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An Investigation of the Mechanism of the Hydrodesulfurization of Thiophene over Sulfided Co–Mo/Al_2O_3 Catalysts

II. The Effect of Promotion by Cobalt on the C–S Bond Cleavage and Double-bond Hydrogenation/Dehydrogenation Activities of Tetrahydrothiophene and Related Compounds

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The C–S bond cleavage reactions of tetrahydrothiophene and but-1-thiol with and without hydrogen, the dehydrogenation of tetrahydrothiophene, and the hydrogenation of but-1,3-diene and of but-1-ene at a temperature of 521 K have been examined at relatively low pressures and temperatures over three related Mo/Al_2O_3 catalysts; one was unpromoted with Co and the others had different Co contents. The catalysts were activated prior to use by treatment in hydrogen sulfide at 573 K followed by hydrogen at 521 K. The products (but-1-ene, but-2-enes, butane, and but-1,3-diene) and product distributions from the reactions of tetrahydrothiophene were similar to those reported in Part I for the hydrosulfurization of thiophene; although but-1-thiol gave similar products, the product distribution was very different, there being much higher proportions of butane. There was no evidence under these conditions for interconversion of tetrahydrothiophene and but-1-thiol. It is concluded that ring hydrogenation of thiophene occurs prior to C–S bond cleavage rather than vice versa; the hydrogenation and C–S bond cleavage sites are distinct but interrelated and are both promoted by Co. These results and conclusions are compared and contrasted with those in the literature.

INTRODUCTION

In Part I of this investigation, the activation procedure for a Co–Mo/Al_2O_3 catalyst was reported (*1*). It was found that the activity of the catalyst for thiophene hydrodesulfurization (HDS) resided in a partially reduced sulfide produced by reaction of the calcined (oxide) material with H_2S, followed by treatment with H_2. The effect of different Co and Mo contents upon activity and selectivity was also investigated using two series of related catalysts. Promotion by the Co was found to have a large effect upon the thiophene HDS reaction, but a much smaller effect upon the butene hydrogenation activity. On the basis of these results, two types of reactive site were postulated, one for C–S bond cleavage and the other for hydrogenation. This suggestion is in agreement with the results of other workers (*2–5*). There exist several views on the nature of these surface sites, and these have recently been reviewed by de Beer and Schuit (*6*).

The results presented in the present paper are an extension of the work presented in Part I, the aim being to examine the reactions of possible intermediates

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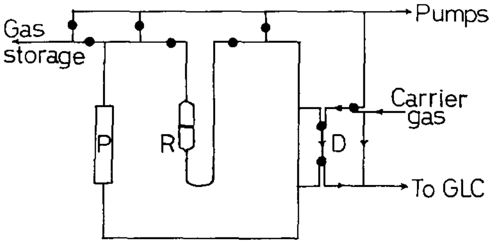


FIG. 1. Schematic representation of the reaction system. P, glass piston pump; R, reaction vessel; D, dosing volume for sample introduction to the gas–liquid chromatograph (GLC).

using several of these catalysts and to gain a further insight into the mechanism of the HDS of thiophene by examining the activities and selectivities of these reactions. Three of the catalysts used in Part I were chosen for study, two of these representing the extremes in activity and the third representing an intermediate behavior, all being used in their active forms (reduced sulfide). The C–S bond cleavage reactions of tetrahydrothiophene and but-1-thiol were investigated, the choice of these particular sulfur compounds being based on their ability to undergo C–S bond cleavage without requiring hydrogenation; they are therefore likely to react predominantly on the C–S bond cleavage site. The choice is further justified on the grounds that these molecules may play some part in the steps leading up to sulfur abstraction during the HDS of thiophene. Particular attention has therefore been paid to the product distributions of these reactions. With regard to the hydrogenation activity of the catalysts, experiments were carried out with but-1-ene and but-1,3-diene; we had observed previously (*1*), in agreement with the observations of Kolboe and Amberg (*7*), that butadiene as formed in small amounts during the HDS reaction and that but-1-ene was the major primary desulfurized product. Although it would have been desirable to study the hydrogenation of thiophene to form tetrahydrothiophene, this is not possible (see Results); however, the reverse reaction, dehydrogenation of tetrahydrothiophene to thiophene, has been studied, and the results are also presented.

All these experiments were carried out on the fully activated (reduced) sulfide. It is possible that the two types of active sites show different characteristics during activation, and therefore a freshly sulfided catalyst was examined with respect to both C–S bond cleavage and hydrogenation activity during its activation in a tetrahydrothiophene–hydrogen mixture. Some experiments were also carried out to investigate the activity of the alumina support for both types of reaction.

The results are discussed in terms of mechanisms which have been put forward in the literature for the HDS of thiophene and related reactions [see Ref. (*2*) and also Refs. (*5*), (*8*), and (*9*)]. It is concluded that the most likely reaction route over our present catalyst involves hydrogenation of the thiophene ring on one site followed by dehydrosulfurization (DHS) on another closely related site.

EXPERIMENTAL

Apparatus. Figure 1 shows the low pressure recirculation system used for both this work and that reported earlier (*1*); it is essentially a constant volume reactor but a piston-type recirculation pump (P) is included which ensures that the reaction mixture is adequately mixed at all stages of the reaction. The recirculation rate and the mass of catalyst were adjusted as required to give a conversion of less than ~5% per pass over the catalyst. The catalyst sample (either 0.1 or 0.02 g; see Results section) was supported on a glass sinter in a Pyrex reaction vessel (R) which was maintained in a furnace kept at a chosen temperature with a controller operated in conjunction with a platinum resistance thermometer and giving temperatures accurate within ±2 K. Reaction mixtures were made up in the gas-handling line using a mercury manometer for pressure measurement.

Analysis was carried out using a Perkin-Elmer F11 gas–liquid chromatograph (GLC) with a flame ionization detector. Samples were introduced through a dosing system (D) composed of greased glass high-vacuum taps. For hydrocarbon analyses, a 4-m GLC column (column A) containing 13% bis-2-methoxyethyl adipate +6% di-2-ethylhexyl sebacate on Chromosorb P (80–100 mesh) in 3-mm-internal-diameter copper tubing maintained at 273 K was used. Analysis of sulfur-containing molecules, where necessary, was carried out using a 2-m column containing 20% polyethylene glycol on celite (60–80 mesh) in 5-mm-internal-diameter nylon tubing maintained at 353 K. Unless otherwise stated, column A was used, and the rates of reactions were determined from the rates of formation of hydrocarbon products.

The technique used is particularly suitable for measuring reaction rates for catalysts which have not achieved steady-state conditions; in the experiments reported here, it was possible to measure rates for catalysts activated in exactly the same way even for reactions which cause deactivation of the catalyst (see Results section).

Catalysts. For the work described here, three samples have been chosen from the series of catalysts described previously (*1*). They were prepared by sequential impregnation of pseudo-boehmite [$Al(OH)_3$] with cobalt formate followed by ammoniacal MoO_3 solutions without calcination between the two steps; this was followed by drying at 383 K, grinding and sieving (particle size, 250–350 μm), and calcination at 823 K. The nominal compositions of the calcined catalysts are as follows (balance γ-alumina): Catalyst 1.1: no cobalt, 11.5% MoO_3; Catalyst 3.2: 2.93% CoO, 11.6% MoO_3; Catalyst 3.5: 4.93% CoO,11.6% MoO_3; In addition to these, a sample of the alumina support was used for some of the experiments. This was prepared by the same procedure used for the catalysts but with the omission of the impregnation steps. Although this procedure may not result in the optimum catalyst, it corresponds quite closely to commonly used industrial methods.

It was found in the previous work (*1*) that sulfidation of the catalyst was an essential step in producing activity. Thus, for the catalysts used here, sulfidation was carried out prior to the reactions and according to the conditions arrived at in the previous paper. For each experiment or sequence of experiments, accurately weighed samples of freshly calcined materials were treated with H_2S at a temperature of 573 K for 17 hr; the pressure of H_2S was 100 Torr (1 Torr $\equiv$ 133.3 N m^{-2}) for 0.1-g samples and 20 Torr for 0.02-g samples. The sample was then treated in H_2 (22 Torr) at 521 K for 1 hr; this procedure was shown previously to produce the optimum activity for HDS of thiophene (*1*).

Chemicals. Thiophene, hydrogen, hydrogen sulfide, and but-1-ene were all the same grades as in the previous work. But-1-thiol and tetrahydrothiophene were BDH laboratory reagents purified by freezing–pumping cycles in the gas mixing system. The but-1,3-diene was supplied by Matheson Inc. (C.P. Grade), and the helium was from the British Oxygen Co. (Research Grade).

Reaction conditions. All reactions were carried out at 521 K with reaction mixtures containing 1.33 Torr of sulfur compound or hydrocarbon plus 22 Torr of H_2 or He; the sequence of reactions is given in the Results section. (At higher temperatures, carbon–carbon bond cleavage occurred for most of the reaction mixtures examined; as this confused the interpretation of the experiments, the temperature of 521 K was chosen as standard.) Outgassing of the catalyst ($P < 10^{-5}$ Torr) was carried out at appropriate points in the pretreatment process described above and again after each of the reactions. Samples of the reaction mixtures were taken at intervals during each reaction, and these were analyzed with the appropriate column. Each experiment lasted for ~15 min unless otherwise stated.

In addition to the experiments using activated catalysts, a series of but-1-ene hydrogenation reactions was carried out on a sample of Catalyst 3.5 which had been sulfided but not treated in hydrogen. The HDS of thiophene was similarly studied on another freshly sulfided sample. The reactions of the alumina support were examined using a sample (0.1 g) which had been subjected to the sulfidation and reduction procedures described above for the supported catalysts.

RESULTS

HDS of Thiophene

The initial rates of reaction of the various molecules over the three Catalysts, 1.1, 3.2, and 3.5, measured from the initial rates of formation of hydrocarbon products, are listed in Table 1; the experimental error is considered to be less than ±10%. The first row of this table (Experiment 1) shows the rates of the HDS of thiophene; the values in parentheses relate to earlier experiments (*1*) in which the thiophene pressure was 3.14 Torr, the other conditions being the same as here. As these figures show, the lower thiophene pressure in the present work (1.33 Torr) using Catalysts 1.1 and 3.5 resulted in a lower reaction rate; this is not so for Catalyst 3.2, which suggests that the present result may be anomalously high (but see the results for tetrahydrothiophene below). The effect of thiophene pressure upon the rate of HDS has been examined by several investigators (*2*, *10*), and values of the exponent of the pressure dependency ranging from 0.5 to 1 are reported, which is consistent with the results for Catalysts 1.1 and 3.5. The ratio of the rate of reaction over Catalyst 3.5 compared with that over Catalyst 1.1, shown in Table 1 for the thiophene HDS reactions, is close to the value previously obtained, i.e., 9.50 compared 10.0. The rates of two thiophene–H_2 reactions were measured over Catalyst 3.5 after the sequence of Experiments 2, 4, and 5 (Table 1), and the rates were found to be 101×10^{-9} and 89×10^{-9} mol s^{-1} g^{-1}, respectively, representing an increase of about 60% in the activity compared with the freshly activated material.

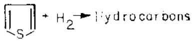
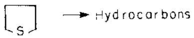
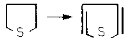
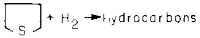
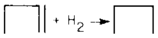
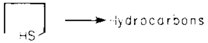
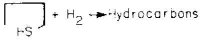
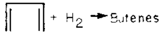
The product distributions in all these reactions of thiophene were found to be similar to those previously reported (*1*); i.e., small amounts of but-1,3-diene were found along with but-1-ene (in excess of the equilibrium proportion with respect to the but-2-enes), *cis*- and *trans*- but-2-ene (in equilibrium with one another), and relatively small amounts of butane.

Decomposition Reactions of Tetrahydrothiophene without Hydrogen

Tetrahydrothiophene reacted in the absence of hydrogen (with He as diluent) to give both hydrocarbon products (Table 1, Experiment 2) and thiophene (Experiment 3), but no butan-1-thiol or half-hydrogenated thiophene was observed. The hydrocarbon products included appreciable quantities of but-1,3-diene, but-1-ene (in excess of its equilibrium amount with respect to the but-2-enes), and the but-2-ene isomers (in equilibrium proportions), but little or no butane. Figure 2 shows the results of an experiment over Catalyst 3.5 in which the hydrocarbon products only were analyzed. This was carried out on a sample previously used for experiments, described in a later section, on the activity and selectivity of catalyst which had been sulfided but not treated in hydrogen. The results of Fig. 2 show clearly that but-1,3-diene is the primary hydrocarbon product of the reaction at low conversions, and that butane is formed only at high conversions.

TABLE 1

Rates of Various Reactions over Catalysts 1.1, 3.2, and 3.5 and the Ratio of the Reaction Rates over Catalysts 3.5 and 1.1[a]

Experiment No.	Reaction	Initial rate ($mol\ s^{-1}\ g^{-1} \times 10^{-9}$)			Ratio of initial rates (rate 3.5/ rate 1.1)	Remarks
		Catalyst 1.1	Catalyst 3.2	Catalyst 3.5		
1		6.26 (9.26)	54.0 (37.7)	59.5 (93.0)	9.50 (10.0)	$P_{C_4H_4S}$ = 1.33 Torr; freshly treated sample (0.1 g) $P_{C_4H_4S}$ = 3.14 Torr; results for maximum activity from (*1*), GLC Column A
2a		5.03	57.9	58.3	11.6	Standard reaction conditions Sequential experiments after Experiment 1
b		4.22	28.3	40.5	9.60	GLC Column A
3a		16.7	25.7	48.0	2.87	Standard reaction conditions Sequential experiments on fresh sample (0.1 g)
b		18.2	23.2	29.0	1.59	GLC Column B
4a		31.0	220	267	8.61	Standard reaction conditions Sequential reactions after Experiment 2
b		32.1	179	400	12.5	GLC Column A
5a		1.99	—	6.19	3.10	Standard reaction conditions Sequential experiments after Experiment 4
b		2.66	5.80	7.60	2.86	GLC Column A
6a		368	1150	2650	7.20	Standard reaction conditions Sequential experiments on fresh sample (0.02 g)
b		226	454	763	3.38	GLC Column A
7a		361	761	1380	3.80	Standard reaction conditions Sequential experiments after Experiment 6
b		431	1150	2210	5.13	GLC Column A
8a		276	531	819	2.97	Standard reaction conditions Sequential experiments after Experiment 7
b		304	673	1220	4.01	GLC Column A

[a] See text for reaction conditions.

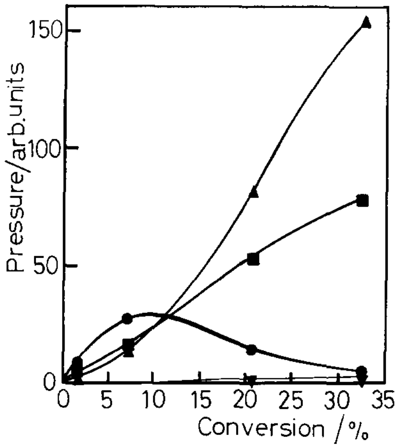


FIG. 2. The production of hydrocarbons in the reaction of tetrahydrothiophene ($P = 1.33$ Torr) without hydrogen over Catalyst 3.5 at 521 K. ▲, *cis*- and *trans*- but-2-ene; ■, but-1-ene; ●, but-1,3-diene; ▼, butane.

The results for the rates of production of hydrocarbons are shown in the second row of Table 1 (Experiment 2); two consecutive experiments are shown for each catalyst. There is a decrease in activity for each material for the second experiment, and this was particularly marked for Catalyst 3.2; a third experiment was carried out for this sample and the rate was found to be very similar to that of Experiment 2b. The order of the activities in Experiment 2b is very similar to that reported previously for the HDS of thiophene (1b) and the ratios of the rates over 3.5 and 1.1 are similar for each of the Experiments 1a, 1b, 2a, and 2b. It would therefore appear that the first rates measured over Catalyst 3.2 are anomalous, but that the subsequent rates are self-consistent; as the anomaly does not appear in the results of Experiment 3 (using a fresh sample), it seems that it is due to some slight difference in the pretreatment procedure prior to Experiment 1a. The next row of Table 1 (3a and b) shows the results of experiments in which the rates of dehydrogenation of tetrahydrothiophene to form thiophene were measured over freshly activated samples of each of the catalysts; there is a smooth gradation in the rates from Catalyst 1.1 to 3.5, and as mentioned above, Catalyst 3.2 appears to behave normally. With Catalyst 1.1, there was a slight increase in the rate in Experiment 3b; with 3.2, there was a slight decrease, and with 3.5 there was a more marked decrease. The ratio of the rates of reaction over Catalysts 3.5 to 1.1 was 2.87 in Experiment 3a, and this dropped to 1.59 in 3b; these ratios compare with a value of 2.85 for the rates reported (*1*) for the formation of butane during thiophene HDS. The rates of formation of thiophene are clearly sufficiently high to provide hydrogen for the hydrogenation reactions referred to above. The production of thiophene is not shown in Fig. 2, as thiophene analysis could not be carried out concurrently with the analysis of the individual hydrocarbons.

Decomposition of Tetrahydrothiophene in Hydrogen

When the reactions of tetrahydrothiophene in the presence of hydrogen were examined over the catalysts used for Experiments 2a and 2b described above, it was found that the rates of reaction were considerably greater than those without hydrogen (see Experiment 4 of Table 1). No poisoning was observed; indeed, the rate of reaction increased appreciably in the second reaction over Catalyst 3.5, and this indicates that the catalyst poisoned in the reaction without hydrogen (Experiment 2) was reactivated when hydrogen was added. The ratios of the rates of reaction over Catalysts 3.5 and 1.1 were 8.6 and 12.5 for the first and second reactions, respectively, and these are similar to those obtained in the absence of hydrogen. The changes in the ratios are probably significant, the ratio dropping in the second reaction without hydrogen and increasing again in the second reaction with hydrogen; this is possibly due to the fact that the

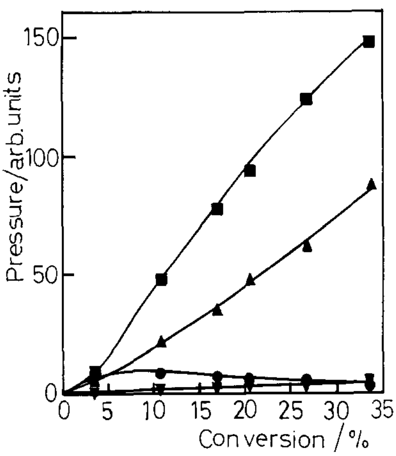


FIG. 3. The production of hydrocarbons in the reaction of tetrahydrothiophene (P = 1.33 Torr) with hydrogen (P = 22 Torr) over Catalyst 3.5 at 521 K. Symbols as in Fig. 2.

conversions were greater with Catalyst 3.5 than with 1.1, and so the partial pressure of product H_2S, and the extent of poisoning by this molecule, would be greatest with the former. It is therefore likely that the most significant rate ratios for the fully activated catalysts are 11.6 for reaction without hydrogen and 12.5 with hydrogen. As above, the hydrocarbon product distributions were examined over a wide range of conversions; this was done using a separate reaction carried out on the sample of Catalyst 3.5 which had been used for Experiments 6, 7, and 8, discussed below. The product distribution is shown in Fig. 3, and this is qualitatively similar to that of Fig. 2; again, but-1-ene appears in excess of its equilibrium proportion with respect to the but-2-enes, and the ratio of the *trans*- to-*cis*-but-2-ene isomers is at the equilibrium value throughout. The proportion of butane in the products is slightly higher than in the reaction without hydrogen, and but-1,3-diene production is decreased. No but-1-thiol was observed among the products.

Hydrogenation of But-1-ene

When the hydrogenation of but-1-ene to butane was examined on the catalysts used for the reactions of tetrahydrothiophene (Experiments 2 and 4, Table 1), a further slight increase in activity occurred. The rate ratios for the reaction on Catalyst 3.5 compared with 1.1 are much lower than those for the desulfurization reactions and are of the same order as for the hydrogenation of but-1-ene during the HDS of thiophene, discussed previously (*1*); concurrently with hydrogenation to butane, a much more rapid isomerization to *cis*- and *trans*-but-2-ene also occurred. These results were quoted in reference (*1*).

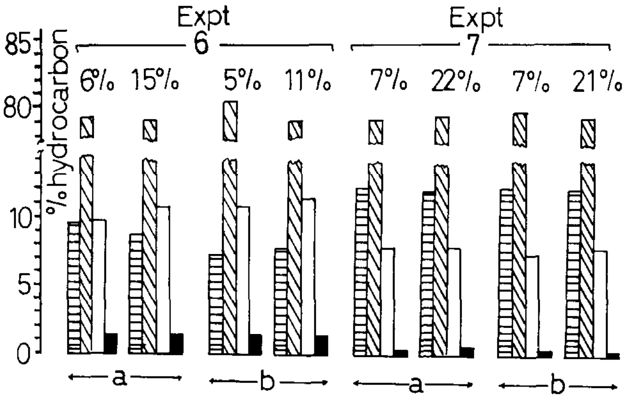


FIG. 4. Histograms showing the product distributions for the reactions of but-1-thiol (P = 1.33 Torr) without hydrogen (Experiments 6a and b) and with hydrogen (P = 22 Torr, Experiments 7a and b) over Catalyst 1.1 at 521 K; the distributions are given at two conversions in each case. ▤, butane; ▧, but-1-ene; □, *cis*- and *trans*- but-2-ene; ■, but-1,3-diene.

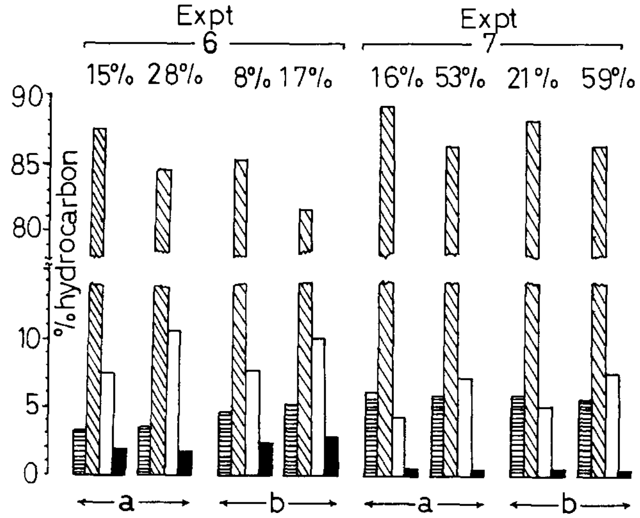


FIG. 5. Histograms showing product distributions over Catalyst 3.5 for the same reactions and conditions as shown in Fig. 4.

Reactions of But-1-thiol without and with Hydrogen

The product distributions for the reactions of but-1-thiol without and with hydrogen are shown schematically by the histograms in Figs. 4 and 5, which give results for Catalysts 1.1 and 3.5, respectively; Experiments 6a and b and 7a and b are shown for both, and the distributions at two conversions are shown for each. The predominant product of the reaction over both catalysts is but-1-ene (~80% at all conversions for 1.1 and slightly higher for 3.5). The but-2-enes are formed in less than the equilibrium amount with respect to but-1-ene, and their formation seems to be hindered by the presence of hydrogen. Butane is a significant product at all conversions, particularly with Catalyst 1.1, and its proportion is increased by the presence of hydrogen; but-1,3-diene is also a significant product throughout the reaction and its proportion is decreased by the presence of hydrogen. The fact that the relative proportions of but-1-ene, butane, and but-1,3-diene do not change markedly during the course of a reaction seems to indicate that they are all formed directly from the surface rather than by readsorption and further reaction as in the production of butane from the butenes during thiophene HDS .

The changes in catalyst activity during the but-1-thiol reactions (Experiments 6 and 7, Table 1) showed a similar pattern to those found for the tetrahydrothiophene reactions; i.e., the activity decreased during reactions in He and then increased during reactions in H_2. The rates of reaction are considerably higher than those of thiophene, tetrahydrothiophene, and but-1-ene discussed above; it is also interesting to note that the thiol reactions in the absence of hydrogen are quite similar to those in the presence of hydrogen, which is in contrast to the results with tetrahydrothiophene. The ratios of the rates on Catalyst 3.5 to those on 1.1 are given in the last column of Table 1 and have values of 7.20 (reactions without H_2) and 5.13 (reactions with H_2) for the reactions in which the catalysts show the highest activities; as discussed above, the catalysts deactivated by the reactions without H_2 give lower values for the ratios.

The initial rates of formation of butane and of but-1,3-diene in Experiments 6 and 7 are shown in Table 2, along with the ratios of the rates of these reactions on Catalysts 3.5 and 1.1. As can be seen, the rate of formation of butane is much higher than the rate of formation of butane from but-1-ene (Experiment 5, Table 1), and this helps to strengthen the conclusion reached above that butane is formed by a different route in this reaction. The formation of but-1,3-diene in the absence of H_2 occurs at a rate similar to its rate of formation during the first reaction of tetrahydrothiophene without H_2 for Catalysts 1.1 and 3.5. The ratios of the rates over the two catalysts show relatively high values for but-1,3-diene formation and low values for butane formation; these are characteristic of C–S bond cleavage and hydrogenation reactions, respectively.

Hydrogenation of But-1,3-diene

The results for the hydrogenation of but-1,3-diene are given in Table 1 (Experiment 8). The predominant products of the reaction were butenes, only small quantities of butane being formed. The rates given in Table 1 therefore refer predominantly to the hydrogenation of one double bond; comparison of the rates for Experiments 5 and 8 in Table 1 shows that the rate of hydrogenation of the first double bond is more than 100-fold greater than that of the second.

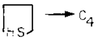
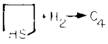
As was observed for other reactions, the activity of but-1,3-diene hydrogenation increased from the first to the second reaction. The ratios of the rates over Catalyst 3.5 to those over 1.1 were 2.97 and 4.01, respectively, which are similar to those referred to above for but-1-ene hydrogenation.

Effect of the Activation Procedure on the Relative Rates of C–S Bond Cleavage and Double-Bond Hydrogenation

We have previously reported (*1*) that the optimum activity of the sulfided catalysts is achieved after exposure of the catalyst either to a sequence of four short thiophene/hydrogen reactions (~15 min each) or to hydrogen alone for an equivalent period of time. The experiments reported in this section were designed to see whether the selectivity of the catalyst changed during this activation procedure; i.e., whether or not the desulfurization and hydrogenation activities developed separately. Table 3 shows the rates of formation of C_4 hydrocarbons for a sequence of experiments with tetrahydrothiophene–H_2 mixtures over Catalyst 3.5. The product

TABLE 2

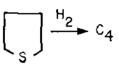
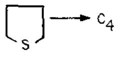
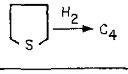
Initial Rates of Product Formation in the Reactions of But-1-thiol[a]

Reaction	Experiment No.	Initial rate of butane formation (10^{-9} mol g^{-1} s^{-1})		Initial rate of but-1,3-diene formation (10^{-9} mol g^{-1} s^{-1})		Ratio of initial rates (rate 3.5/rate 1.1)	
		Catalyst 1.1	Catalyst 3.5	Catalyst 1.1	Catalyst 3.5	Butane	But-1,3-diene
	6a	35.4	84.8	5.20	50.0	2.40	9.62
	b	16.7	35.4	3.03	17.2	2.12	5.68
	7a	44.0	83.8	1.41	4.83	1.90	3.43
	b	53.0	130	1.72	9.95	2.45	5.78

[a] See text for reaction conditions.

TABLE 3

Initial Rates of Product Formation for Reactions of Thiophene over Catalyst 3.5 and Alumina[a]

Catalyst	Reaction	Reaction No.	Initial rate (10^{-9} mol g^{-1} s^{-1})
Freshly sulfided catalyst 3.5		1	47.6
		2	335
		3	374
		4	386
		5	407
Freshly sulfided catalyst 3.5		1	37.1
		2	25.3
Sulfided Al_2O_3			2.05

[a] See text for reaction conditions.

distribution was similar to that reported for the tetrahydrothiophene reactions described above and did not change as the activity increased by a factor of 10. This increase of activity as a function of the number of reactions is similar to that reported previously for thiophene (*1*) and must be explained in a similar way.

Table 3 also shows results for the reaction of tetrahydrothiophene in the absence of hydrogen (in helium). In this case, the activity of the catalyst decreased from the first reaction to the second, but the product distribution was unchanged. This result confirms the fact that hydrogen is necessary for the activation procedure, as concluded previously.

An experiment involving tetrahydrothiophene was carried out using a sample of alumina sulfided in the same way as the catalyst samples; the rate under conditions similar to those for the other experiments was 2.1×10^{-9} mol g^{-1} s^{-1} which is a factor of more than 20 slower than the rate for the first reaction on Catalyst 3.5 (see Table 3). The product distribution was similar to those obtained for similar reactions over the various catalysts.

DISCUSSION

The Nature of the Active Sites

In the previous paper of this series (*1*), we showed that the optimum activity for the HDS of thiophene was obtained after pretreating the catalyst in H_2S followed by exposure to H_2 or to a thiophene/H_2 mixture; we explained this by suggesting that the initial treatment in H_2S gave surface phases akin to Co_9S_8 and MoS_3 and that the latter were partially reduced to species related to MoS_2 on exposure to H_2. We examined the HDS reaction with two series of catalysts containing various quantities of Co and Mo; in all cases, the primary product of the reaction was but-1-ene which was relatively rapidly equilibrated to give a mixture of the butenes, and this mixture was slowly hydrogenated to give butane. Both the desulfurization and hydrogenation activities increased with increasing Co/Mo atomic ratio, but the latter activity was increased to a lesser extent; we concluded that the two reactions occurred on different types of site and suggested that desulfurization took place on a site which involves interaction between Co and Mo sulfides whereas the hydrogenation reaction involves Mo sites less affected by Co promotion.

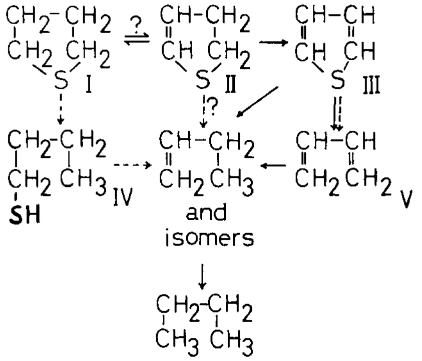
Since our paper (*1*) was submitted for publication, Martinez *et al.* (*11*) have examined samples of our catalysts in the oxide (unsulfided) form; they have reported uv-visible spectroscopic and magnetic measurements as well as results obtained for the desorption of Co and Mo from the calcined materials into aqueous solution. The spectroscopic data showed that the inclusion of Co increased the dispersion of the Mo on the surface; it was also shown from the desorption results that not all the cobalt was present in the surface, although the spectroscopic measurements related to the total Co content. Martinez *et al.* compared our data for production of butane (hydrogenation) with their Co desorption data and concluded that, apart from Catalyst 3.5, there was a good correlation between the two sets of data; they therefore suggested that the hydrogenation site is associated with the Co species. We find it difficult to accept this conclusion for a number of reasons. For example, we feel that undue weight is attached to the data for butane formation which, as it relates to relatively low partial pressures, can only be regarded as being semiquantitative; the most reliable results were those obtained for Catalyst 3.5, and yet this does not fit the correlation. Second, Catalyst 1.1, which contains no cobalt, has significant hydrogenation activity, and this was not included in the correlation. Third, it is difficult to justify correlations between the activities of materials which have been subjected to our sulfidation/reduction treatment with the measurements on the freshly prepared oxidic samples.

Our original suggestion that the hydrogenation occurs at a site associated with the molybdenum and which is also involved in the desulfurization activity and yet less influenced by the cobalt promoter was made for several reasons. These included the facts that (i) the unpromoted catalyst has both desulfurization and hydrogenation activities, (ii) the presence of thiophene inhibits the hydrogenation of but-1-ene [the rate of production of butane in thiophene–butene mixtures was of the same order of magnitude as in the absence of butene, and yet the reaction in the absence of thiophene proceeded about 10 times faster (*1*)], and (iii) the selectivity of the catalyst for HDS of thiophene did not change during the activation procedure. The results in this paper are also in agreement with the model. For example, Catalyst 1.1 has considerable activity for butadiene hydrogenation as well as for dehydrogenation of tetrahydrothiophene to form thiophene. The results for the activation of Catalyst 3.5 with tetrahydrothiophene/H_2 mixtures showed identical hydrocarbon product distributions throughout, and this also confirms the suggestion that the two functions of the catalyst are closely interconnected.

The results presented in Table 1 also reinforce the conclusions of the first paper on separate but related desulfurization and hydrogenation sites; the ratios of the rate on Catalyst 3.5 to that on 1.1 are almost all in the region of 10 for desulfurization reactions and in the region of 3 for hydrogenation and dehydrogenation reactions. The only exception is the value for but-1-thiol which probably reacts by a different mechanism (see below).

Mechanism of the Reaction

A series of papers on the mechanism of the hydrodesulfurization reaction have been published by Amberg and co-workers. In a paper concerning the desulfurization reactions of tetrahydrothiophene, Desikan and Amberg (*5*) suggest that the reaction occurs according to Scheme A. A solid arrow indicates a strong acid site, a dotted arrow a weaker site, and the question mark a route not positively identified. The Scheme implies that the reaction of thiophene (III) to form but-1,3-diene (V), butenes, and butane proceeds by a different route to the desulfurization of tetrahydrothiophene (I), which takes place predominantly via but-1-thiol (IV), with a small contribution to the rate by the alternative route via dehydrogenation to dihydrothiophene and thiophene and subsequent reaction. More recent results by Furimsky and Amberg for the desulfurization of benzothiophene and 2,3-dihydro-



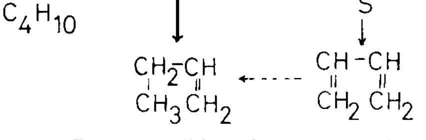
SCHEME A. Scheme given by Desikan and Amberg (*5*) to explain their results for the HDS of thiophene and related reactions.

benzothiophene (*9*). have been interpreted as showing that the initial step is again the cleavage of the hetero-ring. It is interesting to note that Kolboe, a co-worker of Amberg, has suggested (*12*) a refinement of the mechanism involving dehydrosulfurization of adsorbed species; this implies that the initial product from but-1-thiol will be but-1-ene, that from tetrahydrothiophene will be but-1,3-diene (or but-1-thiol, if desorption occurs before rupture of the second C–S bond) and that for thiophene is likely to be an acetylenic residue, unlikely to desorb itself but instead being hydrogenated to give but-1,3-diene as well as butenes and butane.

We believe that the results presented in this paper can be explained using a different mechanism involving the hydrogenation of thiophene (III) to give tetrahydrothiophene (I) followed by dehydrosulfurization to give but-1,3-diene (V) which may subsequently be hydrogenated further to give the butenes and butane. This alternative mechanism was considered but rejected by Amberg and co-workers; the probable reason for the difference between our results and theirs is the very different reaction conditions (particularly of pressure) used in the two sets of experiments, but the difference may also be due to different methods of catalyst preparation. In the following paragraphs, we will compare and contrast our results with those of Amberg and co-workers and will then put forward arguments for our interpretation of the present results.

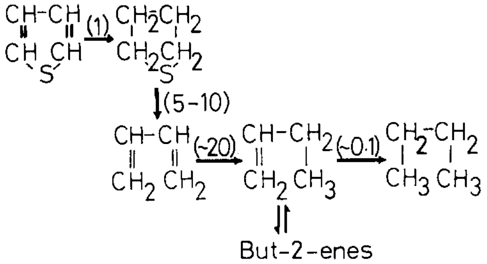
We will first discuss the product distributions of the various reactions. Our observation that the HDS of thiophene gives traces of but-1,3-diene, but-1-ene (in excess of the equilibrium distribution), *cis*- and *trans*-but-2-ene, and small quantities of butane over all our catalysts is in agreement with the observations reported by Owens and Amberg (*8*). In the absence of hydrogen, tetrahydrothiophene is both dehydrogenated to give thiophene and desulfurized (see Fig. 2) to give but-1,3-diene (in much higher proportions than from thiophene) together with the butenes and traces of butane, the butane becoming appreciable only at high conversion; no trace of but-1-thiol was observed, in contrast to the observations of Desikan and Amberg (*5*). Slight poisoning of the catalyst occurs in these experiments, but the activity is regenerated after hydrogen has been introduced. The rate of desulfurization of tetrahydrothiophene in H_2 is about five times faster than that of thiophene. Hydrogen considerably increased the rate of the reaction and dehydrogenation no longer occurred; the hydrocarbon product distribution (see Fig. 3) was qualitatively the same as that for the reaction without hydrogen but with the but-1,3-diene lower throughout, so we conclude that the main function of the hydrogen is either to keep the surface sites unblocked or to keep the surface in its partially reduced state, and although hydrogen does not participate in the formation of the but-1,3-diene, it increases the rate of the hydrogenation to give butenes. The results of Desikan and Amberg for the tetrahydrothiophene H_2 reaction (*5*), on which they based their scheme, are different in some essential features: they observed only the butenes and butane among their products together with thiophene and but-1-thiol (depending on the history of the sample); they observed no but-1,3-diene and could not distinguish whether but-2-ene or but-1-ene was the primary product of the reaction. We find that but-1-thiol reacts both without and with hydrogen (at comparable rates; see Table 1) to give but-1,3-diene and but-1-ene, in excess over the but-2-enes, and butane is also a significant product; Desikan and Amberg also report for the same reaction that butane is formed in substantial quantities, but they do not give a breakdown of the butene analysis. Our results for hydrogenation of but-1,3-diene are similar to those reported by Owens and Amberg (*8*), the predominant product being but-1-ene, and the hydrogenation of the second bond occurs relatively slowly; the hydrogenation of the first double bond of but-1,3-diene occurs ~100 times faster than the hydrogenation of but-1-ene (Table 1, Experiments 5 and 8).

We believe that our results argue against the participation of but-1-thiol as an intermediate product (see Scheme A, species IV) under our experimental conditions. The product distribution from this molecule was very different from that from thiophene and tetrahydrothiophene: But-1,3-diene was formed relatively rapidly, and the rate of production of butane (see Table 2) was greater than that from but-1-ene. But-1-ene is most probably formed by dehydrosulfurization (DHS) of the thiol, and butane is also formed directly from the parent molecule by substitution of the –SH group by hydrogen; the DHS is formally equivalent to dehydration of an alcohol and, by analogy, could conceivably even occur on the alumina support. The production of but-1,3-diene could take place by dehydrogenation of but-1-ene, but this step is not possible on thermodynamic grounds ($K_p \simeq 10^{-6}$). In consequence, we suggest that dehydrocyclization to a tetrahydrothiophene species followed by DHS is more probable; the production of part of the but-1-ene from the but-1,3-diene so formed is also possible although this cannot be the major route for its formation (compare the results for Expeiiments 3 and 4 with those of 6 and 7 in Table 1, remembering that but-1-ene is the major product in the reactions of but-1-thiol). These ideas are embodied in Scheme B. If but-1-thiol was a significant intermediate in the HDS of thiophene or tetrahydrothiophene under our conditions, we would expect to find larger proportions of but-1,3-diene and particularly butane among the products of the reaction, i.e., approaching 10% of butane in the products instead of approximately 1% as observed (*1*).



SCHEME B. A possible scheme to explain the results for the HDS of but-1-thiol.

In their scheme for the reaction (Scheme A), Desikan and Amberg (*5*) show the dehydrogenation of tetrahydrothiophene to form thiophene but argue against the reverse reaction, saying that tetrahydrothiophene was not observed in reactions of thiophene. The nonobservance of tetrahydrothiophene does not rule out its presence in small quantities or of surface species directly related to it. The faster reaction of the tetrahydrothiophene, in our opinion, argues in favor of its possible inclusion as an intermediate in our experiments, and its rapid dehydrogenation in the absence of hydrogen indicates that the interconversion of the two sulfur-containing molecules is rapid. Also in favor of such a sequence is the very similar product distributions from both molecules. We suggest that Scheme C explains the results.



SCHEME C. A possible scheme to explain the results for the HDS of thiophene and related reactions. Approximate relative rates for reactions over Catalyst 3.5 are given in parentheses.

In this scheme, horizontal arrows indicate a hydrogenation reaction, and vertical arrows indicate desulfurization; these conclusions are strengthened by the relative rates for Catalysts 1.1 and 3.5 given in Table 1. We do not attempt to show possible surface entities and do not necessarily imply that all molecules shown in

Scheme C are formed in the gas phase. The numbers in brackets refer to the approximate relative rates of the various reactions, these being based on the results for Catalyst 3.5 shown in Table 1.

Mikovsky and co-workers (*13*) have argued against such a scheme for the desulfurization reaction based on their observation that H_2S only is formed initially in experiments involving thiophene–D_2 mixtures over Co–Mo/Al_2O_3 catalysts; this implies that the first step is the breakdown of thiophene to form acetylenic residues, in agreement with the ideas of Kolboe (*12*). However, Eyre *et al.* (*14*) have observed isotopic mixing in similar experiments with unsupported MoS_2, and we have made similar observations with our catalysts (*15*).

The results and interpretation presented in this paper, contrasting as they do with those of Amberg and co-workers, should not be thought of as negating their work; rather, they illustrate the differences which can result when apparently the same reaction and catalysts are examined under different conditions. In this case, the main difference is probably that of the pressures used, although the differences in methods of catalyst preparation may also be of some importance. It is possible that the mechanism which we have put forward may occur to a minor extent under Amberg's conditions and vice versa.

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