JOURNAL OF CATALYSIS 3, 426–437 (1964)

Catalytic Reactions of Methyl Mercaptan on Disulfides of Molybdenum and Tungsten

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Received March 31, 1964

The exchange reaction between methyl mercaptan and deuterium has been followed in the temperature range 150° to 190°C on a molybdenum disulfide catalyst and in the range 40° to 100°C on a tungsten disulfide catalyst. The mercaptyl hydrogen atom was replaced on both catalysts and some exchange of the methyl hydrogen atoms also occurred over the molybdenum catalyst.

The decomposition of methyl mercaptan in the presence of hydrogen occurred in the temperature range 230° to 270°C over molybdenum disulfide by two reactions: (a) a disproportionation to yield dimethyl sulfide and hydrogen sulfide and (b) a hydrogenolysis to yield methane and hydrogen sulfide. Reaction (a) took place over tungsten disulfide between 130° and 230°C but reaction (b) only occurred above 230°C. Some allied reactions of dimethyl sulfide and the exchange of methane with deuterium were also examined on both catalysts.

Activation energies and frequency factors were measured for a number of the reactions and the mechanisms are discussed. The relative ease of activation of various chemical bonds on both catalysts is given by the order H–H > H–S > C–S > C–H but the catalytic behavior of the tungsten catalyst is more selective than that of the molybdenum catalyst.

INTRODUCTION

The exchange reactions between hydrogen and deuterium and between hydrogen sulfide and deuterium have been examined recently (*1*) on the disulfides of molybdenum and tungsten. That investigation gave data about the efficiency of the sulfide catalysts for the activation of the H–H and H–S bonds and some information about the mechanism of the exchange reactions. We selected methyl mercaptan as a suitable reactant to examine in order to extend this fundamental approach to the study of these sulfide catalysts.

The first object of the work was to compare the ease of activation of the C–H and S–H bonds in the molecule by following the exchange reactions of the different types of hydrogen atoms with deuterium. The second object was to learn about the catalytic activation of the C–S bond by following reactions of the mercaptan in the presence of hydrogen at higher temperatures. Preliminary investigations showed that two different types of decomposition of methyl mercaptan were involved.

Disproportionation

$$2CH_3SH \rightleftharpoons (CH_3)_2S + H_2S \qquad (1)$$

Hydrogenolysis

$$CH_3SH + H_2 \rightarrow CH_4 + H_2S \qquad (2)$$

Reaction (1), for which the equilibrium constant is small at 200°C, involves both the rupture and the formation of H–S and C–S bonds. Reaction (2), for which the equilibrium at 200°C strongly favors the products, involves the formation of C–H and H–S bonds as well as the rupture of H–H and C–S bonds.

There is little information in the literature about heterogeneous exchange reactions of mercaptans with deuterium although studies on the homogeneous exchange of the mercaptyl hydrogen with heavy water in the liquid phase, reviewed by Kirshenbaum (*2*), have attracted attention partly because of the possibility of using the reactions in a dual temperature process for the concentration of deuterium. The adsorption and hydrogenolysis of methyl mercaptan on nickel subsulfide (Ni_3S_2) have been investigated (*3, 4*). The reaction of the mercaptan took place at an appreciable rate in the temperature range from 200° to 250°C and was first order with respect to the sulfur compound in the presence of excess hydrogen. The adsorption of methyl mercaptan was activated in this temperature range and was believed by the authors to be the slow step of the reaction.

The chemisorption of dimethyl sulfide on supported nickel catalysts was studied by Den Besten and Selwood (*5*) and they obtained evidence for decomposition which was extensive above 120°C. The interaction of methyl mercaptan with evaporated films of nickel and tungsten (*6*) was studied in this laboratory concurrently with the present investigation; dissociative adsorption occurred on both metals at $-80°C$ and sulfidation of nickel took place at 0°C and higher temperatures. Some hydrogen and methane were desorbed from both metals and nickel also yielded small quantities of dimethyl sulfide above 40°C.

EXPERIMENTAL

The apparatus and the experimental technique for following the exchange reaction between methyl mercaptan and deuterium were identical to those used for the study of the exchange of hydrogen sulfide and deuterium (*1*). The reaction took place in a static system and was interrupted at appropriate intervals by freezing out the condensable gases so that the dilution of the deuterium by hydrogen could be determined by thermal conductivity measurements.

The apparatus for following the decomposition of methyl mercaptan in hydrogen was essentially similar to the type used by Kemball (*7*) for other catalytic studies. The gas mixture was admitted to a vessel containing a sample of catalyst and linked by a glass capillary leak to a Nier-type mass spectrometer. The temperature of the reaction vessel was then raised to the required value and the reaction followed by observing the changes in the mass spectra at intervals.

Hydrogen, deuterium, and hydrogen sulfide were purified as before (*1*). Methyl mercaptan and dimethyl sulfide, obtained from British Drug Houses Ltd. were purified by vacuum distillation and their purity was then checked by mass spectrometric analysis and by vapor pressure measurements. Methane from a cylinder was purified by alternate freezing and pumping until its vapor pressure at liquid nitrogen temperature corresponded to the published data. The samples of the molybdenum disulfide and tungsten disulfide were similar to those used in the previous work (*1*) and they were subjected to the same pretreatments as before.

Mass spectrometric analyses were carried out using 15 v electrons to ionize the molecules. As some of the sulfur compounds were fairly strongly adsorbed in the spectrometer, the gas mixture was allowed to leak into the spectrometer for a period of 15 to 20 min at room temperature before the reaction vessel was heated to the temperature for reaction. The ion source of the mass spectrometer was also baked and evacuated thoroughly between experiments in order to minimize the background spectrum. The peaks corresponding to values of m/e of 62, 48, 34, and 16 were used, after correction for naturally occurring isotopes, to estimate the amounts of dimethyl sulfide, methyl mercaptan, hydrogen sulfide and methane, respectively. A small correction was made to peak 34 to allow for a fragment ion (3.5% of the parent ion) formed from methyl mercaptan; similar but smaller corrections were made to peak 16 for fragment ions from the mercaptan (0.5%) and the disulfide (0.7%). Accurate analyses for mercaptan could not be made in the presence of excess dimethyl sulfide because a large amount of the fragment ion with $m/e = 47$ from the latter compound interfered with the estimation of peak 48 due to the limited resolving power of the spectrometer. Calibration mixtures were used to determine the relative sensitivities of the peaks for the various compounds.

RESULTS

Exchange of CH_3SH and D_2 on MoS_2

Details of the experimental conditions are given in Table 1. The course of the reaction was accurately represented by the first order equation, used previously (*1*),

$$-\log_{10}(\lambda - \lambda_\infty) = k_1 t/2.303 - \log_{10}(\lambda_0 - \lambda_\infty) \quad (3)$$

where λ is the resistance of the thermal conductivity cell at time t, and λ_0 and λ_∞ are the corresponding initial and final values. The experimental λ_∞ corresponded to 23% hydrogen in the "deuterium" and this indicated that about 1.2 hydrogen atoms in each molecule of mercaptan were being exchanged. Mass spectrometric analyses of samples from partially completed experiments confirmed that more than one hydrogen was being replaced; the main product when the exchange was half-completed was a monodeuteromercaptan but about 5% of more highly exchanged species were present. Unfortunately, the technique was not valid at temperatures above 190°C because the decomposition of the mercaptan (described later) gave rise to some methane which interfered with the analysis of the "deuterium" by thermal conductivity.

As before (*1*), the rate constants k_1 were converted into absolute initial rates of exchange R in atoms/sec cm^2 of catalyst surface and the Arrhenius parameters for R are given in Table 1.

Some analyses were made by means of the mass spectrometer of the proportions of H_2, HD, and D_2 in samples from partially completed experiments. The values of $q = [HD]^2/[H_2][D_2]$ are given in Table 2 and they were substantially smaller than K, the equilibrium constant for the reaction

$$H_2 + D_2 \rightleftharpoons 2HD \quad (4)$$

Exchange of CH_3SH and D_2 on WS_2

Exchange followed Eq. (3) except for a sudden change in the resistance of the thermal conductivity cell at the beginning of each experiment [a similar behavior had been observed in the exchange of hydrogen sulfide and deuterium; see Fig. 2 of ref. (*1*)]. The final hydrogen content in the "deuterium" was approximately 24% but part (4%) was attributable to the sharp initial change and the remaining change corresponded closely to the amount expected for the replacement of one hydrogen atom in each molecule of mercaptan. Mass spectrometric analyses of samples from partially completed runs confirmed that monodeuteromercaptan was the only isotopic species of mercaptan formed, although traces of "hydrogen sulfide" were also observed.

The Arrhenius parameters for the absolute initial rate of exchange are given in Table 1 and the values of q for some partially completed runs in Table 2. The order of the exchange reaction was investigated at 80°C by using a series of mixtures of the reactants. The order with respect to deuterium, determined by varying the

TABLE 1
EXCHANGE OF METHYL MERCAPTAN WITH DEUTERIUM

Catalyst	Weight of catalyst (g)	Size of reaction vessel (ml)	P_{CH_3SH} (mm)	P_{D_2} (mm)	Temp. range (°C)	E (kcal/mole)	$\log_{10}A$ (A in atoms/sec cm^2)
MoS_2	2.53	78.7	62.4	125	150–190	15.0 ± 0.5	19.1 ± 0.6
WS_2	2.90	76.7	63	126	40–100	9.1 ± 0.4	15.7 ± 0.3

TABLE 2

VALUES OF $q = [HD]^2/[H_2][D_2]$ DURING EXCHANGE OF METHYL MERCAPTAN

Catalyst	Temp. (°C)	% of reaction completed	q	Equilibrium const. K of reaction (4)
MoS_2	168	32.3	0.72	3.56
MoS_2	190	39.8	0.73	3.59
WS_2	60	12.9	0.24	3.34
WS_2	80	29.6	0.72	3.38
WS_2	100	42.3	1.34	3.43

initial pressures from 32 to 190 mm, was 0.95; the order with respect to mercaptan, determined by using initial pressures from 42 to 252 mm, was −0.1.

The hydrogen released at the start of each reaction was believed to arise from an irreversible adsorption of the mercaptan and, if this occurred by the reaction

$$2CH_3SH(g) \rightarrow 2CH_3S(a) + H_2(g) \qquad (5)$$

an adsorption of one molecule for each 600 $Å^2$ of surface would have been sufficient to account for the hydrogen liberated. Some confirmation of this hypothesis was obtained from the pressure-dependence experiments, as the percentages of hydrogen released initially varied from 2.4 to 8% as the ratio of deuterium/mercaptan in the reaction mixture decreased and the calculated percentages according to reaction (5) ranged from 4 to 8%.

Evidence for the exchange of the hydrogen atoms in the methyl group of the mercaptan was obtained at 155° and 180°C. At these temperatures the exchange of the first hydrogen atom (the mercaptyl hydrogen) was rapid and further exchange occurred slowly, e.g. after 6 hr at 180°C over 2.5 hydrogen atoms per molecule had been replaced and the reaction was still continuing. Mass spectrometric analysis confirmed the presence of a range of isotopic mercaptans and also showed that some decomposition, yielding hydrogen sulfide, dimethyl sulfide, and methane, had occurred as well. An approximate activation energy of 16.5 ± 2.0 kcal/mole and a frequency factor ($\log_{10}A$ in atoms/sec cm^2) of 16.8 ± 1.0 was derived for the slow exchange. The ratio of the rate of the fast exchange (based on an extrapolated value) to that of the slow exchange was about 400 at 155°C.

Decomposition of CH_3SH and Allied Reactions on MoS_2

A blank experiment was carried out at 300°C with a mixture of methyl mercaptan and hydrogen in the absence of catalyst. The decomposition was extremely slow, being about 1% per hour, and so the influence of any homogeneous reaction or catalysis by the glass walls could be neglected in comparison with the faster reactions on both sulfide catalysts.

The normal reaction mixture consisted of 53.8 mm of mercaptan and 113 mm of hydrogen; the sample of catalyst weighed 2.43 g and the reaction vessel (119 ml) contained 2.13×10^{20} molecules of mercaptan. Reaction occurred at measurable rates in the temperature range 230–270°C and a typical experiment is shown in Fig. 1. The amounts of methyl mercaptan, hydrogen sulfide, and dimethyl sulfide were expressed as percentages of the total sulfur-containing molecules present at each stage of the reaction; the amount of methane was expressed as a percentage of the carbon atoms present in the three compounds containing carbon. The total sulfur and carbon contents of the gas phase remained constant within 10–15% throughout all experiments; this variation was attributed to experimental error associated with the mass spectrometric analyses but we cannot exclude the possibility that a small percentage of the material was taken up by the catalyst or converted to some other products.

TABLE 3

INITIAL RATES OF REACTION OF METHYL MERCAPTAN ON MOLYBDENUM DISULFIDE

Temp. (°C)	Rates (%/min g)			
	CH_3SH	H_2S	CH_3SCH_3	CH_4
230	−0.117	0.065	0.044	0.012
250	−0.259	0.137	0.115	0.020
270	−0.489	0.265	0.196	0.076

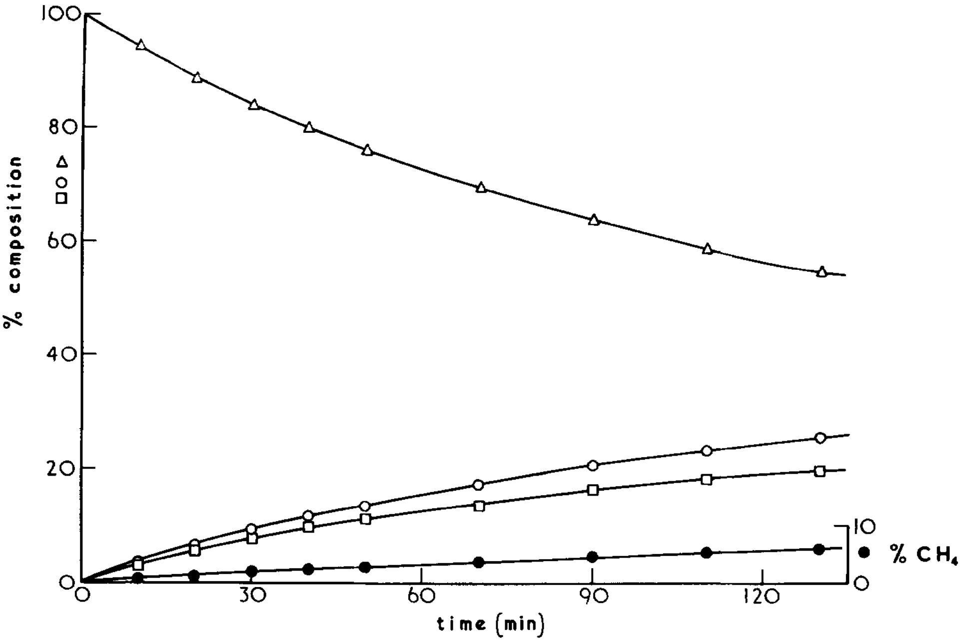

FIG. 1. Reaction of 54 mm methyl mercaptan and 113 mm hydrogen on MoS_2 at 250°C: % composition refers to total sulfur content of the gas phase; △, CH_3SH; ○, H_2S; □, CH_3SCH_3; and ● gives % CH_4 based on total carbon content of the gas phase.

TABLE 4
ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR REACTIONS OF METHYL MERCAPTAN AND HYDROGEN

Catalyst	Temp. range (°C)	Reaction	E (kcal/mole)	$\log_{10}A$ (A in molecules/sec cm^2)
MoS_2	230–270	(1)	19.7	19.5
MoS_2	230–270	(2)	22.9	20.4
WS_2	130–230	Decomposition of CH_3SH	13.8	17.3
WS_2	130–230	Formation of H_2S	12.4	16.4
WS_2	130–230	Formation of $(CH_3)_2S$	15.9	17.8
WS_2	230–310	(2)	28.8	21.8

Some results for the initial rates of reaction, expressed as per cent per minute per gram of catalyst are reported in Table 3. These show that both reactions (1) and (2) occurred simultaneously on molybdenum disulfide. The Arrhenius parameters for the absolute initial rates of reaction are given in Table 4.

Experiments using one-fifth of the normal pressure of mercaptan at 210°, 230°, and 250°C indicated that the order of reaction (1) was 0.5 with respect to the mercaptan pressure. This reduction of pressure had no influence on the rate of reaction (2) and this confirmed the internal evidence from all runs that the formation of methane was independent of the amount of mercaptan present; the constant rate of methane formation, shown in Fig. 1 was observed at all temperatures. A series of experiments at 250°C with a fixed pressure of 21.6 mm of mercaptan and pressures of hydrogen ranging from 27 to 237 mm gave orders with respect to hydrogen of 0 and

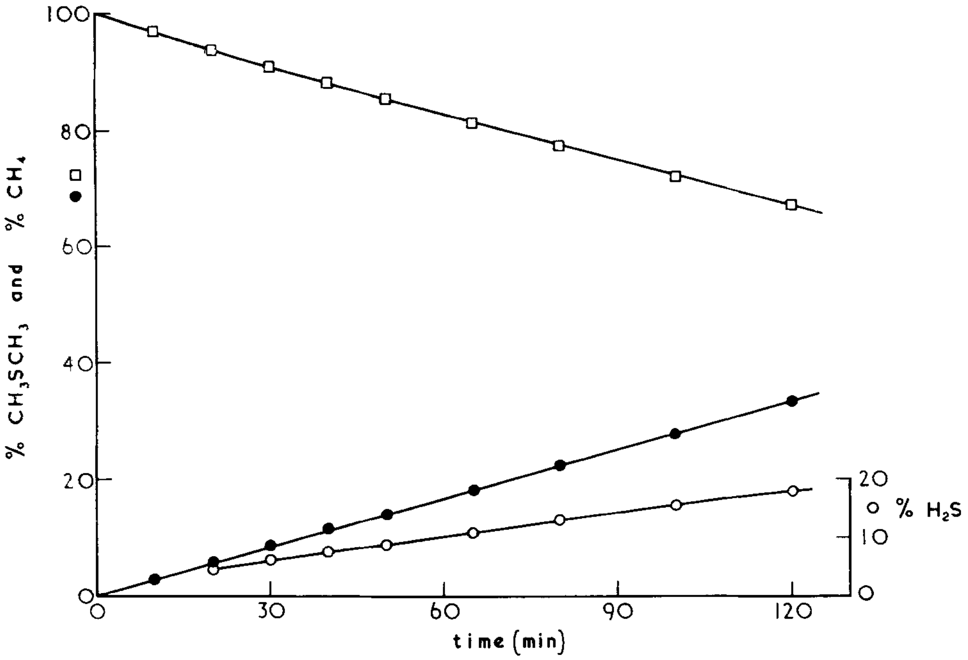

FIG. 2. Reaction of 53 mm dimethyl sulfide and 112 mm hydrogen on MoS$_2$ at 290°C: □, CH$_3$SCH$_3$; ●, CH$_4$ based on carbon content; and ○, H$_2$S based on sulfur content of the gas phase.

0.65 for reactions (1) and (2), respectively. The decomposition of mercaptan without added hydrogen occurred at 250°C and gave the usual products but, as expected, the rate of formation of methane decreased rapidly with time.

Reaction of dimethyl sulfide and hydrogen (54 mm and 113 mm, respectively) occurred in the range from 250° to 320°C and a typical experiment is shown in Fig. 2. A constant rate of formation of methane was observed at each temperature and the products corresponded to the reaction

$$CH_3SCH_3 + 2H_2 \rightarrow 2CH_4 + H_2S \qquad (6)$$

The slight decrease in the rate of formation of hydrogen sulfide in the later stages of the runs was probably associated with the formation of methyl mercaptan by the reverse of reaction (1), although the resolution of the mass spectrometer prevented the detection of small quantities of the mercaptan in excess dimethyl sulfide. The rate of decomposition of dimethyl sulfide by reaction (6) was about one-sixth of the rate of loss of mercaptan by reaction (2) at 270°C; the activation energy for the reaction of the dimethyl sulfide was 22.0 kcal/mole and the frequency factor 2 × 10^{19} molecules/sec cm^2.

Experiments were carried out on the exchange of methane and deuterium in order to obtain more information about the rates of dissociative adsorption of methane on the catalyst and the reverse process of desorption. With 20 mm of methane and 242 mm of deuterium, the exchange was extremely slow at 300°C and a typical analysis of the methane after 40 min is given in Table 5. The rate of exchange of methane was about 40 times as slow as the rate of formation of methane from mercaptan at 300°C.

Decomposition of CH$_3$SH and Allied Reactions on WS$_2$

The normal reaction mixture consisted of 54.9 mm of mercaptan and 115 mm of hydrogen; the sample of catalyst weighed 0.55 g and the reaction vessel (117 ml) contained 2.13 × 10^{20} molecules of mercaptan. Reaction (1) occurred readily in

TABLE 5

PRODUCTS FROM THE EXCHANGE OF METHANE WITH DEUTERIUM

Catalyst	Temp. (°C)	Time (min)	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
MoS_2	300	40	96.9	1.60	0.85	0.41	0.21
WS_2	320	105	91.0	0.51	0.98	1.32	6.43

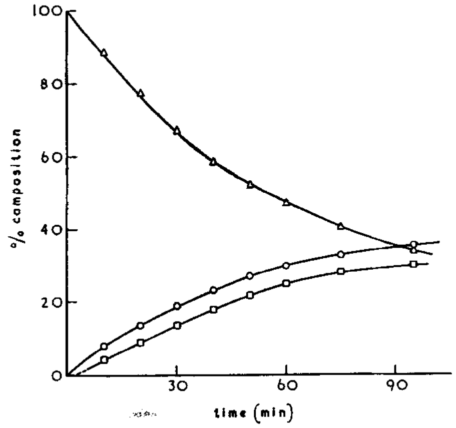

FIG. 3. Reaction of 54 mm methyl mercaptan and 115 mm hydrogen on WS_2 at 210°C; symbols as in Fig. 1.

the temperature range 130–230°C and at the higher temperatures, as shown in Fig. 3, the rate decreased as equilibrium was obtained. Common features of all experiments were the appearance of hydrogen sulfide before the increase of dimethyl sulfide was observed and the constant difference in the percentage of the two products in the later part of each run. The Arrhenius parameters for the reactions are given in Table 4 and they reflect the differences observed in the formation of the two products of reaction (1). Some experiments were carried out using only 12.1 mm of mercaptan with the normal pressure of hydrogen. The initial rate of formation of dimethyl sulfide was proportional to the pressure of the mercaptan but the pressure dependence

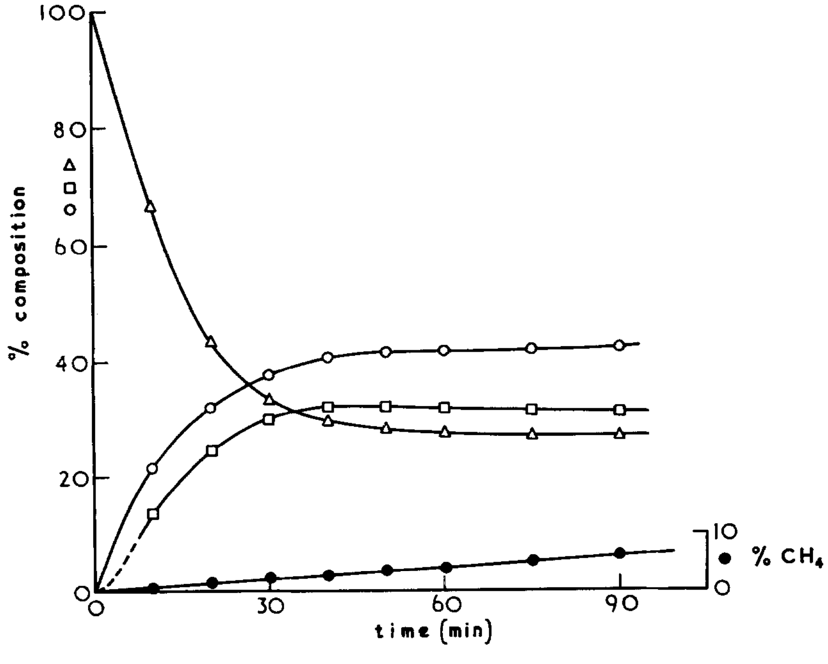

FIG. 4. Reaction of 55 mm methyl mercaptan and 115 mm hydrogen on WS_2 at 250°C; symbols as in Fig. 1.

of the formation of hydrogen sulfide varied from about 0.3 at 140°C to 0.7 at 210°C. A variation of the pressure of hydrogen from 50 to 560 mm had little effect on the initial rates of formation of both products; there was some scatter in the results but the rates changed by a maximum factor of 2 for the 11-fold change in pressure. An experiment at 180°C using 54 mm of mercaptan without added hydrogen gave the same products but the rate of reaction was about one-third of the rate with the normal mixture.

The formation of methane by reaction (2) was observed at 230°C and higher temperatures. The rate of formation of methane, as shown in Fig. 4, was constant at each temperature and this indication of a zero order dependence on the pressure of mercaptan was confirmed by the results with different reaction mixtures. A series of experiments was carried out at 270°C using a constant pressure 22 mm of mercaptan and pressures of hydrogen from 84 to 313 mm to establish the influence of the pressure of hydrogen on the rate of production of methane. The results are shown in Fig. 5 and they indicated an order which decreased from about 0.5 at low pressures to approximately zero at the higher pressures.

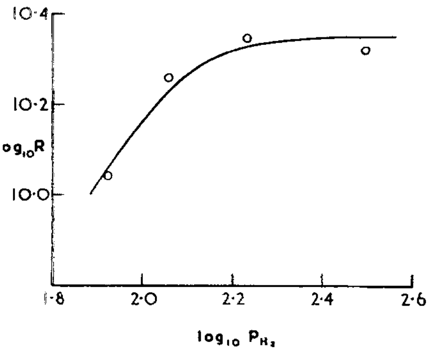

FIG. 5. Effect of hydrogen pressure on the initial rate of formation of methane from 22 mm of methyl mercaptan on WS_2 at 270°C; R is rate in molecules/sec cm^2 and p_{H_2} is in mm.

Dimethyl sulfide and hydrogen (55 and 115 mm, respectively) reacted at temperatures between 250° and 310°C to form methane and hydrogen sulfide but the distribution of products did not correspond closely to reaction (6) because some hydrogen sulfide and dimethyl sulfide were converted into mercaptan by the reverse of reaction (1). The activation energy for the reaction of dimethyl sulfide to form methane was 27 kcal/mole and the frequency factor 2×10^{20} molecules/sec cm^2.

The exchange of methane and deuterium (20 and 211 mm, respectively) occurred slowly at 320°C at a rate which was about 1/100th of the extrapolated rate of formation of methane from mercaptan. A typical distribution of products is given in Table 5 and this shows that the compound CD_4 is the most abundant species in the products in contrast to the results with molybdenum disulfide.

DISCUSSION

Irreversible Adsorptive Processes

The experimental results showed that approximately one molecule of methyl mercaptan was adsorbed rapidly for each 600 Å^2 of surface when exchange reactions were carried out on tungsten disulfide. This process, which was assumed to occur by reaction (5), must be irreversible under the conditions used for the exchange experiments in order to account for the observed final percentages of hydrogen in the "deuterium," because the mass spectrometric evidence indicated clearly that only a single hydrogen atom in each molecule of mercaptan was exchangeable at 100°C. An additional adsorption process of the type

$$2CH_3SH(g) + H_2(g) \rightarrow 2CH_3(a) + 2H_2S(g) \quad (7)$$

must occur at higher temperature because the formation of hydrogen sulfide began slightly earlier than the formation of dimethyl sulfide and thereafter the amount of the former product remained in excess of the amount of the latter. The differences in the percentages of the two products corresponded to an adsorption of one molecule of mercaptan on about 200 Å^2 of surface, on the basis of reaction (7) for normal reaction mixtures. As expected, the excess percentage of hydrogen sulfide was greater with mixtures containing smaller pressures of mercaptan and showed a slight increase from 3% to 8% as the pressure of hydrogen was raised from 50 to 560 mm with a constant pressure of mercaptan. Further confirmation of reaction (7) was found from a slight initial decrease in the amount of carbon-containing compounds in the gas phase during the initial stages of reactions on tungsten disulfide.

The absence of any evidence for such adsorptive processes on molybdenum disulfide does not necessarily imply a difference in the behavior of the two catalysts. The surface area of the molybdenum disulfide was only 2.18 m^2/g compared with 78.2 m^2/g for the tungsten disulfide and so adsorptions of the same extent as those on the tungsten catalyst would not have been detectable with molybdenum disulfide.

The Exchange of Methyl Mercaptan with Deuterium

Since one hydrogen atom in the mercaptan exchanged more rapidly than the remaining three atoms, it is obvious that both catalysts can activate the S–H bond more readily than the C–H bonds in the methyl group. However, the difference in the reactivity is less marked on molybdenum disulfide, which gave some exchange of the methyl hydrogens concurrently with that of the mercaptyl hydrogen, than on tungsten disulfide. This difference in selectivity is analogous to the behavior in the earlier results (*1*) which indicated that tungsten disulfide catalyzed the exchange of hydrogen and deuterium at lower temperatures than the exchange of hydrogen sulfide and deuterium but both reactions occurred in the same range of temperature with the molybdenum catalyst.

A comparison of the present results with the earlier work (*1*) shows that, on tungsten disulfide, the temperature ranges, activation energies, and frequency factors are almost identical for the exchange of the mercaptyl hydrogen and the hydrogen atoms in hydrogen sulfide. The temperature ranges for both reactions are the same with molybdenum disulfide but the activation energy is about 4 kcal/mole lower for the reaction of mercaptan than for that of hydrogen sulfide and this difference is offset by a compensating decrease of 1.8 in $\log_{10}A$.

In exchange reactions, the principle of microscopic reversibility must apply to the rate-determining step, i.e. if the rate is controlled by an adsorption process there will be a corresponding desorption process occurring at the same rate. Thus, the exchange of methyl mercaptan might be controlled by the pair of reactions

$$CH_3SH(g) \rightarrow CH_3S(a) + H(a) \qquad (8a)$$

and

$$D(a) + CH_3S(a) \rightarrow CH_3SD(g) \qquad (8b)$$

Since the order with respect to mercaptan on tungsten disulfide was —0.1, it is clear that the mercaptan is strongly adsorbed and the coverage of the surface by $CH_3S(a)$ will not be influenced greatly by the pressure of mercaptan. It is obvious that the rate of (8b) cannot involve an order with respect to deuterium of more than 0.5 and this does not agree with the observed order of 0.95 on tungsten disulfide. Thus, although some exchange may occur by reactions (8a) and (8b), we are forced to conclude that the rate-determining steps are probably

$$CH_3S(a) + D_2(g) \rightarrow CH_3SD(g) + D(a) \qquad (9a)$$

and

$$H(a) + CH_3SH(g) \rightarrow CH_3S(a) + H_2(g) \qquad (9b)$$

The expected kinetics of reaction (9a) will be first order in deuterium and zero order in mercaptan in agreement with the observed orders. The values of q reported in Table 2 show that the "hydrogen" returned to the gas phase during the initial stages of the exchange reactions on both catalysts consisted mainly of H_2 with comparatively little HD. If HD had been the only initial product the values of q would have been equal to K, the equilibrium constant of the interconversion reaction (4), throughout the course of the exchange reaction of the mercaptan. On the other hand, if H_2 had been the only initial product, the value of q would have been zero initially and risen gradually as reaction occurred. The formation of H_2 as a product implies that the concentration of H(a) must be greater than the concentration of D(a) in the early stages of the exchange and also that the equilibration between gas-phase "deuterium" and adsorbed "hydrogen" is not much faster than the rate of exchange of the mercaptyl hydrogen atom. Thus, the character of the exchange processes with methyl mercaptan is similar to that observed previously with hydrogen sulfide (1) and the presence of the mercaptan must, like hydrogen sulfide, partially poison the exchange of hydrogen and deuterium on both catalysts.

Decomposition of Mercaptan on WS_2

It is simpler to discuss the results on tungsten disulfide before those on molybdenum disulfide because the two main types of decomposition of the mercaptan begin in different temperature ranges on the tungsten catalyst.

The disproportionation of the mercaptan to form dimethyl sulfide and hydrogen sulfide occurs readily on tungsten disulfide and the results indicate that equilibrium for reaction (1) is attained fairly rapidly at temperatures above 200°C. The experimental values of the equilibrium constant for this reaction decreased from 1.8 to 1.2 over the temperature range from 250° to 310°C and calculated values based on the most recent thermodynamic data (*8, 9*) are 1.8 and 1.4 for the two temperatures. An analysis of the course of reaction (1) was carried out on the assumptions that the forward reaction was directly proportional to the pressure of mercaptan, as observed experimentally, and that the additional decrease in rate was attributable to the build-up of the back reaction as equilibrium was approached. As the rate of the forward reaction is given by

$$r_1 = k_2 P_{\mathrm{CH_3SH}} \qquad (10)$$

the rate of the reverse reaction should be given by

$$r_2 = k_3 P_{\mathrm{(CH_3)_2S}} P_{\mathrm{H_2S}} / P_{\mathrm{CH_3SH}} \qquad (11)$$

under the conditions of our experiments, in order that the equilibrium constant of reaction (1) will be established when the rates of the forward and back reactions become equal. The apparent rates of the forward reaction were determined from a composition–time plot at a series of times by drawing tangents. These were subtracted from the expected rates based on the initial rate and Eq. (10) in order to give values for the back reaction at each time and the values, thus obtained, are shown in Fig. 6 plotted according to Eq. (11). The activation energy of the back reaction was 15.9 kcal/mole which, together with the value of 13.8 kcal/mole for the disappearance of mercaptan, gives ΔH for reaction (1) as —2.1 kcal/mole. The agreement with the known heat content change of —2.4 kcal/mole provides further confirmation that an interpretation of the results in terms of an approach to equilibrium is correct.

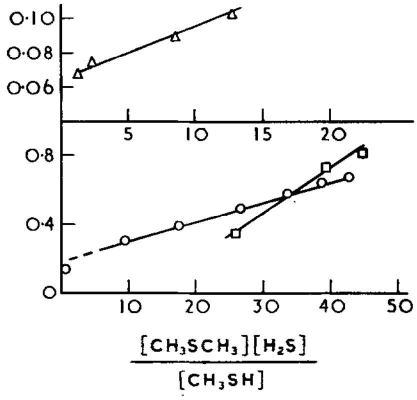

FIG. 6. Plots to test Eq. (11) for the reaction of methyl mercaptan and hydrogen on WS_2; △, 190°C; ○, 230°C; □, 250°C.

It is probable that the rate-determining step of reaction (1) involves the formation of the C–S bond. The evidence from the exchange experiments shows that the rupture and formation of H–S bonds occurs at lower temperatures and with smaller activation energy than the decomposition of mercaptan by reaction (1). Furthermore, the fact that hydrogen sulfide is formed with an activation energy which is 3.5 kcal/mole lower than that for the production of dimethyl sulfide is some evidence that the rupture of C–S bonds is not rate determining. The actual mechanism of the slow step is not clear; it could be formulated as

$$CH_3S(a) + CH_3(a) \rightarrow (CH_3)_2S(g) \qquad (12)$$

but this is difficult to reconcile with the first order dependence on mercaptan pressure. The kinetics of the exchange experiments were interpreted on the assumption that the species CH_3S is strongly adsorbed and that the concentration is not greatly influenced by the pressure of mercaptan. Also, the kinetics of the formation of methane, to be discussed later, do not support the conclusion that the concentration of adsorbed methyl groups is influenced by the pressure of mercaptan. A formulation of the mechanism as

$$CH_3SH(g) + CH_3(a) \rightarrow (CH_3)_2S(g) + H(a) \qquad (13)$$

would agree with the kinetics but it would imply a rather complex, and perhaps unlikely, transition state.

The exchange of the hydrogen atoms in the methyl group of the mercaptan is about 10 or 20 times slower at 155°C than the formation of dimethyl sulfide. This means that the methyl group, adsorbed on the surface either as CH_3 or CH_3S, is a comparatively stable entity at this temperature and it does not readily undergo a reversible dissociative adsorption involving rupture of C–H bonds.

The slow step in the formation of methane by reaction (2) probably involves desorption by the process

$$CH_3(a) + H(a) \rightarrow CH_4(g) \qquad (14)$$

The characteristics of the reaction in regard to both activation energy and the zero order dependence on the pressure of the sulfur-containing molecule are similar in the cases where methyl mercaptan or dimethyl sulfide are used as the initial reactant. This is a consequence of the ease with which the equilibrium corresponding to reaction (1) is established on tungsten disulfide. Both sulfur compounds must give rise to a substantial coverage of the surface by adsorbed methyl radicals and the concentration of these species cannot depend very markedly on the pressure of the reactant because the rate of formation remained constant throughout the experiments at each temperature.

The fact that the exchange of methane with deuterium is about 100 times slower than the formation of methane from mercaptan at 320°C is interesting. Dissociative adsorption and the reverse desorption reaction must occur at identical rates in the exchange process and so the rate-determining step of the exchange reaction must be the same as (14). The difference in rates can be explained on the basis that the coverage of the surface by methyl groups is very substantially higher when the sulfur compounds are decomposing than when methane is being exchanged and support for this suggestion can be obtained by introducing the concept of a "virtual pressure" of methane. The equilibrium constant for reaction (2) at 327°C is about 3×10^6 and so, since the desorption of methyl groups is slow, the concentration of these groups on the surface when mercaptan is decomposing will be approximately the same as if the surface had been exposed to a pressure of 10^5 or 10^6 atm of methane. Thus, the zero order kinetics observed for the formation of methane by reaction (2) do not necessarily imply that methyl groups are strongly adsorbed; the adsorption of methane as methyl groups and hydrogen atoms may only take place to a limited extent when the gas phase contains methane, but substantial coverages by methyl groups will be maintained in the presence of mercaptan because of the position of the equilibrium of reaction (2).

The results of this work and of the earlier investigation (*1*) show that tungsten disulfide can activate chemical bonds in the order

$$\text{H–H} > \text{H–S} > \text{C–S} > \text{C–H}$$

Decomposition of Mercaptan on MoS_2

The most obvious difference between the results on molybdenum disulfide and those on tungsten disulfide is that both reactions (1) and (2) occur in the same range of temperature. The relative ease of activation of the different chemical bonds is similar to the order set out above for tungsten disulfide but the differences are much less marked because molybdenum disulfide is a less selective catalyst.

It is interesting that an apparent value of the equilibrium constant of reaction (1) of 8 is obtained over molybdenum disulfide at 270°C which is well above the true value. This arises because hydrogen sulfide is formed more rapidly by reaction (2) than it can be removed by the reverse of reaction (1). The mutual interaction of the two reactions in this way makes it unlikely that a simple explanation can be given of the course of reaction (1).

Since the activation energies and rates of formation of both hydrogen sulfide and dimethyl sulfide are identical we cannot rule out the possibility that the cleavage of the C–S bond might be rate determining for reaction (1) on this catalyst.

The main features of reaction (2) and of the exchange of methane are essentially similar on both catalysts. The only significant difference is in the pattern of products from the exchange reaction. Less multiple exchange of methane occurs with molybdenum than with tungsten disulfide and this indicates that less reversible dissociation of methyl groups takes place on the molybdenum catalyst.

ACKNOWLEDGMENTS

The authors wish to thank the Agricultural Division of Imperial Chemical Industries Ltd. for the gift of the catalyst samples and one of us (R.L.W.) acknowledges the award of a research studentship by the Ministry of Education, N. Ireland.

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