Adsorption and Catalytic Decomposition of Dimethyl Sulphide and Dimethyl Disulphide on Metal Films of Iron, Palladium, Nickel, Aluminium and Copper

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The interaction of dimethyl sulphide (Me,S) and dimethyl disulphide (Me₂S₂) has been studied with metal films of Fe, Pd, Ni, Al and Cu over the temperature ranges 193-500 K with Me₂S and 223-600 K in the case of Me₂S₂. At 193 K mainly molecular chemisorption of Me₂S occurred on the films. With Me₂S₂, multilayer adsorption, involving both chemisorption and van der Waals adsorption, took place on the films at 223 K. Dissociative chemisorption of Me₂S or Me₂S₂ began above 300 K and was accompanied by the evolution of gaseous products. The latter involved H_2 , CH_4 and C₂H₆ gases with Me₂S and H₂, CH₄, C₂H₆, MeSH and Me₂S subsequent to the dissociation of Me₂S₂. Additional gaseous products throughout the decomposition on the oxidized films were CO, H₂O and C₂H₄. The rate of Me₂S or Me₂S, chemisorption depended on the pressure of the reacting gas, and the kinetic data indicated the operation of a compensation effect throughout the interaction of Me₂S or Me₂S₂ with the films. On the basis of kinetic data it was possible to arrange the metal films in the order of decreasing activity toward Me₂S or Me₂S₂ adsorption. The transition-metal films showed greater activity than Al and Cu, and among the former films Fe showed the greatest activity, for chemisorption of Me₂S and Me₂S₂. All the metals have higher tendencies for Me_2S adsorption than for Me_2S_2 .

Methyl sulphide and dimethyl disulphide are discharged during industrial processes into the atmosphere and are listed as substances having an offensive odour in many countries. Both substances are highly corrosive¹ under various conditions and can also act as corrosion inhibitors when used in small amounts under certain circumstances.^{1, 2} Poisoning of catalytic surfaces by compounds containing unshielded sulphur atoms, including dimethyl sulphide and dimethyl disulphide, is of widespread interest.³ The poisoning effects of such compounds on a number of catalysts are well known.⁴

This investigation contributes to a series of studies on the adsorption of sulphurcontaining gases on various solids.⁵⁻¹⁰ In the present work the adsorption and the decomposition of dimethyl sulphide and dimethyl disulphide was investigated on a number of clean and oxidized metal films over a wide range of temperatures (193–600 K). The product phase was analysed mass-spectrometrically and the kinetics of adsorption were followed at each stage. Although there have been some studies¹¹⁻¹⁴ of the adsorption of dimethyl sulphide and dimethyl disulphide, very few have dealt with such fundamental aspects.¹⁵⁻¹⁷

Experimental

The apparatus and general techniques utilized in the outgassing, preparation and sintering of the films have been described elsewhere.¹⁸⁻²¹ The metal films were prepared from Johnson Matthey spectroscopically standardized wires (0.5 mm in diameter) which were first degassed at as high a temperature as possible (*ca.* 1300 K) for a

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minimum of 8 h. Each film was prepared at 78 K and sintered for 30 min at 350 K. During the deposition and sintering of the films the reaction vessel was pumped and the pressure was always $< 10^{-6}$ N m⁻².

The reaction vessel was connected through a leak device to a Quadruvac 200 massspectrometer partial-pressure gauge (Leybold-Heraus); details of the construction and operation have been given elsewhere.¹⁸⁻²⁰

Dimethyl sulphide (Me₂S) and dimethyl disulphide (Me₂S₂) with purity > 98% were obtained from Rideal Dehan. Each substance was purified by vacuum distillation twice at room temperature into a receiver at 78 K followed by cold pumping. Only middle fractions of the distillate were used, and mass-spectrometric analysis showed these to be > 99.6% pure. The stored samples were further outgassed, purified and then analysed prior to use. All the materials used in the cracking-pattern determination were obtained from Matheson and B.D.H. and had stated purities exceeding 99.5%. Each substance was subjected to the same purification treatment as for Me₂S and Me₂S₂.

The surface area of each film was determined from the krypton adsorption isotherm at 78 K before the admission of Me₂S or Me₂S₂ doses. The extent (θ) of dimethyl sulphide or disulphide adsorption on the film was expressed as

$$\theta = V_{\rm g}/V_{\rm Kr} \tag{1}$$

where $V_{\rm Kr}$ represents the volume of the krypton monolayer on the surface at 78 K and $V_{\rm g}$ is the volume of Me₂S or Me₂S₂ adsorbed subsequent to the determination of the area.

In a series of experiments, each film was first saturated with oxygen gas at 300 K and a pressure of 2.0 N m⁻². The oxygen pressure was then reduced to 10^{-4} N m⁻² and the area of the oxidized film was redetermined prior to the addition of Me₂S or Me₂S₂ to the surface. The extent (X) of metal oxidation was estimated from the relation

$$X = V_{\rm O_0} / V_{\rm Kr}.$$
 (2)

The extent (θ) of the subsequent Me₂S or Me₂S adsorption was calculated from eqn (1) using the volume of the krypton monolayer ($\bar{V}_{\rm Kr}$) on the oxidized surface instead of $V_{\rm Kr}$; all the volumes were measured in units of mm³ at s.t.p.

Results

Adsorption of Me₂S

Fast adsorption of Me₂S occurred on all films at 193 K, the pressure falling to 10^{-4} N m⁻² in < 1 min. Further adsorption took place in a similar manner until the rate of uptake decreased rapidly to 10^{12} molecule cm⁻² s⁻¹, corresponding to 1% of the monolayer per second at values of θ ranging from 0.57 to 0.881 for the transition-metal films Pd, Ni and Fe and from 1.14 to 1.34 on Al and Cu. Table 1 gives the volumes of the krypton monolayer ($V_{\rm Kr}$) on the films, the subsequent maximum Me₂S adsorption ($V_{\rm g}$) at 193 K and the corresponding values of θ . Ca. 15% of the adsorption on Al and Cu films at 193 K was reversible. Some CH₄ and H₂ gases, amounting to ca. 5% of adsorbed Me₂S, was desorbed at 193 K. Slow Me₂S uptake continued on all surfaces in the temperature range 250–340 K without liberation of significant amounts of product gases; the values of θ increased by ca. 15% over a period of 1 h of the reaction at such temperatures.

Adsorption of Me₂S on the films above 340 K was accompanied by the evolution of gaseous products; these involved H_2 , CH_4 and C_2H_6 gases on Fe, Pd, Al and Cu and only CH_4 and C_2H_6 on Ni. Hydrogen evolution was appreciable only on Fe and Al films forming the dominant gaseous product of Me₂S decomposition on these metals. The extent of CH_4 liberation at any temperature was generally greater on Fe, Pd, Ni and Cu

film	$V^a_{ m Kr}$	$V^a_{\mathrm{O}_2}$	X	$ar{V}^a_{ m Kr}$	$V^a_{ m g}$	θ
Fe	101.0				89.0	0.881
Pd	79.5				46.0	0.578
Ni	36.0		_		25.2	0.700
Al	17.5				20.1	1.148
Cu	8.4				11.3	1.345
oxidized Fe	80.0	79.3	0.991	70.5	58.1	0.824
oxidized Pd	76.5	84.2	1.100	60.8	37.5	0.616
oxidized Ni	50.0	57.2	1.144	39.9	26.4	0.663
oxidized Al	18.0	24.3	1.350	21.7	19.1	0.880
oxidized Cu	15.4	18.0	1.168	22.0	22.2	1.009
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Table 1. Adsorption of dimethyl sulphide (Me₂S) on clean and oxidized films of Fe, Pd, Ni, Al and Cu at 193 K

^a The volumes of the gases were expressed in mm³ at s.t.p.

Table 2. Analysis of the gas phase, given as percentage of eachgas, throughout the decomposition of dimethyl sulphide (Me²S)on various films

film	T/K	H ₂	CH ₄	C_2H_6	H ₂ O	CO	Me ₂ S
Fe	301	21.24	6.03	11.21		_	61.52
	338	31.26	21.72	10.00			37.02
	498	32.69	38.77	10.87			17.67
Pd	338	8.19	17.59	9.41			61.26
	383		58.37	10.82	—	—	30.81
	498		72.06	10.94			17.00
Ni	383		40.31	23.04			36.65
	498		55.77	25.28			18.95
Al	383	29.21	7.18	18.90			44.71
	448	35.77	10.33	19.38			34.52
Cu	573	7.87	39.28	11.90			40.95
oxidized Fe	383	29.41	16.98	3.95	2.81	1.23	45.62
	498	43.64	21.11	4.76	3.46	2.28	24.75
oxidized Pd	453	9.04	46.69	4.70	1.50	3.13	34.94
	498	27.98	45.63	5.11	2.17	3.03	16.08
oxidized Ni	448	11.10	20.05	2.32	1.07	6.29	59.27
	498	17.77	50.17	2.23	1.88	6.66	21.29
oxidized Al	383	33.81	6.04	3.34	3.95	4.06	48.80
	498	33.37	12.01	3.20	4.53	4.83	42.06
oxidized Cu	573	12.79	31.55	1.38	1.75	3.15	49.38

films than of C_2H_6 . On Al, the percentage of ethane in the gas phase exceeded that of CH_4 . Table 2 gives the composition of the gas phase on the films at two or three temperatures. Fig. 1(*a*) shows the interaction of Me₂S with Fe film at 383 K.

Adsorption of Me₂S on oxidized films at 193 K occurred also rapidly to the extent (θ) which are indicated in table 1 at which the rate of adsorption decreased to $< 10^{11}$ molecule cm⁻² s⁻¹ (< 0.1 % monolayer s⁻¹). Some 10% of the adsorption at 193 K on all films was reversible. No gaseous products were identified subsequent to Me₂S adsorption on oxidized surfaces at this temperature. Further slow Me₂S adsorption



Fig. 1. Interaction of Me₂S with Fe film at 383 K (*a*), and of Me₂S₂ with Pd film at 448 K (*b*). \bigcirc , H₂; \triangle , CH₄; ×, C₂H₆; \Box , MeSH; \blacktriangle , Me₂S and \blacktriangle , Me₂S₂.

film	V _{Kr}	V_{0_2}	X	V _{Kr}	$V_{\rm g}$	θ
Fe	73.10	_			110.0	1.504
Pd	65.81		<u></u>		124.9	1.807
Ni	54.00	_			104.4	1.933
Al	15.56	_			50.70	3.258
Cu	11.31		—		35.7	3.156
oxidized Fe	80.8	82.1	1.096	70.5	144.0	2.042
oxidized Pd	71.7	78.5	1.094	67.3	140.1	2.081
oxidized Ni	57.2	63.1	1.103	48.7	114.5	2.351
oxidized Al	16.9	21.8	1.289	20.2	63.0	3.118
oxidized Cu	12.5	19.7	1.576	15.1	48.8	3.231

Table 3. Adsorption of dimethyl disulphide (Me_2S_2) on clean and oxidized films of Fe, Pd, Ni, Al and Cu at 223 K

occurred at temperatures ≤ 340 K. Dissociative chemisorption of Me₂S was the main feature of the interaction above 340 K resulting in the formation of gaseous products (table 2). The composition of the gas phase consisted (table 2) of H₂ and CH₄ gases, together with small amounts of C₂H₆, H₂O and CO. The dominant product was H₂ on oxidized Fe and Al films and CH₄ on oxidized Pd, Ni and Cu (table 2). Fig. 2(*a*) shows the interaction of Me₂S with oxidized Fe film at 383 K.

Adsorption of Me₂S₂

Rapid Me_2S_2 uptake occurred on films at 223 K until θ became 1.5–1.9 on Fe, Pd and Ni and 3.15–3.25 on Cu and Al. The rate of uptake at this stage decreased to 10^{12} molecule cm⁻² s⁻¹ under an Me_2S_2 pressure of 8.0 N m⁻².

Table 3 gives the values of $V_{\rm Kr}$, $V_{\rm g}$ and the corresponding maximum values of θ on the films at this temperature. No gaseous products were observed subsequent to the adsorption of Me₂S₂ on the films at 223 K. On warming the films to 273 K desorption of Me₂S₂ took place, lowering the values of θ to *ca.* 1.0.

Adsorption of Me_2S_2 on all films above 340 K was accompanied by the evolution of H_2 , CH_4 , C_2H_6 , MeSH and Me_2S gases. The rate of adsorption and dissociation increased with the rise of temperature above 340 K. The major gaseous products on Fe and Ni films at any temperature in the range 340–600 K was Me_2S , while H_2 was the

Table 4. Analysis of the gas phase, given as percentage of each gas, throughout the decomposition
of dimethyl disulphide (Me_2S_2) on various films

film	T/K	H ₂	CH4	C ₂ H ₆	MeSh	Me ₂ S	H ₂ O	СО	Me_2S_2
Fe	394	6.47	17.82	11.37	4.18	9.26			50.90
	443		21.22	23.01	5.18	35.93			14.66
	493	_	25.67	23.07	7.55	40.45			3.26
Pd	448	48.87	9.14	22.08	2.89	3.40			13.62
	498	49.26	10.83	22.45	7.69	4.30		_	5.47
Ni	433	14.37	13.03	19.23	6.73	12.33			33.93
	483	21.54	20.24	20.53	7.65	27.33			2.71
	523	23.70	21.21	21.15	6.66	26.95	_		0.33
Al	383	4.39	7.21	13.03	8.31	4.48			62.58
	443	18.54	14.94	12.23	13.02	10.08			31.19
	513	28.64	16.26	12.39	15.48	23.65			3.58
Cu	343	5.88	4.83	26.26	4.2				58.83
	433	20.29	7.27	27.8	5.02	3.55	_		36.03
	573	38.40	15.77	29.95	5.29	5.62	_	-	4.97
oxidized Pe	343	20.67	9.48	8.17	15.94	5.91	2.37	_	37.46
	453		41.82	8.48	15.46	6.28	4.10	1.81	22.05
	493		40.21	10.44	20.97	15.78	4.89	2.06	5.65
oxidized Pd	383	20.15	32.65	7.17	11.87	5.65	3.20		19.31
	498	19.53	28.56	8.69	21.10	10.37	4.80	2.35	3.60
oxidized Ni	348	15.90	11.73	12.42	18.61	13.32	2.50		25.52
	498		32.82	13.67	25.48	18.16	2.60	3.41	3.86
oxidized Al	383	11.45	4.17	16.56	17.90	13.84	2.30		33.78
	513	24.15	10.19	18.34	18.10	14.93	3.31	2.89	8.09
oxidized Cu	348	11.92	11.58	10.34	13.00	21.45	5.89		25.82
	498	10.70	20.66	12.91	18.08	23.83	4.04	1.72	8.05



Fig. 2. Interaction of Me₂S with oxidized Fe at 383 K (a) and of Me₂S₂ with oxidized Pd at 498 K (b). \bigoplus , CO and \bigoplus , H₂O. Other symbols as in fig. 1.

main product on Pd, Al and Cu films at similar temperatures. The extent of MeSH formation on all films was very small, even when the temperature was raised to 600 K. Table 4 shows the percentages of the gaseous products throughout the interaction of Me_2S_2 with the films at various temperatures. Fig. 1(b) shows the interaction of Me_2S_2 with a Pd film at 448 K.

Adsorption of Me₂S₂ on oxidized films at 223 K was also rapid, and the extent of



Fig. 3. Values of \Box , N; \bigcirc , M and \triangle , R plotted as a function of temperature for Me₂S adsorption on clean (a) and oxidized (b) films.

adsorption on oxidized Fe, Pd, and Ni films was greater than on the corresponding clean metals (table 3). Ca. 50% of the adsorption on oxidized Fe, Pd and Ni and ca. 68% on oxidized Al and Cu at 223 K were reversible.

Above 340 K dissociative chemisorption of Me_2S_2 occurred on the oxidized surfaces, and the adsorption was followed by the liberation of such gases as H_2 , CH_4 , C_2H_6 , MeSH and Me_2S , together with small amounts of H_2O and CO. Methane and methanethiol were the main products on oxidized Fe, Pd and Ni films, while CH_4 and Me_2S were the dominant products on oxidized Cu. H_2 evolution on oxidized Fe and Ni films occurred at 343 K but discontinued at higher temperatures. A summary of the results at various temperatures is presented in table 4, and fig. 2(b) describes the behaviour of Me_2S_2 on an oxidized Pd film at 498 K.

Surface Composition

The composition of the surface phase on each film is expressed as $C_n H_m S_l$, where n, m and l represent, respectively, the number of carbon, hydrogen and sulphur atoms remaining in the surface phase per adsorbed Me₂S or Me₂S₂ molecule. Values of n, m and l have been obtained from the volumes of the resulting gases for a given volume of adsorbed Me₂S or Me₂S₂, taking into consideration the number of carbon, hydrogen and sulphur atoms in each gas; the procedure of estimating these parameters is similar to that presented previously.^{18, 19} These data were then used to calculate the values of N and M, indicating, respectively, the number of carbon and hydrogen atoms to sulphur adatoms, and R, the number of hydrogen to carbon adatoms. Thus N, M and R correspond, respectively, to the ratios n/l, m/l and m/n.

The value of *l* remained equal to unity throughout Me_2S decomposition on both clean and oxidized films, as none of the gaseous products contained sulphur atoms at any temperature < 600 K; this makes n = N and m = M with respect to the surface composition of the adsorbed Me_2S . Fig. 3 shows the values *N*, *M* and *R* for Me_2S plotted as a function of temperature on both clean and oxidized films over the temperature range 195–600 K; the points on each plot represent a general trend for the temperature dependence of the respective parameter. Values of these parameters are shown in fig. 3 to decrease considerably with the rise in temperature, but the extent is slightly greater

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on the oxidized films than on clean surfaces. Some specific values of the three parameters for Me_2S at four temperatures which are involved in fig. 3 may be arranged as follows, where c and o refer, respectively, to the clean and oxidized films.

	Ì	N	Ι	М	1	१
T/K	с	0	с	0	с	0
193	2.0	2.00	6.0	6.00	3.00	3.00
400	1.6	1.70	4.2	4.40	2.62	2.59
500	1.4	1.35	3.5	3.25	2.50	2.40
600	1.2	1.10	2.5	2.00	2.10	1.80

Values of N and M are thus shown to be higher at 400 K, but lower at 500 and 600 K, on oxidized surfaces than on clean films. Values of R decreased steadily with increasing temperature, attaining values of 2.1 and 1.8 on clean and oxidized films, respectively.

Decomposition of Me_2S_2 , as indicated in fig. 4 and 5, was less dependent on temperature on Al and Cu films than on Fe, Ni and Pd. Moreover, the variation of n, m and l (fig. 4) with temperature was greater on clean Al and Cu than on the oxidized surfaces of these films; the reverse of this trend existed with respect to Fe, Pd and Ni (fig. 4). Some specific values for n, m and l on Fe, Pd, and Ni may be arranged as follows:

	n		n m			l	
T/K	с	0	с	0	c	0	
223	2.0	2.0	6.0	6.0	2.0	2.0	
400	1.8	1.4	4.5	4.8	1.9	1.9	
500	1.2	0.7	2.0	1.8	1.8	1.7	
600	0.5	0.3	0.7	0.5	1.2	1.2	

Thus the change in the values of n, m and l is substantial, particularly over the temperature range 500-600 K. On Al and Cu the values of these parameters are considerably higher than those on Fe, Ni and Pd. Values of l in the case of Me₂S₂ also decreased with increasing temperature as a consequence of the removal of adsorbed sulphur-containing species (MeSH and Me₂S) from the surface.

Owing to the temperature dependence of l, another plot was necessary to represent the ratios n/l, m/l and m/n as expressed in terms of N, M and R vs. temperature as in fig. 5. The drop in N values to below unity with increasing temperature reflects the fact that more carbon is removed from the surface phase than sulphur. There is a sharp fall in the values of M (fig. 5) over the temperature range 500-600 K, attaining at the latter temperature a value as low as ca. 0.5. The variation of R on clean films of Fe, Ni and Pd became less temperature-dependent over the temperature range 500-600 K as compared with the range 400-500 K; on oxidized surfaces of these films a steady temperature dependence continued at all temperatures > 400 K.

Kinetics of Adsorption

The rate of Me₂S and Me₂S₂ adsorption on each surface was determined at various surface coverages (θ) and temperatures. At a given temperature and Me₂S or Me₂S₂ pressure the velocity (r_1) of uptake was measured at an initial pressure p_1 ; the pressure



Fig. 4. Composition of the surface phase plotted against temperature for Me_2S_2 adsorption on clean (a) and oxidized (b) films. \Box , n; \bigcirc , m and \triangle , l for Fe, Pd and Ni and \blacksquare , n; \bigcirc , m and \triangle , l for Al and Cu.



Fig. 5. Values of N, M and R plotted as a function of temperature for Me_2S_2 adsorption on clean (a) and oxidized (b) films. Symbols as in fig. 2 for Fe, Ni and Pd and a similar filled symbol for Al and Cu.

Table 5. Activation energies $(E_a/kJ \text{ mol}^{-1})$, pre-exponential factors $(A/\text{molecule cm}^{-2} \text{ s}^{-1})$ and entropies of activation $(\Delta S^*/J \text{ mol}^{-1} \text{ K}^{-1})$ for the adsorption of dimethyl sulphide (Me₂S) on various films

film	T/K	heta	E_{a}	A	ΔS^*
Fe	301-498	0.881-1.525	50.228 ± 2.9	2.891 × 1018	-460.94
Pd	301-498	0.578-1.452	56.678 ± 2.1	4.686×10^{18}	-457.97
Ni	338-498	0.700-1.941	53.281 ± 1.8	3.697×10^{18}	-459.46
Al	338-498	1.148-2.119	65.756 ± 3.3	1.560×10^{19}	-451.41
Cu	443-533	1.345-2.414	78.268 ± 4.2	4.808×10^{19}	-442.94
oxidized Fe	338-498	0.824-1.195	58.382 ± 3.5	4.882×10^{18}	-453.28
xidized Pd	383-498	0.616-0.853	68.593 ± 2.7	1.625×10^{19}	-448.61
oxidized Ni	383-498	0.663-0.930	72.419 ± 2.2	2.517×10^{19}	-445.18
oxidized Al	338-498	0.880-2.055	79.392 ± 3.1	4.01×10^{19}	- 441.40
oxidized Cu	383-553	1.009-2.089	83.992 + 3.5	8.914 × 10 ¹⁹	-434.85

Table 6. Activation energies $(E_a/kJ \text{ mol}^{-1})$, pre-exponential factors $(A/\text{molecule cm}^2 \text{ s}^{-1})$ and entropies of activation $(\Delta S^*/J \text{ mol}^{-1} \text{ K}^{-1})$ for the adsorption of dimethyl sulphide (Me_2S_2) on various films

film	T/K	θ	$E_{ m a}$	A	ΔS^*
Fe	343-493	1.504-3.906	43.503 ± 2.1	3.890 × 1017	-473.79
Pd	343-498	1.897-3.467	49.138 ± 1.7	7.687×10^{17}	-472.10
Ni	343-523	1.933-3.503	58.395 ± 1.4	1.493×10^{18}	-466.21
Al	348-493	3.255-5.396	61.690 ± 1.9	2.517×10^{18}	-465.18
Cu	348-573	3.156-6.151	72.510 ± 2.3	6.622×10^{18}	-457.28
oxidized Fe	348-493	2.042-4.559	47.692 ± 2.6	4.886×10^{17}	-473.81
oxidized Pd	348-498	2.081-4.051	55.839 ± 2.9	1.119×10^{18}	-467.83
oxidized Ni	348-498	2.351-5.167	63.633 ± 1.6	2.328×10^{18}	-463.78
oxidized Al	348-493	2.351-5.167	68.799 ± 1.7	4.204 ± 10^{18}	-460.08
oxidized Cu	393-583	3.118-6.871	80.478 ± 2.5	1.005×10^{19}	-452.16

was then rapidly changed to a different constant pressure p_2 at the same surface coverage (θ) , and the new velocity r_2 measured. These data were then used to estimate the pressure dependence, S, from the relation:^{18,19}

$$(p_1/p_2)^s = r_1/r_2. (3)$$

The values of S obtained for both sulphur compounds were close to unity. Moreover, the plots of log p for each adsorbate at a constant temperature against time were found to be adequately linear.

From the rates of adsorption of each sulphur compound at two different temperatures, but essentially the same adsorbate pressure and value of θ , the activation energy of adsorption (E_a) was determined, and the results are given in tables 5 and 6. The value of E_a for each adsorbate did not vary with temperature or with the extent of adsorption (θ). Values of E_a could also be estimated from Arrhenius plots, provided the rates at different temperatures are derived under similar adsorbate pressures. The extent (θ) of adsorption did not influence the values of E and A, as these values remained constant over an increase of θ to ca. 3.0 in the case of Me₂S and to ca. 6.0 for Me₂S₂ (tables 5 and 6). The kinetics of Me₂S and Me₂S₂ adsorption are thus shown to be independent of the nature and amount of adsorbed species remaining on the surface over the experimental values of θ that are given in tables 5 and 6. Interaction of Me₂S and Me₂S₂ on Metal Films



Fig. 6. log A vs. E_a for Me₂S (a) and Me₂S₂ (b) adsorption on clean and oxidized films. \bigcirc , Fe; \square , Pd, \triangle , Ni, \square , Al; \bigtriangledown , Cu, and similar filled symbols for the oxidized films.

The rate of adsorption (r) and the appropriate value of E_a were then used to calculate the pre-exponential factor (A) in the rate equation:

$$r = A \exp\left(-E_{\rm a}/RT\right). \tag{4}$$

The entropy of activation (ΔS^{\ddagger}) for Me₂S and Me₂S₂ was then calculated from the value of A using relationship

$$A = (\mathbf{k}T/\mathbf{h}) C_{\mathbf{g}} C_{\mathbf{s}} \exp\left(\Delta S^{\dagger}/\mathbf{R}\right)$$
(5)

where C_g and C_s are, respectively, the concentrations of the sulphur compounds per unit volume (cm³) and the surface sites per unit area (cm²). Plots of E_a values against log A are shown in fig. 6.

Discussion

Me₂S

The results indicated that mainly molecular adsorption of Me_2S occurred on all surfaces at 193 K, as only very small amounts of CH_4 , alone or together with H_2 , appeared in the gas phase at this temperature. Magnetization measurements¹⁵ on supported nickel catalysts have shown that Me_2S is associatively chemisorbed at room temperature with the formation of two bonds with two nickel atoms of the surface. Molecular adsorption of Me_2S on the surface may also occur *via* coordination to a single metal site through a lone pair of electrons on sulphur in a similar manner to those reported earlier^{10, 13, 22} for the adsorption of mercaptans and alkyl sulphides on a number of surfaces; the relatively large size of the adsorbed Me_2S molecule may then cause the blockage of an additional (adjacent) site. The formation of very small amounts of CH_4 and H_2 on certain films at 193 K shows that some dissociative chemisorption is also possible through the rupture of both C—S and C—H bonds.

The dissociative chemisorption which began above 350 K may take place as

$$Me_2S(g) \rightarrow Me_2S(a) \rightarrow MeS(a) + Me(a)$$
 (6)

involving the rupture of the C—S bond of the methyl sulphide. This is similar to the adsorption behaviour of alkyl sulphides on silica-supported nickel^{13, 23} and of mercaptans on a number of surfaces.^{9, 10, 24} The formation of appreciable amounts of hydrogen and alkanes as a result of chemisorption of methyl sulphide above 350 K requires at least

partial dissociation of C—H bonds of the chemisorbed Me(a) and MeS(a) residues in addition to the dissociation of C—S bonds. The dissociation of methyl sulphide on supported-nickel catalysts was reported to be highly temperature-dependent.¹⁵ At *ca.* 400 K extensive dissociation of Me₂S occurred through the cleavage of both C—S and C—H bonds, and magnetization experiments indicated¹⁵ the formation of 8–10 bonds at this temperature for each Me₂S molecule adsorbed, depending on the nature of the products formed in the surface phase.

Surface recombination reactions between chemisorbed methyl (or thiolate) groups and between these residues and atomically chemisorbed hydrogen lead to the formation of hydrogen, methane and ethane as

$$\Delta H/\text{kJ mol}^{-1}$$
Me(a) \rightarrow CH₂(a) + H(a) -98.0 (7a)

$$H(a) + H(a) \rightarrow H_2(g) \tag{8}$$

$$Me(a) + Me(a) \rightarrow MeMe(g)$$
 334.0 (9*a*)

$$Me(a) + H(a) \rightarrow MeH(a) \qquad 238.0 \qquad (10a)$$

The Me(a) species in reactions (7a), (9a) and (10a) may be replaced by MeS(a) species to give such reactions as

	$\Delta H/\text{kJ} \text{ mol}^{-1}$	
$MeS(a) \rightarrow CH_2S(a) + H(a)$	-187.0	(7 <i>b</i>)
$Me(a) + MeS(a) \rightarrow MeMe(g) + S(a)$	-48.0	(9 <i>b</i>)

$$MeS(a) + MeS(a) \rightarrow MeMe(g) + 2S(a) - 450.0$$
 (9*c*)

$$MeS(a) + H(a) \rightarrow MeH(a) + H(a) - 143.0$$
 (10b)

An attempt was made to calculate the enthalpy changes [$\Delta H(a)$ associated with these and previous reactions from the heats of adsorption, enthalpies of formation and the bond dissociation energies, using the procedure already adopted in previous publications,^{21,25} the resulting data for Fe film are indicated in reactions (7)–(10).

A similar trend operates among the ΔH_a values of reactions (7)–(10) on other metals. The results generally show that reaction (7b) is more exothermic than reaction (7a), and that reactions (9a) and (10a) are endothermic while the corresponding reactions (9b), (9c) and (10b) are exothermic. If the enthalpy changes were roughly treated as equivalent to the changes in the free energies of the corresponding reactions, through ignoring the accompanying changes in entropy, the calculated values of ΔH_a should reflect the thermodynamic feasibilities of the various proposed reactions. Dissociation of C—Cl and C—H bonds has been found¹⁹ to occur throughout the chemisorption of hydrocarbons and hydrogen on such surfaces proceeded through reaction steps similar to those of reactions (7)–(10). Methyl sulphide was also shown to be chemisorbed dissociatively \geq 300 K on silica-supported nickel¹⁷ by the rupture of C—S and C—H bonds, and surface recombination reactions as followed by thermodesorption and i.r. transmission measurements gave rise to hydrogen and hydrocarbons.

The extensive production of H_2 subsequent to the dissociative adsorption of Me_2S on Fe and Al films indicates the significance of reaction (7) on these films. The predominance of CH_4 over C_2H_6 on most surfaces may be attributed to an abundant supply of atomic hydrogen at or near the surface which can migrate on or through the lattice and hydrogenate the bound MeS or Me groups. A significant amount of atomic hydrogen has been found to be incorporated in a number of metals during adsorption of H_2S^{26} and MeSH.^{24,27} Diffusion to the surface of hydrogen atoms contained in the lattice is proposed^{24,27} to be the probable source of the broad intense H_2 desorption peak on rutile throughout H_2S and CH_3SH adsorption at 600 K.

3054 Interaction of Me₂S and Me₂S₂ on Metal Films

Dissociative chemisorption of Me₂S on oxidized surfaces above 300 K may take place

$$Me_2S(g) + O(a) \rightarrow MeS(a) + MeO(a)$$
 (11)

where the thiolate group (-SMe) bound on a metal site and the methyl group (-Me) attached to preadsorbed oxygen site, the latter probably forming a methoxide radical on the surface. The chemisorption of Me₂S on silica was enhanced by high-temperature pretreatment of the oxide; the adsorbed species consisted of methyl groups attached to oxide sites and thiolate groups on silicon atoms.¹³ Reaction (11) resembles in some respects the adsorption behaviour of methanethiol on TiO₂²⁸ and on a number of supports²⁹ and oxidized films.¹⁰ The formation of CO subsequent to the decomposition of Me₂S on oxidized films suggests that dissociation of Me₂S via reaction (11) does occur.

The production of ethane and methane gases from the decomposition of Me₂S on oxidized films above 300 K may proceed through reactions similar to those of (9b), (9c)and (10b). Methl groups bound to oxide sites are less susceptible to such recombination reactions than those attached to sulphur owing to the fact that the C-O bond is relatively stronger than C-S. Thermochemical calculations indicated that the recombination reactions (9b), (9c) and (10b) are more exothermic than the corresponding reactions involving MeO.

The methoxide radicals OMe(a) resulting from the dissociative adsorption of Me₂S on the oxidized films decompose mainly to CO in similar steps to those suggested for the production of this gas from methanol decomposition on oxidized metals.³⁰

Values of R (fig. 3) dropped to below 3.0 at 400 K and decreased further to ca. 2.0 when the temperature of the film was raised to 600 K. This is an indication of substantial cleavage in the C-H bonds of Me₂S subsequent to chemisorption on the films at such temperatures. This also reflects the extent of the contribution of surface species to production of hydrogen atoms in the surface phase. Comparatively lower values of N and M were attained on oxidized surfaces than on clean films as a result of the additional reactions which take place entirely on the oxidized films. The drop in R(fig. 3) to values in the range 2-3 in the temperature range 400-600 K may suggest the existence of CH₃ and CH₂ radicals in the surface phase. In the presence of sufficient hydrogen adatoms, any $C_2H_4(a)$ species that may be formed should rapidly be hydrogenated into C_2H_6 gas. This is one likely explanation for the fact that no C_2H_4 gas was detected over such temperatures.

Me₂S₂

Multilayer adsorption of Me_2S_2 took place on all films at 223 K, as the values of θ were considerably higher than unity, and a substantial fraction of the adsorption at this temperature was reversible.

Dissociative chemisorption and subsequent evolution of gaseous products began only at temperatures ≥ 350 K. The chemisorbed Me₂S₂ molecule can act as a precursor state leading to dissociation via either or both of the following paths:

$$Me_{2}S_{2}(g) \longrightarrow Me_{2}S_{2}(a) \xrightarrow{(a) \qquad MeS(a) + MeS(a)}_{(b) \qquad MeS_{2}(a) + Me(a)}$$
(12)

Reaction 12(a) is expected to be the predominant decomposition pathway, as the MeS—SMe bond dissociation energy $(306.6 \text{ kJ mol}^{-1})$ is lower than that of Me—SSMe (327.6 kJ mol⁻¹). Calculation of the enthalpies of adsorption in the manner described in previous papers^{21, 25} indicated that the dissociation of the adsorbed Me₂S, via pathway

as

(a) is more exothermic than according to the pathway (b); the values of ΔH_a on films of Fe, Pd and Ni according to paths (a) and (b) are, respectively, -450 and -380 kJ mol⁻¹. These ΔH_a values may reflect the different tendencies of the dissociation pathways to proceed if entropies associated with such steps could be ignored. Further dissociation of MeS₂(a) to MeS(a) and S(a) is also possible, as the enthalpy change involved in such dissociation is also exothermic on all surfaces by ca. 50–70 kJ mol⁻¹. On oxidizing films, the MeS₂(a) and MeS(a) species resulting from reaction (12) are likely to be attached to the metal sites, while Me(a) is being bound to the oxide site. Cleavage of the C—S bond leaving an adsorbed methyl group on lattice oxygen forming a methoxide radical was a possibility in methanethiol decomposition on a number of surfaces.²⁴

The formation of hydrocarbons as a result of Me_2S_2 chemisorption on the films at temperatures ≥ 350 K requires at least partial dissociation of the C-H bonds of the chemisorbed methyl or thiolate groups, in addition to the dissociation of the C-S bonds. Surface recombination reactions between chemisorbed methyl or thiolate species, and between these species and atomically adsorbed hydrogen, leading to the formation of the various products, proceed in parallel with the dissociation of S-S, C-S and C-H bonds.

Considering the most abundant surface species to involve H, Me and MeS, then reactions similar to those described by eqn (7)–(10) can occur throughout Me_2S_2 decomposition on various surfaces. Additional reactions are possible in the case of Me_2S_2 , probably because of the presence of $MeS_2(a)$ species on the surface. These may include $MeS_2(a) + H(a) + MeSH(a) + S(a)$ (12)

$$MeS_2(a) + H(a) \rightarrow MeSH(g) + S(a)$$
 (13)

$$MeS_2(a) + Me(a) \rightarrow Me_2S(g) + S(a)$$
 (14)

$$MeS_{2}(a) + MeS(a) \rightarrow Me_{2}S + 2S(a).$$
(15)

The formation of MeSH from the reaction of MeS(a) and H(a) has been disregarded, as no such reaction occurred throughout Me₂S decomposition on the same metals where similar species were suggested to exist in the surface phase. The reaction of MeS(a) with adjacent Me(a) or MeS(a) species to produce Me₂S has been ignored, as Me₂S decomposition on the same metals was found to be entirely irreversible. On the basis of thermochemical calculations, reactions (13)–(15) were found to be all exothermic.

Decomposition of Me_2S_2 on the oxidized films may also take place in similar steps to those of reaction (12), the resulting MeS_2 and MeS species covering the metal sites and Me radicals binding to preadsorbed oxygen atoms. The methoxide radicals resulting from the interaction of Me and O(a) species, probably enter into a series of decomposition reactions similar to those mentioned before to produce CO, H_2 and H_2O gases. MeS(a) and MeS₂(a) species, on the other hand, may take part in reactions similar to (7)–(10) and (13)–(15) to liberate such gases as H_2 , CH_4 , C_2H_6 , MeSH and Me₂S. The decomposition of Me_2S_2 on silica-supported nickel at 300 K have been found¹⁷ to produce similar gaseous products.

Surface structure (fig. 4) indicated a steady decrease in the parameters n and m to very low values at 600 K, while l attained a value of 1.2 at the same temperature; the latter reflects the possibility of sulphur adsorption and also possibly incorporation in the metal lattice. The surface sites initially form terminal or bridged bonds to sulphur lone pairs, and at higher temperatures the loss of H_2 , CH_3 and CH_2 species occurs, leaving sulphur anions which may then be incorporated into the lattice.

Values of R (fig. 5), reflecting the ratio of H to C, decreased to below 3 above 400 K, indicating the presence of CH₃ and CH₂ species in the surface phase. Lower N, M and R values (fig. 5) on the transition-metal films (Fe, Pd and Ni) than on Al and Cu may reflect the higher heats of the surface species on the latter films than the former.

Kinetics of Adsorption

It is concluded from the value of $S \approx 1.0$ [eqn (3)] and the direct dependence of the adsorption rate on Me₂S or Me₂S₂ pressure that the rate-controlling step in each case is the adsorption of the sulphide or the disulphide on the surface, which is then followed by the rupture of S—S, C—S and C—H bonds in these adsorbates. The relationships existing between log A and E_a (fig. 6) suggest the operation of a compensation effect³¹ throughout the adsorption of the sulphur compounds on the films. The compensation phenomenon is likely to arise from a relationship between the heat and the entropy of adsorption,^{31,32} which leads to a connection between the activation energy and entropy of activation (and hence the pre-exponential factor).

The kinetic results presented in fig. 6 indicate that the activities of various surfaces towards Me_2S adsorption follow the following sequence:

Fe > Ni > Pd > oxidized Fe > Al > oxidized Pd

> oxidized Ni > oxidized Al = Cu > oxidized Cu (a)

while the activities of Me_2S_2 adsorption on the same surfaces may be arranged as:

Fe > oxidized Fe > Pd > oxidized Pd > Ni > oxidized Ni

= Al > oxidized Al > Cu > oxidized Cu. (b)

Thus the most active metals toward both sulphur compounds are the transition-metal films, among which Fe occupies the highest rank. On the other hand, Al and Cu were the least active metals among the five covered in this investigation, Cu being less active than Al.

The sequence of activity among the oxidized films towards both sulphur compounds was as follows:

oxidized Fe > oxidized Pd > oxidized Ni > oxidized Al > oxidized Cu. (c)

Comparing sequences (a) and (b) it is shown that Ni is far less active than Pd towards Me_2S_2 , while the reverse of this trend holds with respect to Me_2S . A further point is that the oxidized Fe film shows a higher activity for Me_2S_2 chemisorption than do the clean metals Pd, Ni, Al and Cu.

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