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Some Catalytic Reactions of Thiophene on Disulfides of Tungsten and Molybdenum

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The exchange reaction between thiophene and deuterium has been followed over tungsten disulfide and over molybdenum disulfide. All four hydrogens in the molecule are replaced at the same rate over the tungsten disulfide but on molybdenum disulfide the hydrogen atoms on the carbon atoms β to the sulfur atom exchange more slowly than those on the α carbon atoms. Substantially higher temperatures are necessary to exchange tetrahydrothiophene and deuterium and decomposition occurs simultaneously on both catalysts.

The decomposition of thiophene and tetrahydrothiophene in the presence of hydrogen and some allied reactions such as the hydrogenation of butadiene and the isomerization of but-1-ene have been examined. Tungsten disulfide forms similar products from both sulfur compounds which are mainly hydrogen sulfide, an equilibrium mixture of straight-chain butenes and some butane. Relatively more unsaturated products, including some butadiene from tetrahydrothiophene, are formed over molybdenum disulfide.

Some general schemes for the various reactions are discussed. Both catalysts show much lower activity for the rupture of the C–S bond in the cyclic molecules than for the rupture of the same bond in straight-chain molecules such as mercaptans or dialkyl sulfides. Most of the differences between the two catalysts arise because tungsten disulfide is a relatively better catalyst than molybdenum disulfide for the activation of C–H bonds and for bringing about reactions which involve the addition or subtraction of hydrogen atoms from hydrocarbon molecules or from the hydrocarbon portion of the cyclic molecules.

INTRODUCTION

The use of sulfide catalysts in the hydrodesulfurization of thiophene has been the subject of a number of investigations and progress has been reviewed by McKinley (*1*) and more recently by Weisser (*2*). While it is probable that the reaction to form butane and hydrogen sulfide from thiophene always proceeds in a series of consecutive steps (*3*), there have been various proposals as to the nature of the intermediate steps involved with different catalysts. Thus, the initial process has been said to involve the formation of tetrahydrothiophene (*4, 5*) or ring-opening to form butadiene thiol (*6*). Detailed investigations have been made by Amberg and his co-workers (*3, 7, 8, 9*) of reactions on sulfided cobalt molybdate and sulfided chromia. They concluded that the predominant reaction sequence with thiophene or methylthiophenes involves C–S bond fission with the formation of dienes and olefins followed by hydrogenation to saturated products. The main reaction with hydrothiophenes was hydrodecyclization to *n*-butanethiol and conversion of the latter to butenes, butane, and hydrogen sulfide with a second and less prominent desulfurization sequence involving thiophene as an intermediate.

The present work is an extension of previous investigations (*10, 11, 12*) in which the behavior of a series of simple sulfur compounds (hydrogen sulfide, methyl mercaptan, and ethyl mercaptan) has been examined in a static system on the disulfides of tungsten and molybdenum with deuterium as well as with hydrogen. The main objects of the work were to compare the ease of rupture of the C–S bond in cyclic molecules with ease of rupture of the same bond in the mercaptans and to learn by use of a static system and by exchange experiments with deuterium more about the processes which occur with thiophene and tetrahydrothiophene on these two sulfide catalysts.

EXPERIMENTAL

The apparatus, consisting principally of a reaction vessel linked by a capillary leak to a mass spectrometer, the catalysts, and their pretreatment, and the general experimental procedure have been described (*10, 11, 12*).

Thiophene was obtained from British Drug Houses Ltd. and purified using a preparative gas-liquid chromatography column so that benzene, the main impurity, was reduced to less than 0.2%. Tetrahydrothiophene was obtained from L. Light & Co. Ltd. and the purity of both compounds was checked by mass spectrometric analysis and by gas-liquid chromatography.

The isotopic thiophenes produced in exchange experiments with deuterium were analyzed in the mass spectrometer with an accelerating voltage of 17 V for the ionizing electrons. The products from all other reactions were estimated with 15-V electrons in order to reduce uncertainties associated with the formation of fragment ions. The amounts of tetrahydrothiophene, thiophene, butadiene, and hydrogen sulfide were obtained from the peaks corresponding to the parent ions with values of m/e of 88, 84, 54, and 34, respectively. The fragment ions with m/e of 43 and 41 were used to estimate the amounts of n-butanes and the total butenes, respectively, after making a number of minor corrections for the contributions from other molecules to these peaks. A number of calibration mixtures were used to determine the sensitivities of the various peaks for the different compounds and the amounts of the products were expressed either as a percentage of the total sulfur content or the total carbon content of the gas phase.

Detailed analyses of the butenes were obtained at the end of some reactions by withdrawing samples from the reaction mixture and analyzing by GLC. Further information about the composition of the isotopic thiophenes formed by exchange over molybdenum disulfide was also found by examining the products in a Varian Associates, Model HR 100 NMR spectrometer.

RESULTS

Control Experiments

In order to check that the influence of homogeneous reactions or catalysis by the walls of the reaction vessel was negligible compared with the effect of the sulfide catalysts, experiments were carried out in the absence of catalyst. Less than 1% exchange of thiophene with deuterium was found after 5 hr at 420°C and no exchange of tetrahydrothiophene was detectable after 4 hr at 375°C. In neither case was there evidence of decomposition of the molecules to form hydrogen sulfide or other products.

Exchange with Deuterium

The hydrogen atoms in thiophene were replaced by deuterium on both catalysts in temperature ranges which were well below those required for decomposition of the molecule. Results are summarized in Table

TABLE 1
RATES OF EXCHANGE AND ARRHENIUS PARAMETERS FOR THIOPHENE (13 MM) AND DEUTERIUM (130 MM)

On 2.43 g MoS_2			On 0.55 g WS_2	
Temp. (°C)	Initial rates (%/min)		Temp. (°C)	Initial rate (%/min)
	Fast process	Slow process		
165	0.09	—	105	0.19
195	0.49	—	135	1.05
220	0.68	—	155	3.45
240	1.12	(0.01)	205	16.3
265	1.96	0.18		
E (kcal/mole)	14.3 ± 1.5	—	—	16.0 ± 1.0
$\log_{10} A$ (A in atoms/sec cm^2)	16.4 ± 1.0	—	—	19.0 ± 0.8

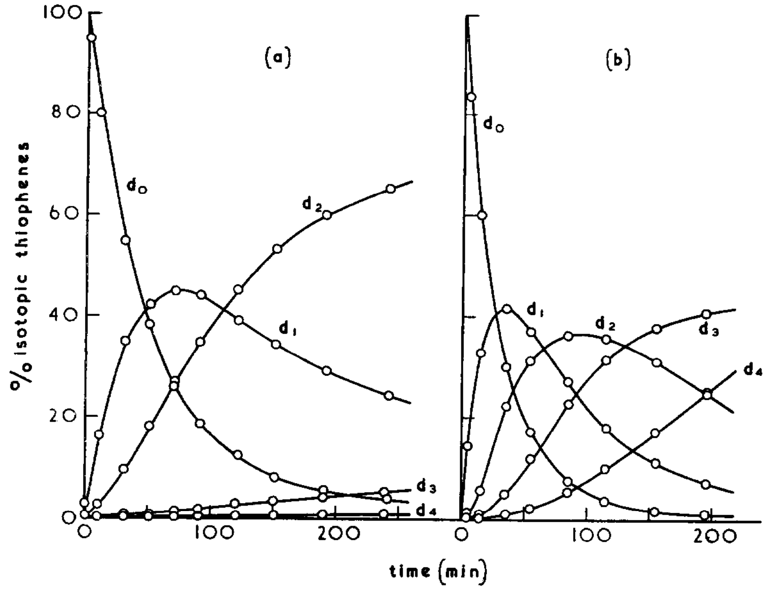

FIG. 1. Exchange reactions of thiophene with deuterium: (a) on MoS$_2$ at 265°C, and (b) on WS$_2$ at 155°C, expressed as per cent isotopic composition of total thiophenes.

1 and typical experiments are shown in Fig. 1. Stepwise exchange with the replacement of a single hydrogen atom at a time was observed on both catalysts and on tungsten disulfide there was no detectable difference in the rate of exchange of the two kinds of hydrogen atoms in the molecule. However, on molybdenum disulfide, two of

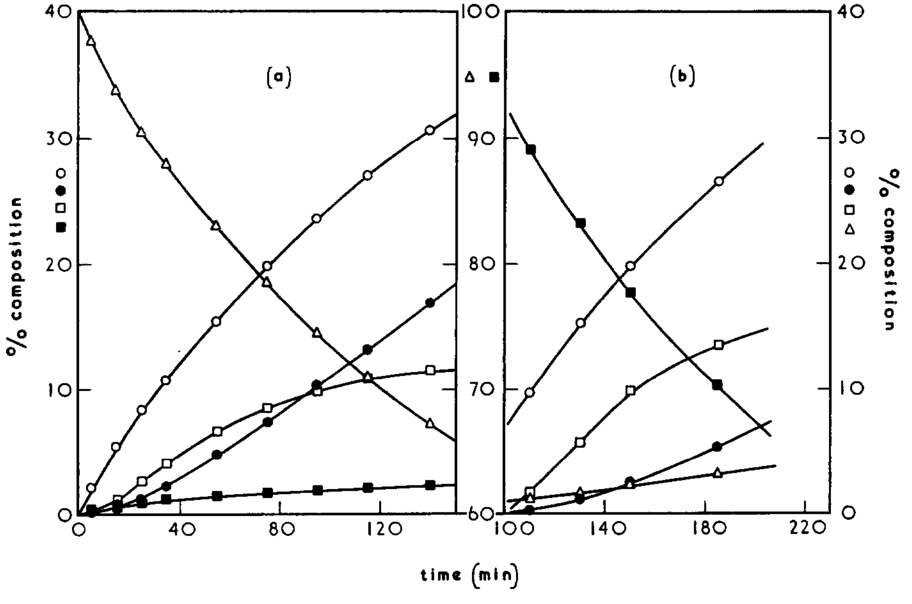

FIG. 2. Reactions with hydrogen on WS$_2$ at 305°C: (a) thiophene (Expt. A2) and (b) tetrahydrothiophene (Expt. A5); ○, H$_2$S; △, C$_4$H$_4$S; ■, C$_4$H$_8$S, expressed as per cent of total sulfur composition; □, C$_4$H$_8$ and ●, C$_4$H$_{10}$ expressed as per cent of total carbon composition. For 100 min, Expt. A5 was at 238°C with formation of some of the sulfur-containing products.

the hydrogen atoms were replaced much more rapidly than the other two, particularly at lower temperatures, as may be seen in Fig. 1. After exchange on molybdenum disulfide at 240°C, a sample consisting of 7% d_0, 32% d_1, 55% d_2, 5% d_3, and 1% d_4 was removed for NMR analysis. The expected ratio of H_β/H_α was 4.19 on the assumption that the hydrogen atoms on the carbon atoms adjacent to the sulfur atom were replaced before those on the β carbon atoms or 0.24 if the converse was assumed. The experimental value of H_β/H_α from the integrated spectrum was 4.02, which showed that the α hydrogen atoms were being exchanged much more rapidly than the β hydrogen atoms. Data such as those shown in Fig. 1 were analyzed by kinetic equations described previously (*13*, *14*) in order to obtain the initial rates of exchange reported in Table 1.

The exchange of the hydrogen atoms in the saturated molecule, tetrahydrothiophene, occurred less readily on both catalysts than the exchange of thiophene and measurable rates were only observed at temperatures which also caused decomposition to take place. Stepwise exchange was found on the molybdenum disulfide at 270°C with the formation of the d_1 compound at a rate of about 1%/hr and the rate of decomposition was some 4%/hr. Similar results were obtained on tungsten disulfide at 215°C with rates of 2%/hr and 4%/hr for exchange and decomposition, respectively.

In order to find out if molybdenum disulfide could bring about the exchange of aromatic molecules as rapidly as the exchange of thiophene, experiments were carried out with benzene and toluene. No exchange of benzene was observed after 4 hr at 340°C and less than 1% of the d_1 compound was formed from toluene in 3 hr at 300°C.

Reactions with Hydrogen on WS_2

The decomposition of thiophene in the presence of hydrogen to form hydrocarbons and hydrogen sulfide occurred at conveniently measurable rates at temperatures of 270°C or upwards on tungsten disulfide. The results are summarized in Table 2 and the course of reaction in Expt. A2 is shown in Fig. 2(a). Satisfactory reproducibility was obtained, as shown by experiments A2 and A3, and the main reactions which occurred initially were the following:

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

$$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S \qquad (2)$$

$$C_4H_4S + 2H_2 \rightarrow C_4H_8S \qquad (3)$$

and then subsequently the butene from reaction (1) was hydrogenated slowly to butane. There was a gradual decline in the total amount of the sulfur-containing molecules in the gas phase which amounted to some 15% after 3 hr, but most of this decline was attributable either to the removal of gas from the reaction vessel by the leak into the mass spectrometer or possibly to changes in the sensitivity of the mass spectrometer to the various compounds. A detailed examination of the mass spectrum at the end of the runs revealed no evidence for the formation of sulfur-containing molecules other than hydrogen sulfide and tetrahydrothiophene. A decrease of about 5% of the total carbon-containing molecules in the gas phase occurred at the beginning of each experiment.

TABLE 2
REACTIONS OF COMPOUNDS WITH 130 MM H_2 ON 0.55 G OF WS_2

				Composition after 25% reaction based on S content					
				As % of S content			As % of C_4 content		
Expt.	Reactant (Pressure in mm)	Temp. (°C)	Initial rate of decomposition (% S/min)	C_4H_4S	C_4H_8S	H_2S	C_4H_8	C_4H_{10}	Total C_4 products
A1	C_4H_4S (13)	272	0.25	75.0	3.8	21.2	5.9	8.9	18.6
A2	C_4H_4S (13)	304	0.40	75.0	1.9	23.1	9.7	9.9	21.5
A3	C_4H_4S (13)	305	0.42	75.0	1.9	23.1	8.2	7.8	17.9
A4	C_4H_4S (6.5)	305	0.6	75.0	1.4	23.6	10.9	7.6	19.9
A5	C_4H_8S (13)	305	0.33	2.6	75.0	22.4	11.3	3.5	17.4

This was associated with the fact that the formation of the hydrocarbon products was initially slower than the formation of hydrogen sulfide and then increased after a few minutes as shown in Fig. 2(a). This effect was caused by the adsorption of hydrocarbons on the surface of the catalyst, which had an area of 78.2 m^2/g and, as shown by the results in the last column of Table 2, the amount of the total carbon products remained some 4% to 8% below the amount of the sulfur products throughout each run.

Approximate activation energies and frequency factors for reactions (1), (2), and (3) were obtained by comparison of the results of Expts. A1 and A2 and these are given in Table 3. Approximate orders of zero for reactions (1) and (2) and first for reaction (3) with respect to the pressure of thiophene were found by comparing Expt. A4 with A2 and A3.

TABLE 3
Approximate Activation Energies and Frequency Factors for Reactions of Thiophene on WS_2

Reaction	E (kcal/mole)	$\log_{10} A$ (A in molecules/sec cm^2)
(1)	18	16.6
(2)	19	16.7
(3)	<10	<11.0

Tetrahydrothiophene (Expt. A5) decomposed at a similar rate to thiophene on tungsten disulfide by reactions analogous to reactions (1) and (2) and a little thiophene was also formed by the reverse of reaction (3). Rather less butane was formed from the saturated molecule than from thiophene but in all other respects the two molecules behaved in a similar way [Fig. 2(b)].

The composition of the butenes formed at the end of experiments on the decomposition of thiophene and tetrahydrothiophene are given in Table 4 together with calculated equilibrium mixtures (*15*). Both compounds gave mixtures of the straight-chain butenes which were close to equilibrium but no evidence was found for the formation of isobutene, which would have necessitated the rearrangement of the hydrocarbon skeleton. It was not possible to determine which, if any, of the butenes was formed preferentially in the initial stages of the decomposition because the isomerization of the butenes occurred rapidly on tungsten disulfide at temperatures below those required for the decomposition of thiophene. This was demonstrated by Expt. A6 using 8 mm of but-1-ene, 8 mm of thiophene, and 130 mm of hydrogen at 238°C and the results in Table 4 show that isomerization was virtually completed after only 55 min. The hydrogenation of butadiene also occurred rapidly on tungsten disulfide at 238°C even in the presence of thiophene. The course of Expt. A7 (8 mm butadiene, 8 mm thiophene, and 130 mm hydrogen) is shown in Fig. 3 and the composition of the butenes

TABLE 4
Comparison of the Experimental Distributions of Butene Isomers with Equilibrium Distributions

Catalyst	Expt.	Temp. (°C)	Duration of expt. (min)	Percentages		
				But-1-ene	*trans*-But-2-ene	*cis*-But-2-ene
Calculated equilibrium at 235°C				15.6	52.3	32.1
WS_2	A6	238	55	19.4	53.6	27.0
WS_2	A7	238	85	20.1	53.6	26.3
Calculated equilibrium at 300°C				19.5	48.9	31.6
WS_2	A3	305	140	19.0	52.4	28.6
WS_2	A5	305	105	19.6	52.2	28.3
Calculated equilibrium at 380°C				28.3	44.9	31.8
MoS_2	B2	378	135	30.6	43.8	25.6
MoS_2	B6	378	200	49.5	32.5	17.9

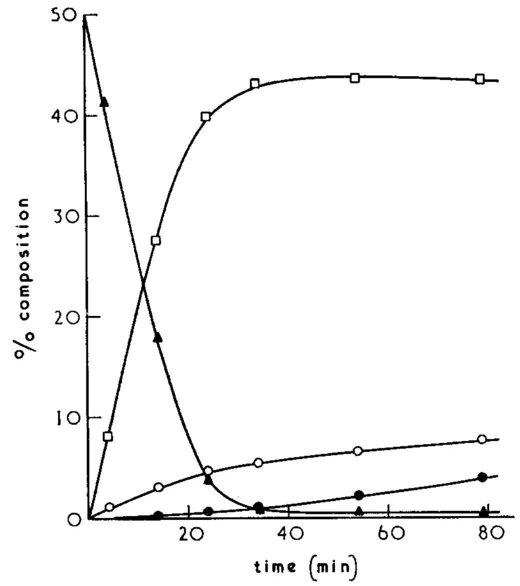

Fig. 3. Hydrogenation of butadiene in the presence of thiophene on WS_2 at 238°C (Expt. A7). Symbols as in Fig. 2 with ▲, C_4H_6, expressed as per cent of total carbon composition.

is given in Table 4. The initial rate of conversion of butadiene to butene was 4.6%/min and the rate remained virtually constant until most of the diene had reacted, indicating that the reaction was zero order with respect to the diene and thus providing evidence for relatively strong adsorption of the molecule. In the latter stages of the reaction, a slow hydrogenation of butene to butane took place. The initial rate of decomposition of thiophene as measured by the formation of hydrogen sulfide was only 0.20%/min and very much slower than the rate of hydrogenation of butadiene.

Reactions with Hydrogen on MoS_2

Temperatures of 350°C or upwards were necessary in order to obtain appreciable rates of decomposition of thiophene over molybdenum disulfide and difficulties were experienced with loss of catalytic activity. Firstly, the rates of reaction in any particular experiment decreased with time and became extremely slow after about 20% to 30% of the thiophene had reacted. Secondly, the type of treatment which was found satisfactory for maintaining catalytic activity in the previous work (*10, 11, 12*) was only partially successful in restoring activity after reactions with thiophene or tetrahydrothiophene. This meant that there was a gradual decline in activity of a catalyst sample used for a series of experiments such as those reported in Table 5 although a comparison of the rates of Expts. B1, B3, and B7 shows that after the catalyst had been used for two or three experiments the subsequent fall in activity was not marked. Finally, increase of reaction temperature, cf. B3 and B4, did not give the expected increase in initial rate.

The course of Expts. B2 and B6 is shown in Fig. 4(a) and 4(b). The main mode of

TABLE 5

Sequence of Reactions of Compounds with 130 mm H_2 on a Sample of MoS_2 (2.43 g) at 378°C

Expt.	Treatment of catalyst[a]	Reactant (pressure in mm)	Initial rate of decomposition (% S/min)
B1	3 cycles at 270°C	C_4H_4S (13)	0.61
B2	2 cycles at 270°C	C_4H_4S (13)	0.21
B3	2 cycles at 270°C	C_4H_4S (13)	0.14
B4[b]	2 cycles at 270°C	C_4H_4S (13)	0.13
B5	1 cycle at 400°C	C_4H_4S(6.5) + C_4H_6(6.5)	0.06 (3.6)[c]
B6	1 cycle at 370°C	C_4H_8S (13)	1.26
B7	1 cycle at 370°C	C_4H_4S (13)	0.10

[a] Each cycle of pretreatment consisted of evacuation for 12 hr or more at the stated temperature followed by heating in the presence of $H_2S + H_2$ (50 mm + 130 mm) for at least 12 hr at the same temperature. Finally the catalyst was evacuated for 4 hr at the temperature to be used for the next reaction.

[b] Reaction carried out at 439°C.

[c] Initial rate of hydrogenation of butadiene (%/min).

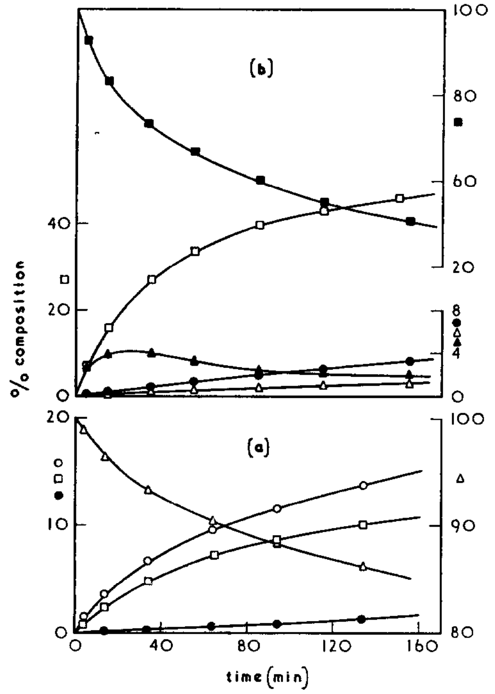

FIG. 4. Reactions with hydrogen on MoS_2 at 378°C: (a) thiophene (Expt. B2) and (b) tetrahydrothiophene (Expt. B6); symbols as in Figs. 2 and 3.

decomposition of thiophene over molybdenum disulfide was by reaction (1) although, as may be seen from Table 4, the butenes formed were not in thermodynamic equilibrium and contained less of the but-2-enes than expected for equilibrium. The ratios of *trans*- to *cis*-but-2-ene were near the equilibrium value and it seemed likely that but-1-ene was the principal primary product. Reaction (2) occurred to a smaller extent than over tungsten disulfide and in all experiments the amount of butane formed was less than one-fifth of the amount of butene after 20% of the thiophene had decomposed. No hydrogenation of thiophene to tetrahydrothiophene by reaction (3) was detected.

The decomposition of tetrahydrothiophene [Fig. 4(b)] was about ten times faster than the decomposition of thiophene at 378°C and showed a number of other interesting features. Butene, mainly but-1-ene (cf. Table 4), butane, and thiophene were all formed as initial products but a further mode of decomposition was by the reaction

$$C_4H_8S \rightarrow C_4H_6 + H_2S \qquad (4)$$

yielding butadiene which was then rapidly hydrogenated to form more butene. With all reactions of thiophene and tetrahydrothiophene on molybdenum disulfide the carbon balance remained equal to the sulfur balance of the gas-phase compounds throughout the runs and there was no apparent loss of carbon to the catalyst as had been found with tungsten disulfide. It is probable that the hydrocarbons like butadiene and the butenes were fairly strongly adsorbed but as the surface area of the molybdenum disulfide was small (2.18 m^2/g) the removal of material from the gas phase was not detectable.

Experiment B5 shows that, as with tungsten disulfide, butadiene was rapidly hydrogenated even in the presence of thiophene and this reaction took place about 60 times as fast as the decomposition of thiophene at 378°C. As the rate of reaction of thiophene was lower in Expt. B5 than in the later run, B7, there is evidence that the presence of butadiene may inhibit the decomposition of thiophene by competing for the catalyst surface.

DISCUSSION

The main point which is established by comparing the present results with the previous work on the decomposition of methyl mercaptan (*11*) and ethyl mercaptan (*12*) is that both catalysts show much lower activity and require the use of higher temperatures in order to break the C–S bond in the ring compounds thiophene and tetrahydrothiophene than to break the same bond in straight-chain compounds such as mercaptans or dialkyl sulfides. However on tungsten disulfide, for which the relevant activation energies and frequency factors are available, it is clear that the low rate of rupture of the C–S bond in the cyclic molecules is more the consequence of a lower frequency factor than of a higher activation energy.

The second point which emerges is that tungsten disulfide is a relatively better catalyst than molybdenum disulfide for the activation of C–H bonds and for bringing about reactions which involve the addition or subtraction of hydrogen atoms from hydrocarbon molecules or from the hydrocarbon portion of the cyclic molecules. This difference of behavior was also noted in the work with ethyl mercaptan (*12*) and it is obvious in the present work for a number of reactions which occur more readily on tungsten disulfide than on molybdenum disulfide. These include (a) the exchange of the hydrogen atoms on the β-carbon atoms of thiophene; (b) the hydrogenation of thiophene to tetrahydrothiophene; (c) the isomerization of the butenes; (d) the formation of butane from unsaturated C_4 hydrocarbons. Another interesting fact is that the exchange of thiophene with deuterium takes place considerably faster than the exchange of the hydrogen atoms in the ethyl group of ethyl mercaptan or the exchange of ethylene with deuterium (*12*) at temperatures around 200°C on tungsten disulfide, but the opposite behavior is found over molybdenum disulfide.

We shall set out schematically the types of reaction which occur over tungsten disulfide and then consider the differences which are found with molybdenum disulfide. It is convenient to divide the complex processes into three stages.

STAGE I

The following reactions occur with the cyclic molecules:

$$\begin{tikzcd}
C_4H_4S(g) \arrow[d, shift right] \\
C_4H_4S(a) \arrow[u, shift right] \arrow[r, shift left] & C_4H_5S(a) \arrow[l, shift left] \arrow[r, shift left] & C_4H_6S(a) \arrow[l, shift left]
\end{tikzcd}$$

$$\begin{tikzcd}
 & & C_4H_8S(g) \arrow[d, shift left] \\
{} \arrow[r, shift left] & C_4H_7S(a) \arrow[l, shift left] \arrow[r, shift left] & C_4H_8S(a) \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

and this part of the scheme can account for the exchange of both thiophene and tetrahydrothiophene as well as the interconversion of the two compounds which has been shown to take place at 305° over tungsten disulfide. It is possible that the exchange of thiophene might involve dissociative adsorption to form species of the type $C_4H_3S(a)$ but there is no evidence to suggest that this mechanism is more likely than one involving the associated species $C_4H_5S(a)$ which must exist as an intermediate in the formation of tetrahydrothiophene from thiophene.

STAGE II

This covers the processes responsible for the rupture of the C–S bonds and the reaction is likely to occur with one or more of the surface entities of intermediate state of hydrogenation in Stage I. We formulate this second stage as

$$\left.\begin{array}{r} C_4H_5S(a) \\ \text{or } C_4H_6S(a) \\ \text{or } C_4H_7S(a) \end{array}\right\} \xrightarrow{(5)} \text{straight-chain } C_4H_nS(a) \qquad (5,\ 6)$$

$$\xrightarrow{(6)} C_4H_m(a) + \left\{\begin{array}{l} S(a) \\ \text{or } HS(a) \end{array}\right.$$

where *n* and *m* are unknown but may be in the range from 4 to 8. We assume that step (5) is probably rate-determining in the decomposition of both thiophene and tetrahydrothiophene and that step (6) takes place very readily because the corresponding reaction with the compounds ethyl mercaptan and diethyl sulfide is known (*12*) to occur at temperatures well below those necessary for the decomposition of the cyclic molecules. The absence of any butyl mercaptan or unsaturated C_4S compound in the reaction products does not constitute evidence against the proposed scheme for Stage II, because if step (6) is sufficiently rapid little desorption of any straight-chain compound like C_4H_nS will be able to occur. The species S(a) or HS(a) are rapidly converted into gas-phase H_2S and the hydrocarbon species $C_4H_m(a)$ enters the next stage.

STAGE III

A complex series of interconversions of the hydrocarbon intermediates is proposed and although we do not have direct evidence for all of the following reactions we believe that they can all occur, but subject to the limitations set by thermodynamic considerations. The proposed scheme is

$$\begin{tikzcd}
C_4H_6(g) \arrow[d, shift right] & & C_4H_8(g) \arrow[d, shift left] & C_4H_{10}(g) \\
C_4H_6(a) \arrow[u, shift right] \arrow[r, shift left] & C_4H_7(a) \arrow[l, shift left] \arrow[r, shift left] & C_4H_8(a) \arrow[l, shift left] \arrow[u, shift left] \arrow[r, shift left] & C_4H_9(a) \arrow[l, shift left] \arrow[u, "(8)"']
\end{tikzcd}$$

We do not detect butadiene as a product in reactions over tungsten disulfide, but these take place at temperatures for which the equilibrium constants for reaction (4) and the following reaction

$$C_4H_4S + 2H_2 \rightarrow C_4H_6 + H_2S \qquad (7)$$

are small. Furthermore the rate of hydrogenation of butadiene is extremely rapid at 238°C and some 20 to 30 times faster than the rate of decomposition of either thiophene or tetrahydrothiophene. We have no evidence to decide whether the rapid isomerization of the butenes occurs via $C_4H_7(a)$ or $C_4H_9(a)$—both are possible routes—but it seems likely that the slowest step in Stage III is step (8) because the amounts of butane formed initially are lower than the amounts of the butenes. We believe that the present work provides further proof of our earlier suggestion (*11*, *12*) that the slow step in the formation of saturated hydrocarbons as products is the desorption of the appropriate adsorbed alkyl radical by union with a chemisorbed hydrogen atom.

The same three stages of reaction probably operate with molybdenum disulfide but a number of minor differences in the patterns of products from this catalyst compared with the patterns from tungsten disulfide arise due to two factors. The first is the lower activity of molybdenum disulfide for hydrogenation reactions, with the consequence that more unsaturated products and less saturated products are formed. The second factor is associated with the higher temperature needed to study decomposition on molybdenum disulfide, which means that the equilibrium constants for reactions such as (4) or (7) are larger and allow the formation of butadiene as a product as was, in fact, observed in the reaction of tetrahydrothiophene. The difference in the rates of decomposition of tetrahydrothiophene and thiophene would seem to indicate that the rate of these reactions is not controlled entirely by the rate of step (5) over molybdenum disulfide but may also be influenced by the relative rates of the various steps involved in Stage I. In contrast, with tungsten disulfide the processes in Stage I take place more readily so that the vital intermediate or intermediates for Stage II are formed equally rapidly from either the saturated or the unsaturated molecule.

The deactivation of the molybdenum disulfide catalyst is probably due to the formation of strongly held and substantially dehydrogenated species, possibly polymeric in nature, on the surface of the catalyst. Some support for this suggestion comes from the fact that the decrease in the rate of decomposition with time is smaller with the saturated molecule tetrahydrothiophene than with thiophene. The alternative possibility that sintering is important is less likely as the activity can be partially restored by treatment with hydrogen and hydrogen sulfide.

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