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ABSTRACT

The thermal decomposition of dimethyl disulphide has been studied in the gaseous state by a static method. The primary reaction, which follows a reproducible induction period, produces one mole of methyl mercaptan per mole of disulphide, together with a product of low volatility believed to be a thioformaldehyde polymer:

CH₃SSCH₃---- \rightarrow CH₃SH + 1/n (CH₂S)_n.

There is also a competing reaction producing a large quantity of hydrogen sulphide. The remaining volatile products, hydrocarbons of two or more carbon atoms (believed to be chiefly ethylene), free sulphur, polysulphides, and carbon disulphide are formed either by the latter reaction or by the extensive decomposition of products. The decomposition is catalyzed by hydrogen sulphide, and more strongly by the complete reaction mixture. A mechanism is proposed for the main reaction.

The present investigation was undertaken as a contribution to our fragmentary understanding of the mechanisms of reactions involving the carbonsulphur bond system in organic sulphur compounds. The C-S-S-C bond system of dimethyl disulphide was of special interest. Little is known about the thermal decomposition of the alkyl disulphides, although the thermal decomposition of aryl disulphides has received some study. The work of Schonberg, Mustafa, and Askar (10) suggests that diphenyl disulphide dissociates at the S-S bond into two free aryl thial radicals. In an early investigation Otto and Rossing (8) found that on distillation at atmospheric pressure diamyl disulphide (b.p. 248° C.) gradually decomposes into sulphur or sulphur-rich substances and a tarry residue. Bezzi (3) reported that dioctyl disulphide decomposes at its boiling point of 190° C. at 15 mm. Faragher, Morrell, and Comay (7) found that decomposition of vaporized naphtha solutions of various alkyl disulphides at 496° C. produces the corresponding alkyl mercaptan, hydrogen sulphide, free sulphur, alkyl sulphides, thiophenes, and saturated and unsaturated hydrocarbons.

In some preliminary experiments in this laboratory it was found by Patrick (9) that dimethyl and diethyl disulphides decompose above 300° C. yielding complex pressure-time curves. The homogeneous decomposition of dimethyl disulphide was found to produce large amounts of mercaptan and hydrogen sulphide.

EXPERIMENTAL

Reagents

The dimethyl disulphide, obtained from Eastman Kodak Co., Rochester, New York, gave negative tests for mercaptans, hydrogen sulphide, free

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sulphur, and carbon disulphide. Its refractive index of $n_D^{20} = 1.5261 \pm 0.0002$ agreed well with Vogel and Cowan's (12) value of 1.5260. It was fractionated in a vacuum apparatus before use. The pure hydrogen sulphide was prepared by the method of Bickford and Wilkinson (4). The other sulphur compounds were fractionated Eastman Kodak products.

Apparatus

The apparatus was an all-glass static system consisting essentially of a heated 250 ml. pyrex reaction vessel connected to an evacuating system, a sampling system, and to storage vessels for the reactants. To avoid difficulties of corrosion and condensation, a glass spoon-type Bourdon gauge was used for pressure measurement. The gauge was used both as a direct measuring instrument and as a null indicator.

The volatile constituents of the reaction mixture were sampled in gas pipettes which were attached to the capillary connections of the reaction vessel. From the results of the analyses of the contents of these pipettes the partial pressures of various substances in the reaction vessel during decomposition were calculated. The less volatile constituents were collected in a dry ice trap and analyzed qualitatively.

Analytical Methods

Carbon disulphide was estimated colorimetrically by means of its reaction with cupric acetate and piperidine (5). Thiophenes were tested for with isatin solution (1). Free sulphur was determined in an AnalaR petroleum ether solution of the sample by the method of Ball (2) using dilute reagents.

Hydrocarbons were estimated approximately by a crude gas fractionation method: hydrogen and methane could be separated off at liquid nitrogen temperature. The remaining hydrocarbons were separated off at the freezing point of *n*-pentane, -130° C., and their pressure was corrected slightly for hydrogen sulphide.

The methods of analysis for mixtures of hydrogen sulphide, methyl mercaptan, and disulphide were developed in this laboratory, and are being reported elsewhere in more detail (6). Hydrogen sulphide was absorbed in dilute base, precipitated as cadmium sulphide, and separated from mercaptan by filtration through asbestos in 0.005 M acid. The cadmium sulphide precipitate was oxidized directly with excess acidified standard iodine and determined by back titration with thiosulphate. This method was sensitive to less than 2.5×10^{-6} moles of hydrogen sulphide (0.5 mm. pressure in the reaction vessel) and was accurate in the presence of mercaptan to within 3%. The direct determination for hydrogen sulphide made it possible to determine mercaptan indirectly from the total sulphydryl content of the reaction mixture as determined by absorption in excess standard iodine and back titration with thiosulphate.

In Ball's method (2) for the determination of disulphides the disulphides are reduced to mercaptans by refluxing with zinc and glacial acetic acid. In the present work AnalaR petroleum ether was used as the solvent. By using a slightly stronger acid (94%), a lower temperature (water bath), and by

heating long enough to transfer the entire methyl mercaptan formed to a trap, it was possible to obtain results with a reproducible error in the range $110\frac{1}{2} \pm 1\frac{1}{2}\%$ reduction. The analyses were corrected appropriately. Unfortunately some of the actual analyses were invalidated by the interference of alkyl polysulphides, compounds of the type R-S_z-R, which reduce to mercaptan and hydrogen sulphide.

The presence of alkyl polysulphides was inferred from an interference with the disulphide determinations and by a reaction with mercury. It was observed that a solution of the volatile products in petroleum ether, although free of elementary sulphur, reacted with metallic mercury to produce a black crystalline compound. This was attributed to a reaction of the type quoted by Sidgwick (11):

$2 \text{ Hg} + \text{CH}_3\text{S}_4\text{CH}_3 \rightarrow 2 \text{ HgS} + \text{CH}_3\text{SSCH}_3.$

RESULTS

A typical family of pressure-time curves for the decomposition of dimethyl disulphide is presented in Fig. 1. There is an initial rapid pressure decrease, followed by a period of constant pressure, after which the rate rises slowly to



FIG. 1. Pressure-time curves for the decomposition of dimethyl disulphide at 341° C. Initial pressure of disulphide respectively (1) 24.0, (2) 57.5, (3) 73.0, (4) 92.5, (5) 108.0 mm.

a maximum. The induction period was reproducible: in a series of 16 runs at 316° C. it had a mean length of 11.6 min. with standard deviation only 0.7 min.

The results of extended experiments showed that, after the rate had decreased quite sharply from the maximum to a low value, there remained a slow residual reaction which continued for some time. This behavior suggests the decomposition of products. Both at 341° C. and at 373° C. the final pressure increase is greater than 105% of the minimum pressure.

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Effect of Packing the Reaction Vessel

A sixfold increase in the surface to volume ratio was achieved by packing the vessel with short lengths of pyrex glass tubing. The induction period and maximum rate of reaction were unaffected, indicating that the decomposition is a homogeneous process. The only effect was a slight reduction of the final pressure, attributable to increased adsorption of the products on the vessel surface.

The Initial Pressure Decrease

By using the Bourdon gauge as a direct reading instrument and by using relatively low pressures, it was possible to fill the reaction vessel in times as short as two seconds. It was possible, therefore, to observe the greater part of the initial pressure decrease. With 95 mm. of disulphide at 316° C. the pressure decrease was about 15 mm., the initial rate of the decrease was of the order of 2 mm. per second, and the process was approximately 90% complete in 15 sec. The magnitude of the decrease was greater at higher initial pressures and at lower temperatures; it was only slightly increased by packing the reaction vessel.

Analysis showed that during the induction period the reaction mixture consists almost entirely of unreacted disulphide. This fact suggested strongly that the pressure decrease is due to adsorption of the reactant disulphide on the walls of the pyrex reaction vessel. Further observations supported this view: (1) A few millimeters pressure of hydrogen sulphide in the reaction vessel reduced the extent of the decrease by 80%. Hydrogen sulphide is known to adsorb on glass. (2) If a part of the reactant were removed from the vessel during the induction period, a short, rapid pressure increase occurred, indicating desorption of the disulphide.

An estimation of the activation energy of the initial rate of the pressure decrease gave a value of 16 kcal. per mole. Whereas this is much less than the usual energies of pyrolytic reactions, it is of the order of magnitude of energies of adsorption. It leads to a frequency factor of 10^4 sec^{-1} . If a simple collision theory of adsorption is accepted, this frequency factor should be equal to the number of times a molecule strikes the wall per second. The latter was calculated from kinetic theory as $1 \times 10^4 \text{ sec}^{-1}$ at 316° C.^4 This excellent agreement is considered additional proof that the initial pressure decrease is due to adsorption.

Dependence of the Rate on Initial Disulphide Pressure

The minimum pressure of the induction period was found to be a suitable 'initial' pressure for correlating the results of different experiments. There is little doubt that it represents the true initial disulphide pressure at the start of the main reaction.

The initial pressure was varied from 24 mm. to 230 mm. at 341° C. The dependence of extent of reaction on the initial pressure is given in Table I. Per cent pressure increases are listed for several reaction times. The results

⁴From kinetic theory the "collision number" is $\frac{1}{4}S(8RT/M)^{\frac{1}{2}}$, where S is the surface to volume ratio of the reaction vessel and M is the molecular weight. $S = 1, M = 94, T = 589^{\circ} K$.

TABLE 1	
Dependence of the extent of reaction on the	
INITIAL PRESSURE. $T = 341^{\circ}$ C.	

Initial pressure,	8 min	% pressure in	ncrease after:	20 min
			10 mm.	20 1111
24.0	45	62	76	85
57.5	36	53	68	74
73.0	38	54	68	74
92.5	38	53	66	73
108.0	43	54	68	73
141.8	35	48	63	68
166.5	42	53	68	74
229.5	42	54	68	73

show a first order dependence. The rate constants calculated from these data had a mean value of 20.8×10^{-4} sec.⁻¹ at 341° C. with a standard deviation of 0.7×10^{-4} sec⁻¹.

At pressures below 150 mm. (temperature 341° C.) the induction period is independent of the initial pressure, but at higher pressures its length is reduced. The time at which the maximum rate occurs varies in the same way.

Dependence of the Rate on Temperature

The significant results are shown in Table II. A plot of $\ln k$ vs. 1/T gave a straight line from which an over-all activation energy of 45 ± 4 kcal. per mole was calculated. The frequency factor was estimated to be 2×10^{13} sec⁻¹.

TABLE II Dependence of the reaction on temperature				
Temperature, °C.	Induction period, sec.	Time of max. rate, sec.	Rate constant, sec. ⁻¹	
$316 \\ 314 \\ 360 \\ 373$	690 120 35 19	$ 1860 \\ 420 \\ 157 \\ 65 $	$\begin{array}{c} 0.00042\\ 0.00208\\ 0.0067\\ 0.0116\end{array}$	

Analytical Results

A temperature of 316° C. and an initial pressure of 80 mm. were the standard conditions used for experiments in which analyses were done for the components of the reaction mixture.

Qualitative analyses of the reaction mixture showed that thiophenes are formed in traces only. The principal volatile products were hydrogen sulphide, mercaptan, carbon disulphide, alkyl polysulphides, and low boiling hydrocarbons of two or more carbon atoms. Hydrogen and methane were not detected; if present at all they appear to total less than 5% of the hydrocarbon. The mercaptan was identified as chiefly or entirely methyl mercaptan by the yellowish-green color of its silver mercaptide; the higher silver mercaptides are white. Of the products which were not sampled by the gas pipettes, free sulphur was identified amongst the accumulated products in the cold trap. An involatile tar was formed in considerable quantity; it appeared black by reflected light and reddish-brown by transmitted light.

The two volatile products formed in largest quantity were methyl mercaptan and hydrogen sulphide. The results of quantitative analyses were used to construct partial pressure-versus-time curves for these two products and for the reactant disulphide. These curves, with other results, are shown in Fig. 2. During the early stages of the reaction the rate of hydrogen sulphide formation is equal to one half the rate of increase in pressure. The rates become nearly equal in the later stages.

The alkyl polysulphides in the reaction mixture interfered so seriously with the determination of disulphide that the only accurate determinations were those which were made in the initial stages of the decomposition. A curve labelled *RSSR*, showing the disappearance of disulphide is given in Fig. 2. The values for the dotted part of the curve are believed to be much too high owing to interference by polysulphides. The estimated pressure of disulphide during this part of the reaction is approximately zero since the main reactions appear to be over at 60 min. A curve representing the amount of disulphide decomposed in the early stages of the reaction is also plotted. It was constructed by subtracting the disulphide present from the initial pressure.



FIG. 2. Analytical results for the "standard" reaction, $T = 316^{\circ}$ C., $P_{min} = 80.0$ mm. RSSR shows analytical results for disappearance of disulphide. $\Delta RSSR$ shows measured amount of disulphide decomposed.

FIG. 3. Dependence of the maximum rate on added hydrogen sulphide. Constant disulphide pressure, 52.2 mm. Temperature, 316° C.

Fig. 2 shows that the reaction producing mercaptan is distinct from that producing hydrogen sulphide. The former appears to reach its maximum rate before 20 min., whereas the latter reaches its maximum rate only after 30 min. The end of the induction period appears to be the same for both reactions. Since the pressure increase does not appear to occur until H₂S is formed, the formation of mercaptan must involve little or no pressure change. This is well illustrated by the fact that at 15 min. with a mercaptan pressure of 10 mm. the total pressure change by all processes is only $1\frac{1}{2}$ mm. Moreover, the reaction producing hydrogen sulphide must account also for much of the remaining volatile products. The reactions which occur after 60 min., the slow

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formation of H₂S for example, appear to be reactions amongst the decomposition products. Probably a number of complex processes occur simultaneously.

The partial pressures of all the volatile constituents of the reaction mixture were measured at 120 min., after the completion of the main reactions. The results of analyses are listed in the first column of Table III. The values for carbon disulphide and for hydrocarbons are significant to the order of magnitude only. Estimates of the remaining constituents are recorded in the second column of Table III. The order of magnitude figure for polysulphides was

TABLE III
VOLATILE CONSTITUENTS OF THE REACTION MIXTURE AFTER
120 min. of reaction at 316° C. $(P_{\min} = 80 \text{ mm.})$

Analytical mn	pressures, 1.	Estimated pressur	res,ª
$CH_{4}SH$ $H_{2}S$ CS_{2} Hydrocarbons $H_{2} + CH_{4}$ Thiophene	$\begin{array}{c} 59 \\ 42 \\ 15 \\ (C_2) \\ 25 \\ 0 \\ 1 \end{array}$	CH₃SSCH₃ CH₃S∡CH₃ Sଃ	0 8 0
1	Measured total	pressure 140 mm.	
^a See text.			_

estimated by assuming an apparent 25 mm. of disulphide, shown by the disulphide test, to be due in reality to tetrasulphide. Elemental sulphur could not be determined quantitatively, but it appeared to be present in small

Effect of Added Hydrogen Sulphide

small pressure has been listed as zero.

The addition of hydrogen sulphide to the reaction mixture had a marked effect on the rate of reaction. The induction period and the period of autoacceleration were shortened, and the maximum rate was increased. The significant results are listed in Table IV. In each case the maximum rate of

amounts only. Since it exists at 317° C. almost entirely as S₈, its necessarily

TABLE IV Effect of hydrogen sulphide on the decomposition of 52.3 mm. of disulphide at 316° C.				
Added H ₂ S, mm.	Induction period, min.	Time of max. rate, min.	Maximum rate, mm./min.	
$ \begin{array}{r} 0.0 \\ 10.2 \\ 34.0 \\ 52.0 \end{array} $	$ \begin{array}{r} 13 \\ $	34.0 20.5 12.0 9.7	$\begin{array}{c} 0.123 \\ 0.147 \\ 0.198 \\ 0.213 \end{array}$	

pressure rise (also of hydrogen sulphide formation) occurred after a total pressure increase of 13.7 mm., corresponding in a normal decomposition to the formation of 6.5 mm. of hydrogen sulphide. The logarithm of 'the added

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$d \operatorname{H}_2 S/dt = k [\operatorname{H}_2 S]^{\frac{1}{4}}.$

The total pressure increase was independent of the amount of added hydrogen sulphide. This suggests that the final ratio of hydrogen sulphide formed to mercaptan is unchanged by the addition of hydrogen sulphide. The general character of the decomposition appears entirely unaffected. If this is so the hydrogen sulphide must also accelerate the reaction producing mercaptan.

Effect of Added Mercaptan

A decomposition in the presence of methyl mercaptan at a pressure equal to 30% of the disulphide, did not differ significantly from the normal. Hence, mercaptan is simply an end product of the decomposition.

Effect of the Complete Reaction Mixture

The effect of the complete decomposition products on the reaction was investigated by admitting a second sample of disulphide to the reaction vessel after the completion of a previous experiment. The induction period was reduced to a much greater extent than can be attributed to hydrogen sulphide alone. Indeed, the true induction period of the mercaptan reaction may have been removed entirely. In contrast to the effect of hydrogen sulphide alone the complete reaction mixture did not accelerate the maximum rate of pressure rise. The final pressure increase was slightly less than for the normal reaction. *Effect of Nitric Oxide*

In the presence of 0.6, 2, and 7% nitric oxide, the induction period was no longer reproducible but the maximum rate was normal and occurred at the usual time.





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Comparison with the Decomposition of Diethyl Disulphide

The decomposition of diethyl disulphide appeared to be considerably different from the decomposition of dimethyl disulphide. Three superimposed pressure-time curves are presented in Fig. 4. Although similar in form to those of dimethyl disulphide they show a much greater total pressure increase. The maximum rate is first order with respect to the initial pressure, except at low pressures. The main rate constant of $19.7(\pm 1.1) \times 10^{-4}$ sec.⁻¹ at 318° C., obtained from runs at 28 mm., 33 mm., and 40 mm., falls off between 28 and 18 mm. This rate is of the same order as that for dimethyl disulphide at the much higher temperature of 341° C. The decomposition of diethyl disulphide produces an involatile tar similar in appearance to that produced by dimethyl disulphide. Unlike the decomposition of dimethyl disulphide, it produces a considerable quantity of a fine yellow solid, presumed to be elemental sulphur.

One feature of Fig. 4 is the "break" in the curve near the 30-min. mark. This suggests that the reaction may involve a second stage which is largely responsible for the pressure increase after 30 min.

DISCUSSION

The over-all reaction for the decomposition of dimethyl disulphide is complex. Two main reactions appear to occur. The first is decomposition of the disulphide with the formation of mercaptan, and the second is the formation of hydrogen sulphide and allied products. Both reactions exhibit an induction period. Extensive decomposition of the products of these reactions also takes place.

The rate curves for the formation of mercaptan and H_2S show that the decomposition of the disulphide comes to an end after about 60 min. for the 'standard reaction', i.e., the reaction illustrated in Fig. 2. This behavior cannot be due to an equilibrium as neither the addition of mercaptan nor the addition of hydrogen sulphide to the reaction mixture has any effect on the final pressure. Nor can it be due to inhibition by the products. It must be concluded that the pressure of the reactant disulphide falls to zero after about 60 min. Accordingly, the disulphide pressure at 120 min. has been listed in Table III as zero.

Hydrogen sulphide and mercaptan, the two products formed in greatest quantity, are both reduced relative to the disulphide. To balance the hydrogen, the hydrocarbon products must be either unsaturated or polymeric (Table III). Since the formation of hydrocarbons of more than two carbon atoms appears unlikely, and, indeed, could not account for the magnitude of the pressure increase, it is suggested that the hydrocarbons may be chiefly or entirely ethylene.

From Table III the estimated pressures of the components of the reaction mixture at 120 min. total 148 mm. This value agrees satisfactorily with the measured total pressure of 140 mm., and suggests that no other volatile products are formed in quantity. It supports the conclusion that the disulphide pressure is zero.

The primary reaction is believed to be the decomposition of one mole of disulphide to form one mole of methyl mercaptan. Since there is no accompanying pressure change the remaining fragment "CH₂S" of the dimethyl disulphide molecule must be removed from the system in some way. The thioaldehydes are well known for their remarkable tendency to polymerize; they are scarcely known in the monomeric state (11). The normal polymerization to cyclic trithioformaldehyde would result in a small pressure increase, but in the presence of foreign free radicals the polymerization would presumably be to higher polymers which are involatile. The following process, for example, would not allow ring closure:

$$R \xrightarrow{CH_2=S} RSCH_2 \xrightarrow{CH_2=S} RSCH_2SCH_2$$

The presence of an involatile tar in the reaction products lends support to this view. If this polymerization mechanism occurs, the primary decomposition may be represented by the following over-all reactions:

$$\begin{array}{c} \text{CH}_3\text{SSCH}_3 \longrightarrow \text{CH}_3\text{SH} + \text{CH}_2 = S \\ n \text{ CH}_2 = S \longrightarrow (\text{CH}_3\text{S})_n \end{array}$$
[1]

Hydrogen sulphide appears to be produced by two reactions. The main reaction occurred under the conditions of these experiments between 10 and 60 min.; the total hydrogen sulphide produced by it is approximately 27 mm.; clearly its rate depends on the disulphide present. The second reaction became evident after the disulphide had disappeared. In the experiments discussed here it produces 10 mm. of hydrogen sulphide between 60 and 120 min. at a nearly constant rate, and would appear, therefore, to account for at least 5 mm. (15%) of the hydrogen sulphide produced before 60 min. This reaction must be due to the decomposition of products of the two main reactions, perhaps polythioaldehyde or alkyl polysulphides.

The disulphide available for the main reaction producing hydrogen sulphide appears to be equal to the hydrogen sulphide produced by it. This disulphide can be estimated by subtracting from the initial disulphide pressure the amount used up in producing mercaptan and polysulphide, 59 mm. and approximately 8 mm., respectively. The reaction producing mercaptan seems well established and the mercaptan analysis appears reliable. The polysulphide is in any case only a small correction and therefore the result of 28 mm. of disulphide available for hydrogen sulphide formation should not be greatly in error. It is roughly equal to the hydrogen sulphide produced. Thus one mole of disulphide appears to produce one mole of hydrogen sulphide in the main reaction. This suggestion appears consistent with the observed pressure change, whatever the complete reaction may be. There are, however, many factors affecting the pressure change and a certain deduction is difficult.

The alkyl polysulphides may be formed by addition reactions of the following type:

$$CH_3SSCH_3 + S_x \longrightarrow CH_3S_{x+2}CH_3$$
[II]

The labile character of polysulphide chains is well known.

The 25 mm. of hydrocarbons found by analysis from the standard experiment appear to be almost entirely ethylene. The ethylene could be formed by a second decomposition reaction along with the H₂S, as follows:

$$CH_3SSCH_3 \longrightarrow H_2S + CH_2 = CH_2 + S$$
[III]

This equation, though speculative, is consistent with the data available. The estimate for ethylene is in the ratio one-to-one with those for hydrogen sulphide and disulphide. When taken together, the three reactions postulated would account reasonably for all the substances observed in the decomposition. The reactant disulphide and the products hydrogen sulphide, mercaptan, and hydrogen, would be accounted for completely. The elemental sulphur of reaction [III] would produce the polysulphides of reaction [II] together with traces of S₈. Carbon disulphide, the only other volatile product could well be attributed to the secondary reactions, to the decomposition of the tar, for example. It is difficult to see how it could be produced from the disulphide directly. Finally, the amount of monomeric thioaldehyde necessary to balance reaction [I] would account quite well for the quantity and composition of the involatile products at 120 min., together with the carbon disulphide and small amounts of secondary hydrogen sulphide.

Although no direct evidence was obtained of the occurrence of free radical chains in the decomposition of dimethyl disulphide, it seems unlikely that the entire decomposition could take place by simple molecular reactions. The complexity of the reactant, the variety of the products, and the peculiar rate laws, all suggest free radical mechanisms.

For the primary reaction a straightforward unimolecular decomposition into methyl mercaptan and thioformaldehyde can be conceived. However, this reaction, being unimolecular, could not be catalyzed by the products, and therefore an explanation of the induction period on this basis would be difficult. On the other hand, a free radical chain mechanism is plausible.

The initiating radical might be CH_3S arising from the dissociation of disulphide at the S-S bond:

$$CH_3SSCH_3 \longrightarrow 2 CH_3S$$
 [1]

The following sequence could result: CH₃S + CH₃SSCH₂-

$$+ CH_3SSCH_2 \longrightarrow CH_3SH + CH_3SSCH_2$$
^[2]

 $CH_3SSCH_2 \longrightarrow CH_2 = S + CH_3S$ [3]

In addition to producing mercaptan to the required extent this mechanism also produces the postulated thioformaldehyde. Polymerization of the latter could arise through:

$$n \operatorname{CH}_2 = \operatorname{S} \longrightarrow (\operatorname{CH}_2 \operatorname{S})_n$$
 [4]

or
$$CH_3SSCH_2 + CH_2 = S \longrightarrow CH_3SSCH_2SCH_2$$
 [5]

A second possibility for the initiating radical of equation [1] is the production of a sulphur atom through an intermediate rearrangement of the type:

$$CH_3SSCH_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow S + CH_3SCH_3 \qquad [6]$$

through the decomposition of polysulphides:

$$CH_3S_xCH_3 \longrightarrow S + CH_3SS_{x-1}CH_3$$
^[7]

or through the reaction [III] postulated for the production of hydrogen

sulphide. The observed catalysis by hydrogen sulphide may be due to the production of sulphur atoms by a reduction process:

$$H_{2}S + CH_{3}SSCH_{3} \longrightarrow S + 2CH_{3}SH$$
[8]

The more marked catalyses by the complete reaction mixture could be attributed to reaction [7]. The autoacceleration and approximate coincidence of the induction periods of the mercaptan and hydrogen sulphide reaction could also be dependent on the production of sulphur atoms.

More experimental work must be done before the details of the over-all reaction can be understood.

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