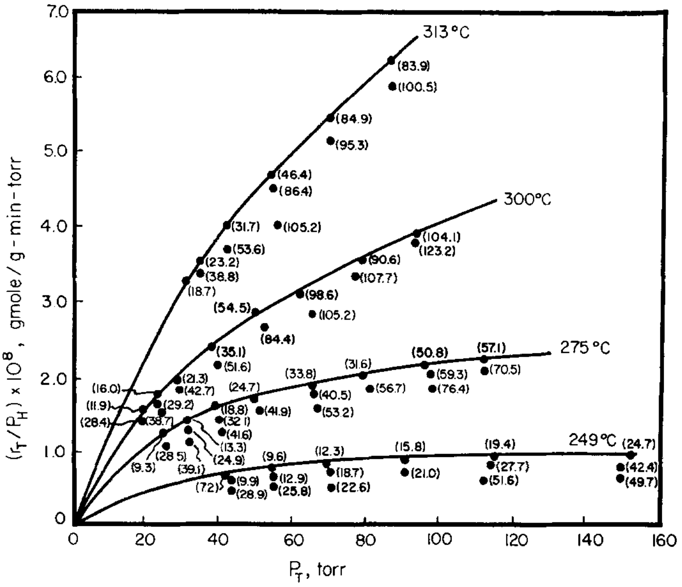

FIG. 1. Rate of reaction of thiophene vs thiophene partial pressure at temperatures in the range of 249–313°C.

Possible kinetic correlations were considered with regard to their pertinence to the following questions: (i) the type of thiophene chemisorption; (ii) dissociative or associative adsorption of hydrogen; (iii) competitive or noncompetitive adsorption of hydrogen and thiophene; (iv) butene hydrogenation on similar or different sites; (v) rate-determining steps other than surface reaction. All these contingencies are contained within the general form (*2*):

$$r_T = \frac{kP_TP_H{}^n}{[1 + K_BP_B + K_TP_T + K_SP_S + (K_HP_H)^n]^m[1 + (K_H'P_H)^n]^l}, \tag{3}$$

where $m = 1, 2$; $n = 0.5, 1$, and $l = 0, 1$.

These forms were examined via a nonlinear least-squares routine (*12*); four expressions were clearly superior in fit to the data and are given in Table 1 as Model 1 ($m = 1$ and 2), Model 2 ($m = 1$), and Model 3 ($m = 1$). The second of these corresponds to the correlation of Satterfield and Roberts (*6*). Of these four, Models 1 ($m = 2$) and 2 ($m = 1$) were essentially equivalent in goodness of fit and about 30% lower in mean square error than Models 1 ($m = 1$) and 3 ($m = 1$). For the two best correlations, the mean square error is $\sim 10^{-14}$, averaged over the temperature range studied, but each has its difficulties. Endothermic chemisorption of hydrogen was indicated by the temperature variation of K_H' in Model 2, while Model 1 is not very specific as to the role of hydrogen in the reaction. The range of P_H investigated ($550 < P_H < 750$) was not sufficiently large to resolve the latter point; Model 2 must, however, be discarded.

Now, the second term in the denominator of Eq. (3) arises from a noncompetitive adsorption of hydrogen, on either different sites or sites inaccessible to thiophene. The former has been suggested by Lipsch and Schuit (*10*), and Massoth (*13*) has reported both reversibly and irreversibly adsorbed hydrogen on MoO_3/Al_2O_3. Hydrogenation by weakly adsorbed hydrogen would correctly be described by Model 1, while any contribution of more strongly adsorbed hydrogen would be described by Model 2. The latter would become more important at higher temperature when hydrogen becomes more mobile on the surface. We then envision a combined process with the major reaction at lower temperature due to weakly adsorbed hydrogen and increasing

TABLE 1

Best Correlations for the Reaction of Thiophene

Model	Rate equation	Comments
1[a]	$\frac{kP_TP_H}{(1 + K_TP_T + K_SP_S)^m}$	Two sites: C_4H_4S and H_2S on one, H_2 on the other (low coverage); surface reaction rds (or H_2 weakly adsorbed).
2	$\frac{kP_TP_H}{(1 + K_TP_T + K_SP_S)^m[1 + (K_H'P_H)^n]}$	As for 1 but with higher surface coverage of H_2.
3	$\frac{kP_T(P_H)^n}{[1 + K_TP_T + K_SP_S + (K_HP_H)^n]^{m+1}}$	Sites of the same kind; competitive adsorption between C_4H_4S and H_2; surface reaction rds.

[a] $m = 1$ for one-point adsorption of thiophene; $m = 2$ for two-point adsorption.

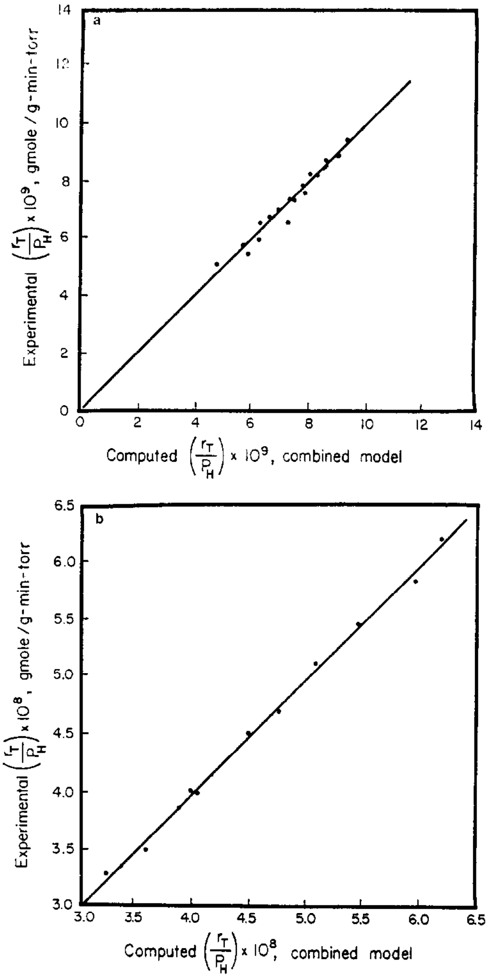

FIG. 2. (a) Computation vs experiment, combined model, 249°C: $44 \leq P_T \leq 153$; $564 \leq P_H \leq 731$; $7.2 \leq P_S \leq 51.6$. (b) Computation vs experiment, combined model, 313°C: $30.9 \leq P_T \leq 87.4$; $529 \leq P_H \leq 786$; $19.5 \leq P_S \leq 105$.

contribution from more strongly adsorbed hydrogen with increasing temperature. The corresponding kinetics involve a combination of Models 1 and 2:

$$r_T = \frac{kP_TP_H}{(1 + K_TP_T + K_SP_S)} \times \left[\frac{1}{(1 + K_H'P_H)} + k''\right], \quad (4)$$

where k'' is a temperature-dependent constant. Indeed, this form consistently provides a slightly better correlation than Model 1. Final discrimination between the two is not possible in view of experimental reproducibility, so results for both are given in Table 2. Figure 2 provides a confrontation of experiment and correlation of the combined model at the extremes of the temperatures investigated.

The Reaction of Tetrahydrothiophene

The rate of reaction of tetrahydrothiophene (THT) was determined at 313°C for this catalyst; it is about twice that of thiophene at comparable conditions of reactant and hydrogen sulfide partial pressure up to the highest pressures investigated (130 Torr). Thiophene and *n*-butanethiol were produced along with the major products; the *n*-butanethiol was always less than 2% of the reactant, but thiophene ranged up to 20% of the partial pressure of THT. As stated before, THT was detected in small amounts (up to

TABLE 2

Correlation Parameters for Thiophene Reaction Rate

Parameter	Model 1 ($m = 2$)	Combined model
k_0	3.4×10^{-5}	1.23×10^{-4}
E_a	11.9	12.9
K_{T_0}	4.91×10^{-8}	5.89×10^{-8}
$-\Delta H_T$	12.2	13.9
K_{S_0}	3.93×10^{-11}	4.77×10^{-14}
$-\Delta H_S$	20.6	29.6
K_{H_0}	—	1.19×10^{-23}
$-\Delta H_H$	—	53.6
k_0''	—	2.81×10^{-7}
E_a''	—	16.2

Temperature (°C)	Mean square error ($\times 10^{14}$) Model 1 ($m = 2$)	 Combined model
249	4.36	3.90
275	4.81	3.95
300	32.91	25.6
313	19.0	13.4

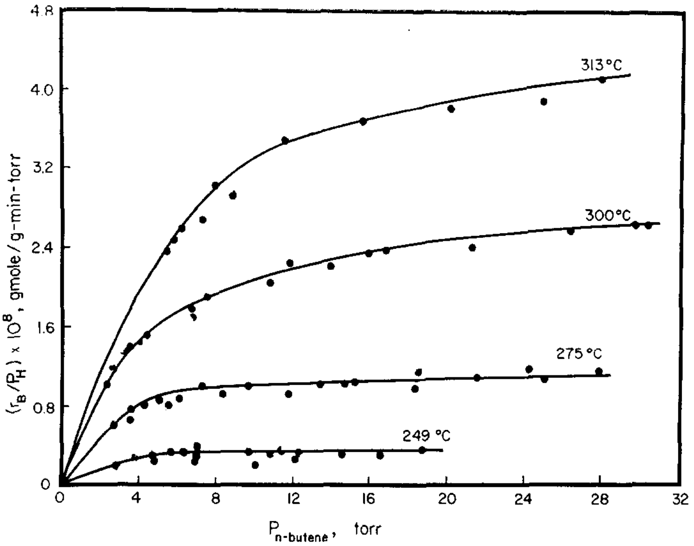

FIG. 3. Rate of formation of butane vs total butene partial pressure at temperatures in the range of 249–313°C for the overall thiophene reaction system.

~3%, based on partial pressure) with thiophene reactant, so the reaction is reversible. The rates of butene formation with either thiophene or THT were about the same, so the higher net rate of reaction of THT is due to dehydrogenation to thiophene.

The Reaction of Butene

Two experiments were used to study butene rates. First the rate of butene formation in the thiophene reaction was measured, as shown in Fig. 3. The inhibition of this reaction by H_2S is much smaller than for thiophene; the P_S varied from 1.5 to 108 Torr in these experiments, and, with few exceptions, the data are represented by a single line at any given temperature.

In the second experiment, the rate of hydrogenation of pure 1-butene (or with H_2S added) in the absence of thiophene was measured to investigate possible differences between hydrogenation and hydrogenolysis sites. These results are given in Fig. 4.

A set of correlations similar to those detailed for thiophene were evaluated for butene hydrogenation. The major points considered were: (i) similar or different active sites for hydrogenolysis and hydrogenation; (ii) competitive adsorption of thiophene with butene on the hydrogenation site (if they differ); (iii) nature of hydrogen chemisorption. The most satisfactory correlation of the data in Fig. 3 is given by Eq. (2), in agreement with Satterfield and Roberts (*6*); parameter values are given in Table 3. There is a much larger H_2S inhibition in the experiments with pure 1-butene, so the correlation does not pertain to these data. Experimental versus computed values for the rate of butene hydrogenation are given in Fig. 5.

Hydrogenation and Hydrogenolysis Sites

A series of experiments with 2% (v/v) pyridine in the thiophene feed was conducted to investigate poisoning of the hydrogenolysis and hydrogenation functions at 250°C; the results are shown in Fig. 6. Pyridine was detected in the reactor effluent at approximately 2.5 hr after initiation of the experiment, corre-

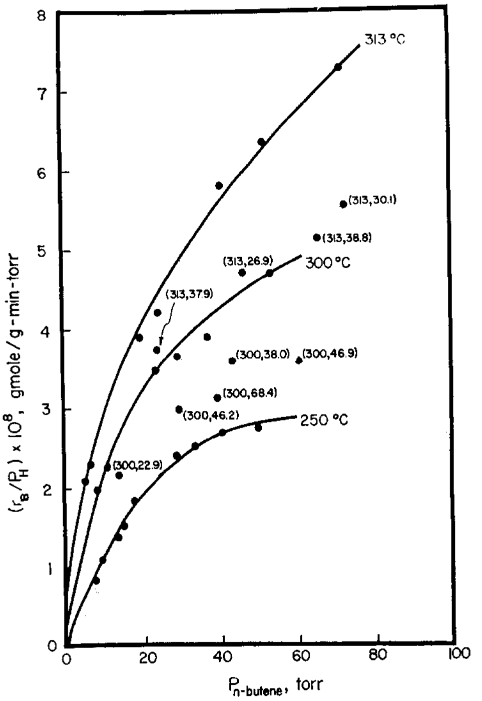

FIG. 4. Rate of hydrogenation of *n*-butene in the absence of thiophene. (—●—) No H_2S present; (● (313, 30.1)) 313°C, 30.1 Torr H_2S.

sponding to an uptake of approximately 3×10^{13} molecules/cm² catalyst surface. These data indicate that butene hydrogenation continues to be poisoned by pyridine well after the thiophene rate has equilibrated. This is suggestive of differences in the hydrogenation and hydrogenolysis sites, although the similar initial declines in activity indicates some parallelism between the two. In particular these results do not preclude hydrogenation on the primary desulfurization site as well as on the hydrogenation site; however, a detailed analysis of the relative hydrogenation and hydrogenolysis rates (2) has shown that this postulate is not consistent with the data.

TABLE 3

Correlation Parameters for Butene Hydrogenation: Equation (2)

Parameter	Value
k_0'	1.37×10^{-7}
E_a'	3.2
K_{B_0}'	4.38×10^{-8}
$-\Delta H_B'$	17.8
K_{S_0}'	1.86×10^{-16}
$-\Delta H_S'$	35.5

Temperature (°C)	Mean square error ($\times 10^{14}$)
275	2.93
300	6.68
313	56.2

Direct Hydrogenation

A confrontation of the results of experiments on hydrogenation of pure 1-butene with model predictions based on parameters determined from the thiophene reaction system is given in Fig. 7. The solid lines correspond to the experimental data of Fig. 4 for no H_2S present, and the dotted lines are computed values from Eq. (2) (experimental points have been omitted for clarity). The prediction falls well below experimental values, although the comparison is somewhat beclouded by the fact

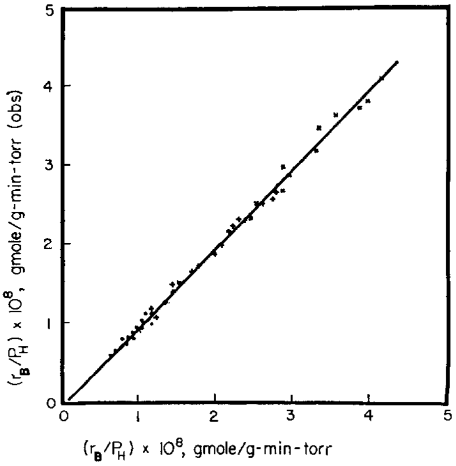

FIG. 5. Experimental vs computed values for butene hydrogenation from Eq. (2): data from the thiophene experiments.

(●) 275°C
(+) 300°C
(×) 313°C
$2.4 \le P_B \le 32.8$ Torr
$9.3 \le P_S \le 123.2$ Torr
$465.0 \le P_H \le 800.1$ Torr.

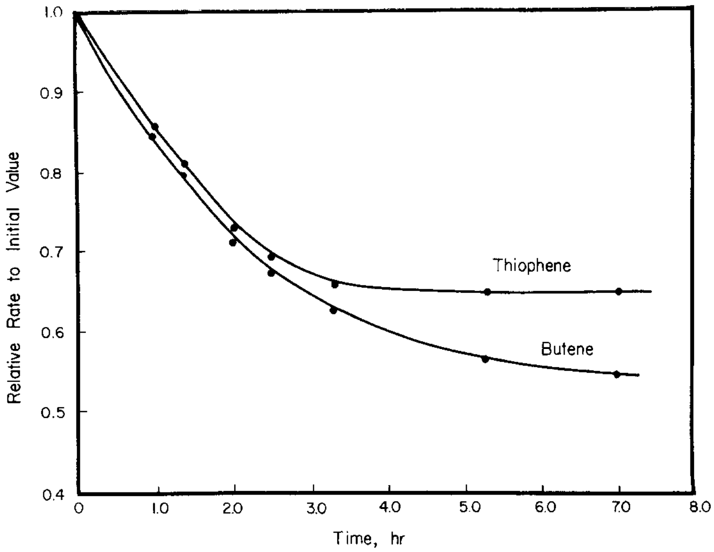

FIG. 6. Poisoning of thiophene and butene reactions by 2% (v/v) pyridine in the feed at 250°C.

that the hydrogenation without thiophene present occurs on an incompletely sulfided surface; this is also the reason that inhibition by hydrogen sulfide was so large in comparison to its effect on hydrogenation in the thiophene reaction system. The discrepancy observed in Fig. 6, however, may be due to the thiophene itself competitively adsorbed on the hydrogenation sites; the point is not clear because kinetic models for butene hydrogenation including thiophene adsorption terms were not as successful as Eq. (2).

Butene Isomerization: Equilibrium

At higher temperatures it was found that the mole fraction ratio among the

TABLE 4

Butene Isomerization Equilibrium

a. Equilibrium constants

T (°C)	x_1	x_{c2}	x_{t2}	K_{1c}	K_{1t}	K_{ct}
249	0.156	0.328	0.516	2.10	3.30	1.64
275	0.173	0.327	0.501	1.89	2.90	1.60
300	0.191	0.321	0.489	1.68	2.56	1.56
313	0.196	0.321	0.484	1.64	2.47	1.54

b. Equilibrium parameters

Reaction	$\Delta H°$ (cal/mole)[a] This work	$\Delta H°$ (cal/mole)[a] Ref. (*14*)	$\Delta S°$ (cal/mole-°K)[a] This work	$\Delta S°$ (cal/mole-°K)[a] Ref. (*14*)
1-to *cis*-2	−2460	−2540	−3.23	−3.04
1-to *trans*-2	−3040	−2960	−3.43	−3.20
cis-2 to *trans*-2	−620	−650	−0.20	−0.20

[a] Determined for 406–560°C in Ref (*14*).

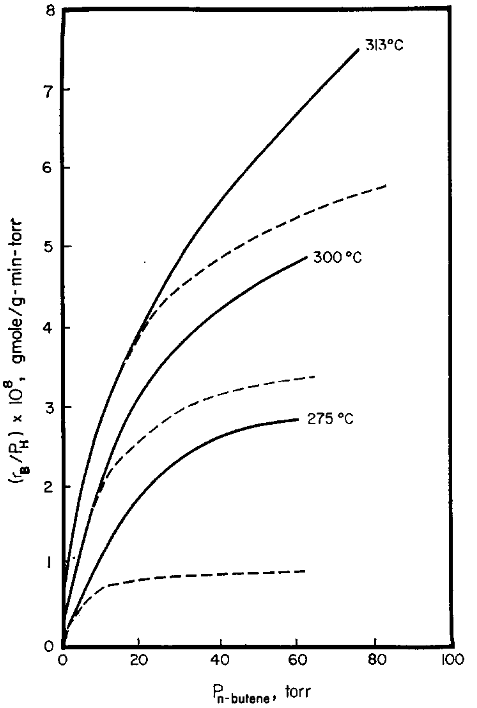

FIG. 7. Comparison of direct hydrogenation results for 1-butene with the prediction of Eq. (2). (——) Data with no H_2S Present (cf. Fig. 4); (- - -) computed from Eq. (2).

isomers 1-butene and *cis*-2- and *trans*-2-butene was invariant with total butene partial pressure. At low temperatures (249°C) there was a small trend in these ratios, approaching a limiting value at low conversion levels. These results agree with those of Owens and Amberg (*4*); the limiting low conversion ratios were taken to represent equilibrium compositions, and the corresponding equilibrium constants were determined and are given in Table 4. The values of $\Delta H°$ and $\Delta S°$ from:

$$\ln(K) = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (5)$$

were obtained from these data via nonlinear estimation, and the results are compared with the reported values of Happel *et al.* (*14*) in Table 4. The agreement is excellent, verifying that the butene isomers are present under the conditions of the present experiment at equilibrium compositions. The kinetic correlation obtained for butene hydrogenation thus represents a lumping of these three species together and reflects the changes in equilibrium composition with temperature level.

TABLE 5

Correlation Parameters for Butene Isomerization: Equation (6)

Parameter	Value
$k_I°$	1.71×10^{-6}
E_I	2.9
$K_1°$	2.45×10^{-4}
$-\Delta H_1$	7.6
$K_2°$	1.98×10^{-3}
$-\Delta H_2$	5.6
$K_S°$	3.05×10^{-11}
$-\Delta H_S$	22.5

Butene Isomerization: Kinetics

From data on the net rate of disappearance of 1-butene, the net rate of appearance of 2-butenes, the equilibrium constants in Table 4, and the relative rates of hydrogenation of 1- and 2-butenes, as reported by Taylor and Dibeler (*15*), it was possible to determine the isomerization rate of 1-butene to 2-butenes as shown in Fig. 8. The *cis*-2 and *trans*-2 isomers are lumped in this analysis. Again, significant inhibition due to H_2S was observed (only some example points are given on the figure to avoid clutter), so it was not possible to use simple power law correlations, as is normally done for this reaction over silica–alumina catalysts. The rate equation was of the form:

$$r_I = \frac{k_I(K_1P_1P_H^{m_1} - K_2P_2P_H^{m_2})}{(1 + K_1P_1 + K_2P_2 + K_SP_S)^n}, \quad (6)$$

with the best individual fit provided by $m_1 = m_2 = 0$ and $n = 1$. Values of the parameters for this model are given in

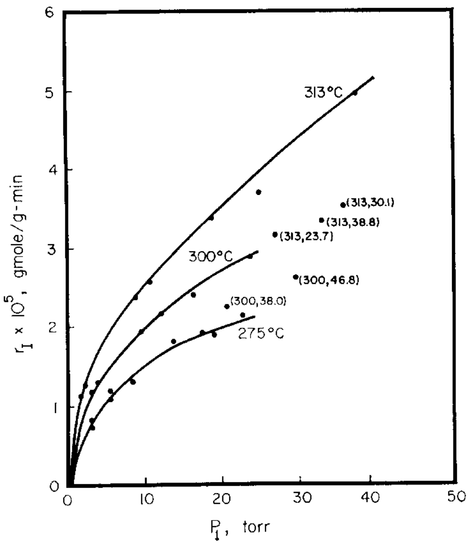

FIG. 8. Isomerization rates for 1-butene to 2-butenes in the thiophene experiments as a function of 1-butene partial pressure. (—●—) no H_2S present; (● (313, 30.1)) 313°C, 30.1 Torr H_2S.

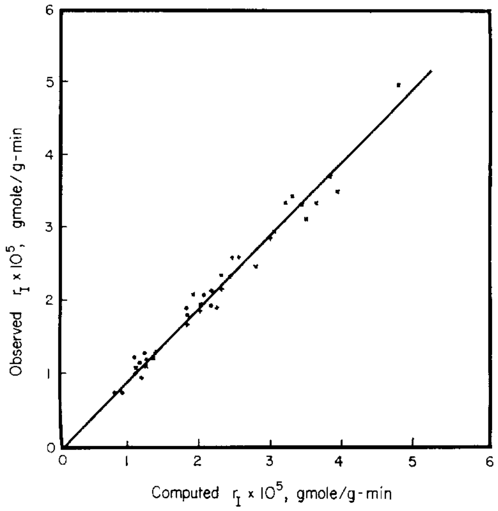

FIG. 9. Experimental vs computed values for butene isomerization from Eq. (6). (●) 275°C; (+) 300°C; (×) 313°C.

Table 5, and the fit provided to the experimental data is illustrated in Fig. 9.

DISCUSSION

The differences in correlation of thiophene kinetics provided by Model 1 and the combined model is small, and discrimination is hampered by the limited range of P_H. The smaller number of parameters in Model 1 should, perhaps, make it preferable; however, that model predicts a maximum in rate with P_T, reported by Satterfield and Roberts (*6*), but not observed here. The combined model requires no such maximum.

Single-site adsorption of thiophene, implied by the combined model, has been visualized as via the heteroatom on the metal site created by an anion vacancy on the oxide surface (*10, 16*), associated with Mo in an oxidation state lower than Mo (IV). Recent studies of deuterium exchange with various heterocyclic sulfur compounds over cobalt-molybdenum oxide surfaces provide evidence that single-site bonding may occur via π complexes as well (*17*).

TABLE 6

Some Reported Values for the Temperature Dependence of Kinetic Parameters for the Reaction of Thiophene

	This work		Ref. (*6*)		Ref. (*7*) (kcal/mole)
	Model 1 (kcal/mole)	*Combined model* (kcal/mole)	*Model 2* (kcal/mole)	*Model 3* (kcal/mole)	
$-\Delta H_T$	12.2	13.9	24	18	—
$-\Delta H_S$	20.6	29.6	19	12	—
E_a	11.9	12.9	3.7	9	20.1 (250–270°C) 9.6 (300–350°C)

In accord with prior findings (*6, 7*), we have found no kinetic evidence for dissociative adsorption of hydrogen. Incorporation of a competitive adsorption term for butene in Model 1 or the combined model for thiophene kinetics resulted in a very small statistically insignificant adsorption constant, which we take as evidence for a difference in hydrogenation and hydrogenolysis sites. Furthermore the large difference between $-\Delta H_S$ for the thiophene correlation and $-\Delta H_S'$ for the butene correlation provides additional support for this view.

The values of $-\Delta H_T$, $-\Delta H_S$, and $-\Delta H_H$ given in Table 2 are, in theory at least, related to some averaged heat of chemisorption on the surface, but intercomparison with other results is risky because such values are obviously dependent on the model employed and the details of catalyst formulation. On this basis, the most appropriate comparison is with the results of Satterfield and Roberts (*6*) and Morooka and Hamrin (*7*). For the former, their Model 2 is equivalent to Model 1 ($m = 2$) here, and their Model 3 is equivalent to Model 1 ($m = 1$) here. The latter have used Model 1 ($m = 2$) for correlation of their data. In both cases, the catalysts are similar: 3.5% CoO, 10% MoO_3 on activated Al_2O_3, 343 m^2/g for Satterfield and Roberts (*6*); 3.5% CoO, 12.5% MoO_3, on Al_2O_3, 270 m^2/g for Morooka and Hamrin (*7*). Some comparisons are given in Table 6; there is good agreement between $-\Delta H_S$ values here and Model 2 (*6*), but large discrepancies for thiophene and the apparent activation energy. Differences in the thiophene parameter may reflect differences in pretreatment procedure [presulfidation with H_2S at 662°C for 3 hr in Ref. (*6*)], and this may also be reflected in the apparent activation energy since the adsorption parameters are lumped into this value. The apparent activation energy obtained in Ref. (*7*) for the higher temperature range is in agreement with the present results from either thiophene model.

The bulk of the present data support the postulate of separate sites for the reactions of thiophene and butene, although, in experiments on direct hydrogenation of butene, there is indirect evidence of the competitive adsorption of thiophene on the hydrogenation sites. The kinetic parameters reported here for butene hydrogenation are not directly comparable with those from Ref. (*6*), since negative apparent activation energies were determined in that work. The value of 17.5 kcal/mole for $-\Delta H_B'$ is vastly different from the 8.5 kcal/mole reported by Owens and Amberg (*4*); however, a thiophene adsorption term may be lumped into the butene constant in the present analysis, as discussed above.

Adsorption parameters obtained from the butene isomerization are comparable with regard to 1-butene, 7.6 kcal/mole vs 8.5 kcal/mole from Ref. (*4*). This must be fortuitous, however, since it is difficult to believe that the same sites are responsible for isomerization and hydrogenation. It is reasonably clear from the present data that, for the temperature ranges involved, the reaction of butene involves the hydrogenation of an equilibrium mixture of 1- and 2-butenes (no skeletal isomerization). Although we have investigated the matter here, a separate kinetic correlation for butene isomerization is thus not required for modeling the rates of the overall desulfurization reaction system.

All activation energy values reported here and in the comparisons are apparent values reflecting the intrinsic activation energy lumped with adsorption parameters. We have attempted no calculation of intrinsic values because of the uncertainty in $-\Delta H_H$. The combined model is the only one in which an independent value was determined for this parameter; the total hydrogen adsorption term is small in comparison to others, thus, large individual errors may be expected due to compensation between $-\Delta H_H$ and K_{H_0}.

NOMENCLATURE

E_a, E_a', E_I	Apparent activation energies for reactions of thiophene, butene hydrogenation, and butene isomerization, kcal/mole
$-\Delta H_T$, $-\Delta H_S$, $-\Delta H_H$	Temperature dependence of adsorption parameters for thiophene, H_2S, and hydrogen (Table 2), kcal/mole
$-\Delta H_B'$, $-\Delta H_S'$	Temperature dependence of adsorption parameters for butene and H_2S (Table 3), kcal/mole
$-\Delta H_1$, $-\Delta H_2$, $-\Delta H_S$	Temperature dependence of adsorption parameters for 1-butene, 2-butenes, and H_2S (Table 5), kcal/mole
k_0, k_0'	Pre-exponential factors for reactions of thiophene and butene (Tables 2 and 3), g mole/[min-g of cat (Torr)^2]
k_I^0	Pre-exponential factor of butene isomerization (Table 5); g mole of 2-butene/(min-g of cat)
K_{T_0}, K_{H_0}, K_{S_0}	Pre-exponential factor of adsorption terms for thiophene, hydrogen, and H_2S (Table 2), Torr^{-1}
K_{B_0}', K_{S_0}'	Pre-exponential factor of adsorption terms for butene and H_2S (Table 3), Torr^{-1}
K_1^0, K_2^0, K_S^0	Pre-exponential factor of adsorption terms for 1-butene, 2-butenes, and H_2S (Table 5), Torr^{-1}
K_{1c}, K_{12}, K_{ct}	Equilibrium constants for butene isomerization: 1 to *cis*-2, 1 to *trans*-2, and *cis*-2 to *tran*-2, respectively (Table 4)
P_T, P_S, P_H	Partial pressures of thiophene, H_2S, and hydrogen (Table 2), Torr
P_B, P_H, P_S	Partial pressures of butene, hydrogen, and H_2S_2 (Table 3), Torr
P_1, P_2, P_S	Partial pressures of 1-butene, 2-butenes, and H_2S (Table 5), Torr
T	Temperature, °C
x_1, x_{c2}, x_{t2}	Mole fractions of 1-, *cis*-2-, and *trans*-2-butenes, respectively (Table 4)

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