this is due to emission from lucigenin which in DMF fluoresces more efficiently than in DMSO.

In AN lucigenin has a high ϕ_f of 0.72 while DBA has a ϕ_f of 0.40. The long-wavelength emission in AN (Figure 5) is seen to be due to lucigenin emission, and this correlates well with the high ϕ_f of lucigenin in this solvent. In ethanol (Figure 3, curve B) lucigenin again has a very low ϕ_f of 0.09 and DBA has a ϕ_f of 0.45. However, DBA is fairly insoluble in EtOH. Thus the DBA concentration at all times is low, lucigenin is a poor emitter, and no long-wavelength emission is observed in EtOH.

The direction of change in the intensity of the long-wavelength band can also be explained. In the case of AN, lucigenin has a high quantum efficiency and is responsible for the long-wavelength emission. At the beginning of the reaction lucigenin is present at a relatively high concentration ($\sim 10^{-3}$ *M*) and the emission is intense. As the reaction proceeds the lucigenin concentration decreases and the intensity of the long-wavelength band likewise decreases. In DMSO and DMF, DBA is responsible for the emission at long wavelengths because lucigenin has a low quantum efficiency. At the beginning of the reaction there is little DBA present, and the long-wavelength emission is of low intensity, but as the reaction proceeds and DBA is built up, the emission at long wavelength increases.

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Thermal Decomposition of Tri- and Tetrasulfanes

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Abstract: An nmr technique has been employed to study the thermal decomposition of H_2S_3 and H_2S_4 in CCl_4 solution at 70.4° in the absence of oxygen. H_2S and elemental sulfur are found to be the ultimate reaction products. It is demonstrated, however, that sulfanes do not decompose directly into H_2S and elemental sulfur but rather form a variety of intermediate sulfanes. H_2S_4 is found to be more stable than H_2S_3. A free-radical mechanism for the reaction is proposed and a possible pathway for the formation of elemental sulfur is suggested.

The study of the thermal stabilities of a variety of polysulfidic chain containing compounds has led to a better understanding of the nature of the sulfur–sulfur bond and of the factors governing the physical and chemical properties of molecules containing sulfur–sulfur linkages. Nevertheless, the understanding of the sulfur–sulfur bond is far from complete. The bond dissociation energies presented in Table I establish that the energy required to break a given sulfur–sulfur bond depends largely on the position of the bond in the sulfur chain of a given system. Thus the central sulfur–sulfur bond in MeS_4Me requires less energy to break than the oxygen–oxygen bond in the relatively unstable hydrogen peroxide. Furthermore, the nature of the group terminating the polysulfide chain seems to have at least some effect on the strength of a given sulfur–sulfur bond in species of the same sulfur chain length.

Thermal stabilities of alkyl polysulfides of varying sulfur chain length have been investigated by several authors (see citations in ref 1), but it was not until the advent of the nmr analytical method that reliable quantitative data on the decomposition products could be obtained.

Thus Tobolsky, *et al.*[1] studied the thermal decomposition of methyl polysulfides by the nmr analytical method. In the early stages of the thermal decomposition of MeS_4Me the main product found was MeS_3Me, while MeS_5Me was found in smaller quantities. These authors postulated a free-radical mechanism initiated by the thermal disproportionation of the parent polysulfide into two resonance-stabilized radicals according to the equation

$$MeS_4Me \overset{80^\circ}{\rightleftharpoons} 2MeS_2\cdot \quad (1)$$

The propagation reactions involved the subsequent attack of these initial radicals on the sulfur chain of the parent polysulfide according to the reaction

$$MeS_4Me + MeS_2\cdot \rightarrow MeS_3Me + MeS_3\cdot \quad (2)$$

followed by termination reactions of the type

$$MeS_2\cdot + MeS_3\cdot \rightleftharpoons MeS_5Me \quad (3)$$

This reaction scheme was postulated to account for the fact that no MeS_2Me had been formed, which would have indicated that $MeS\cdot$ radicals were involved. It was, therefore, concluded that the initial homolytic reaction 1 was more likely than the reaction

$$MeS_4Me \rightleftharpoons MeS\cdot + MeS_3\cdot \quad (4)$$

presumably because the central bond in MeS_4Me is weaker than the other two sulfur–sulfur bonds in this molecule (Table I).

MeS_3Me was found to be considerably more stable than MeS_4Me.[1] This was rationalized by noting that

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[1] T. L. Pickering, K. J. Saunders, and A. V. Tobolsky in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968.

Table I. Dissociation Energies[a]

Compound	Bond dissociation energy, kcal mol^{-1}	Compound	Bond dissociation energy, kcal mol^{-1}
MeS–SMe	69	HS–S–SH	64
HS–SH	72	MeS_2–S_2Me	37
HO–OH	48	$S_8^R \rightleftharpoons S_8^{CH}$	33
MeS–S–SMe	(46)	HS–H	89

[a] Data compiled from T. L. Pickering, K. J. Saunders, and A. V. Tobolsky in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 5; W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., p 17.

MeS_4Me may dissociate relatively easily into two resonance-stabilized radicals by reaction 1, whereas the corresponding homolysis step in MeS_3Me must involve the dissociation of a relatively strong sulfur–sulfur bond (Table I) yielding $MeS\cdot$ and $MeS_2\cdot$ radicals

$$MeS_3Me \rightleftharpoons MeS\cdot + MeS_2\cdot \qquad (5)$$

$MeS\cdot$, however, cannot be stabilized by resonance.

Though the polysulfide chain in hydrogen polysulfides should be expected to react similarly to that of dimethyl polysulfides, a distinctive difference in the reactivity could exist due to the different terminal groups.

Hydrogen polysulfides have been found to be thermodynamically unstable with respect to H_2S and elemental sulfur.[2] When studying the nmr spectra of hydrogen polysulfides in molten sulfur at 130°, Hyne, *et al.*,[3] found that a mixture of hydrogen polysulfides containing originally no H_2S_2 decomposed to yield H_2S and the higher sulfanes with a sulfur chain length of six and higher, while H_2S_2 was formed as an intermediate. Feher reported the preparation of H_2S_2 by thermal cracking of a sulfane mixture which originally did not contain H_2S_2.[4] Obviously, at elevated temperatures, sulfanes higher than H_2S_2 decompose in such a way that one of the intermediate reaction products is H_2S_2. Similarly, Feher observed the disproportionation of pure H_2S_3 upon prolonged standing at room temperature[5] according to

$$2H_2S_3 \rightarrow H_2S_2 + H_2S_4 \qquad (6)$$

The thermal decomposition of pure H_2S_2 at 50° was found to yield H_2S and H_2S_3 in the early stages of the decomposition[6]

$$2H_2S_2 \rightarrow H_2S + H_2S_3 \qquad (7)$$

For this reaction an ionic mechanism was proposed by analogy with the reaction of organic disulfides with KHS. It should, however, be pointed out that in the latter system the reactive SH^- ions were generated by the dissociation of KHS into K^+ and SH^-. Therefore, analogous conclusions drawn from this system and applied to the thermal decomposition of one containing only pure H_2S_2 may be questionable.

The observed disproportionation of various sulfanes under the previously mentioned conditions, and the fact that a disproportionation equilibrium between alkyl polysulfides of varying sulfur chain length has been demonstrated,[1,7] indicates that equilibration between various hydrogen polysulfides at elevated temperatures is to be expected.

Results

At 70.4° sulfanes in 0.2 *M* CCl_4 solutions were found to decompose slowly into sulfur and H_2S by the over-all reaction

$$H_2S_x \rightarrow H_2S + (x - 1)S \qquad (8)$$

By studying the kinetics and the course of these reactions, it was found that H_2S_3 and H_2S_4 and equimolar mixtures of these sulfanes decompose with different rates and do not decompose directly into the final products H_2S and sulfur, but do so through the intermediate formation of daughter sulfanes. The results are summarized in Figures 1–3.

In the course of the decomposition of H_2S_3 and H_2S_4 two rate processes are clearly observed, the first of which involves the relatively fast decomposition of the parent sulfane to form specific intermediate daughter sulfanes. Subsequent to these initial reactions the various sulfanes appear to decompose slowly into H_2S and sulfur. The intermediate sulfane distribution was found to be nearly independent of the nature of the parent sulfane.

The initial decomposition of H_2S_4 resulted in the formation of H_2S_3 and H_2S_5 (Figure 1). The initial buildup of these intermediates was essentially complete after approximately 65 hr. H_2S and H_2S_2 were formed slowly after an induction period of some 30 hr. Ultimately, the sulfane distribution became essentially the same as that which was obtained by the prolonged decomposition of pure H_2S_3 (Figure 2) as reported below.

The initial thermal decomposition of H_2S_3 involved the relatively fast formation of H_2S_4 and approximately equimolar quantities of H_2S_2 and H_2S (Figure 2). In contrast to the observed delay of the appearance of H_2S and H_2S_2 in the thermal decomposition of H_2S_4, these products are formed immediately. Finally, the sulfane distribution approached that observed in the decomposition of H_2S_4.

An equimolar mixture of H_2S_3 and H_2S_4 decomposed to yield initially H_2S, H_2S_2, and to some extent H_2S_5 (Figure 3). The rate of formation of H_2S and H_2S_2 is the highest observed in all experiments (see Figures 1–3).

Considering the time which is needed to decompose 50% of the initially present sulfanes, H_2S_4 turned out to be the most stable sulfane, while H_2S_3 and the equimolar H_2S_3–H_2S_4 mixture exhibited approximately the same thermal stability. Under the prevailing conditions this time was 60 ± 5 hr for H_2S_4, 36 ± 4 hr for H_2S_3, and 33 ± 3 hr for the equimolar H_2S_3–H_2S_4 mixture.

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(2) F. Feher and G. Winkhaus, *Z. Anorg. Allgem. Chem.*, **292**, 203 (1957).

(3) J. B. Hyne, E. Muller, and T. K. Wiewiorowski, *J. Phys. Chem.*, 70, 3733 (1966).

(4) F. Feher, W. Laue, and G. Winkhaus, *Z. Anorg. Allgem. Chem.*, **288**, 113 (1956).

(5) F. Feher and M. Baudler, *Z. Anorg. Chem.*, **254**, 251 (1947).

(6) F. Feher and H. Weber, *Z. Elektrochem.*, **61**, 285 (1957).

(7) D. Grant and J. R. van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964); J. R. van Wazer and D. Grant, *ibid.*, **86**, 1450 (1964).

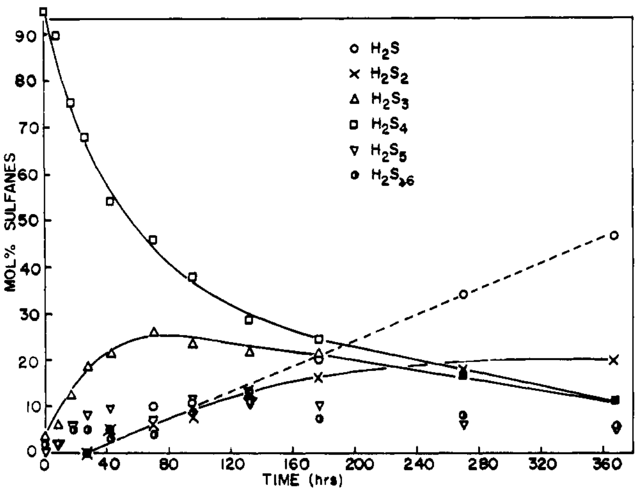

Figure 1. The thermal decomposition of H_2S_4. Variation of the sulfane distribution with time at 70.4°.

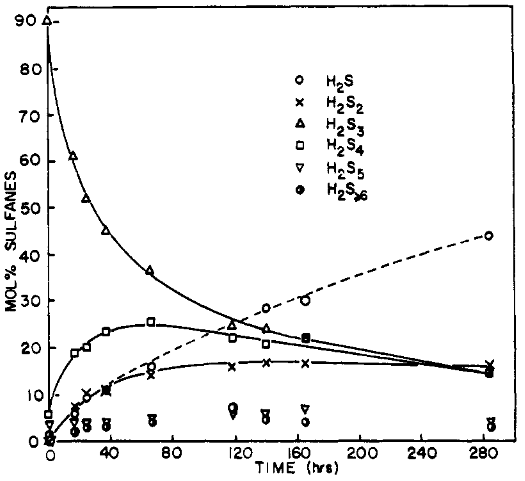

Figure 2. The thermal decomposition of H_2S_3. Variation of the sulfane distribution with time at 70.4°.

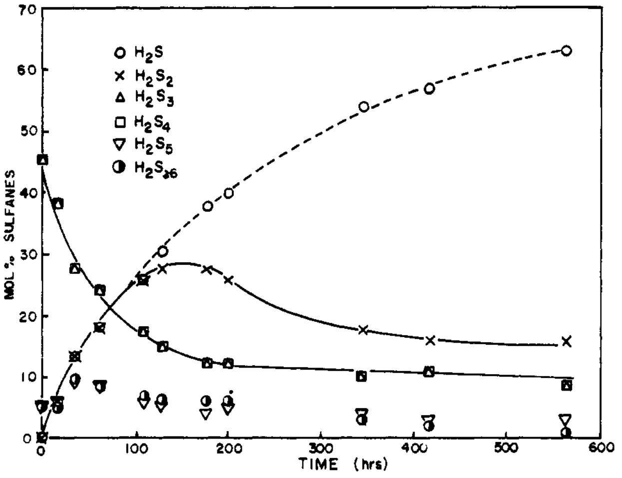

Figure 3. The thermal decomposition of an equimolar mixture of H_2S_3 and H_2S_4. Variation of the sulfane distribution with time at 70.4°.

Discussion of the Reaction Mechanism

Primary Dissociation Steps. In accordance with the present opinion that reactions of this type proceed *via* a free-radical mechanism,[1,7] initiation may be attributed to primary homolytic dissociation steps involving free-radical formation. As the S–S bond dissociation energies in sulfanes are considerably lower than the S–H bond energies (Table I), the primary thermal homolysis almost certainly involves S–S bond cleavages rather than S–H bond scission. Initiation by reactions of the type 9–11 appears, therefore, to be most probable.

$$\mathrm{HS_4H} \rightleftharpoons 2\mathrm{HS_2}\cdot \qquad (9)$$

or

$$\mathrm{HS_4H} \rightleftharpoons \mathrm{HS}\cdot + \cdot\mathrm{S_3H} \qquad (10)$$

$$\mathrm{HS_3H} \rightleftharpoons \mathrm{HS}\cdot + \cdot\mathrm{S_2H} \qquad (11)$$

It should be noted that *statistically* the unsymmetrical cleavage of H_2S_4 by reaction 10 is favored, there being two S–S bonds which can be cleaved to yield unsymmetrical products but only one S–S bond which can be cleaved symmetrically to yield $HS_2\cdot$ (eq 9). However, if the dimethyl polysulfide evidence can be applied to hydrogen polysulfide systems, the more centrally the S–S bond is located in the longer chains, the lower is the dissociation energy. Energetically, therefore, reaction 9 is favored over reaction 10. Finally, the relative stability of the products must be considered. Gee[8] has suggested that radical fragments containing more than one sulfur atom may be stabilized by resonance interaction of the free electron with the sulfur chain. Such stabilization discrimination might be expected to be greatest among the shorter chains. Therefore, the following order of sulfhydryl radical stabilization appears to be likely:

$$\mathrm{HS_{\geq 6}}\cdot \sim \mathrm{HS_5}\cdot \sim \mathrm{HS_4}\cdot > \mathrm{HS_3}\cdot > \mathrm{HS_2}\cdot \gg \mathrm{HS}\cdot$$

Table II summarizes the various factors which may be of importance in determining the primary thermal homolytic dissociation steps for HS_4H. The actual course of the primary dissociation step therefore will be governed by the concerted action of these three factors. In the case of HS_3H the only possible –S–S– homolysis yields $HS\cdot$ and $HS_2\cdot$ radicals.

Subsequent Reactions of the Primary Radical Products. Tobolsky[1] reported $RS\cdot$ radicals to be highly reactive as compared to $RS_2\cdot$ radicals. While $RS\cdot$ radicals were found to abstract hydrogen from triphenylmethane and add to olefinic double bonds, $RS_2\cdot$ radicals were remarkably unreactive. Assuming that the reactivity of sulfhydryl radicals shows a similar dependence on sulfur chain length, the reactivity is expected to decrease as the sulfur chain length increases in the following order: $\cdot SH \gg \cdot S_2H \geq \cdot S_3H$. It is therefore likely that in subsequent reactions the less reactive $HS_2\cdot$ and $HS_3\cdot$ radicals will react primarily by attacking the weaker S–S bonds of the parent sulfane, while $HS\cdot$ radicals will attack S–S bonds but, in addition, may abstract the more strongly bound terminal hydrogen atoms from sulfanes.

Reaction of the Primary Products of HS_4H with the Starting Material. As part of the primary rate process the primary radical products must react initially with the

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[8] F. Fairbrother, G. Gee, and G. T. Merall, *J. Polymer Sci.*, **16**, 459 (1955).

Table II. Factors Affecting the Primary Dissociation of HS_4H

		Relatively favored (+) or not favored (−) by		
	Species	Statistics	Bond dissociation energy	Stability of radical product
HS_4H	$2\ HS_2\cdot$	−	+	+
	$HS\cdot$	+	−	−
	$HS_3\cdot$	+	−	+

parent sulfane which is present in relatively great excess. The various possible reactions are shown below. It should be noted that when a given radical attacks a particular S–S bond two different sets of products are possible depending on the nature of the leaving radical (see eq 13 and 14). All reactions are shown including those which do not yield any net chemical change.

Sulfur Chain Attack

$$HS_3\cdot + \text{H–S–S}\underset{\uparrow}{\text{–}}\text{S–S–H} \rightarrow HS_5H + HS_2\cdot \tag{12}$$

$$HS_3\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–S–H} \rightarrow HS_6H + HS\cdot \tag{13}$$

$$HS_3\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–S–H} \rightarrow HS_4H + HS_3\cdot \quad \text{(no net chemical change)} \tag{14}$$

$$HS_2\cdot + \text{H–S–S}\underset{\uparrow}{\text{–}}\text{S–S–H} \rightarrow HS_4H + HS_2\cdot \quad \text{(no net chemical change)} \tag{15}$$

$$HS_2\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–S–H} \rightarrow HS_3H + HS_3\cdot \quad \text{(principal initial reaction)} \tag{16}$$

$$HS_2\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–S–H} \rightarrow HS_5H + HS\cdot \quad \text{(principal initial reaction)} \tag{17}$$

$$HS\cdot + \text{H–S–S}\underset{\uparrow}{\text{–}}\text{S–S–H} \rightarrow HS_3H + HS_2\cdot \tag{18}$$

$$HS\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–S–H} \rightarrow HS_4H + HS\cdot \quad \text{(no net chemical change)} \tag{19}$$

$$HS\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–S–H} \rightarrow HS_2H + HS_3\cdot \tag{20}$$

Hydrogen Abstaction

$$HS\cdot + \text{H–S–S–S–S–H} \rightarrow HSH + HS_4\cdot \tag{21}$$

As the symmetrical cleavage of HS_4H into two $HS_2\cdot$ radicals is favored (reaction 9) over the asymmetric homolysis (reaction 10), reactions 15, 16, and 17 will be the main reactions of the primary reaction products. Of this group reaction 15 will be the most favored since the weak central S–S bond is attacked, but no change is produced as the reactants and products are identical. Reaction 16 will be favored over reaction 17, since, although both involve terminal S–S bond cleavage, reaction 16 produces a more stable $HS_3\cdot$ species than the $HS\cdot$ species which is produced by reaction 17.

Therefore, in the thermal decomposition of HS_4H, $HS_2\cdot$ is the favored primary radical which, upon subsequent reaction with the starting material, produces preferentially the new polysulfide HS_3H by eq 16. HS_5H, on the other hand, is the less favored new polysulfide generated by reaction of $HS_2\cdot$ with the starting material (eq 17).

Radical–radical reactions will, of course, take place, but these will be termination steps and will not likely be significant in the initial stages of the reaction when the excess of starting material is still high.

Comparison with Results. Inspection of Figure 1 clearly shows that in the initial stages of the decomposition HS_3H and HS_5H are indeed the two principal products in the approximate ratio 2:1. This suggests that reaction 16 is twice as probable as 17 reflecting the enhanced stability of the product $HS_3\cdot$ radical in eq 16.

HS_2H and HSH initially are not produced presumably because eq 20 and 21 which yield them as products depend on $HS\cdot$ which is a product of reaction 17. HSH is obtained by hydrogen abstraction by $HS\cdot$ on any sulfane (*e.g.*, eq 21). HS_2H can be produced by $HS\cdot$ attack on any terminal S–S bond (*e.g.*, eq 20). It, of course, follows that after reactions 16 and 17 have produced significant amounts of $HS_3\cdot$ and $HS\cdot$ all other reactions listed above will come into effect.

Reaction of the Primary Products of HS_3H with the Starting Material. Despite the less favorable type of terminal S–S bond cleavage, HS_3H can only decompose by reaction 11 to form $HS_2\cdot$ and the highly reactive $HS\cdot$ radical. These primary decomposition products initially may react with the parent sulfane as follows.

Sulfur Chain Attack

$$HS_2\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–H} \rightarrow HS_3H + HS_2\cdot \quad \text{(no net chemical change)} \tag{22}$$

$$HS_2\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–H} \rightarrow HS_4H + HS\cdot \quad \text{(principal initial reaction)} \tag{23}$$

$$HS\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–H} \rightarrow HS_2H + HS_2\cdot \tag{24}$$

$$HS\cdot + \text{H–S}\underset{\uparrow}{\text{–}}\text{S–S–H} \rightarrow HS_3H + HS\cdot \quad \text{(no net chemical change)} \tag{25}$$

Hydrogen Abstaction

$$HS\cdot + \text{H–S–S–S–H} \rightarrow HSH + HS_3\cdot \tag{26}$$

Equations 22 and 25 represent exchange reactions only. Reactions 23, 24, and 26, however, are all direct reactions of the primary homolysis radicals, *i.e.*, comparable with reactions 16 and 17 of the decomposition of HS_4H. Reaction 23 produces HS_4H while reactions 24 and 26 produce HS_2H and HSH, respectively.

Since the primary homolysis products $HS\cdot$ and $HS_2\cdot$ are generated in equimolar amounts, the subsequent reactions of these radicals with the parent sulfane are expected to yield products in the molar ratio 2:1:1, if we assume that all these reactions are equally likely. That is

$$2HS_3H \rightleftharpoons 2HS_2\cdot + 2HS\cdot \tag{11}$$

$$2HS_2\cdot + 2HS_3H \rightarrow 2HS_4H + 2HS\cdot \tag{23}$$

$$HS\cdot + HS_3H \rightarrow HS_2H + HS_2\cdot \tag{24}$$

$$HS\cdot + HS_3H \rightarrow HSH + HS_3\cdot \tag{26}$$

Comparison with Results. Inspection of Figure 2 shows that in the initial stages of the HS_3H decomposition HS_4H, HS_2H, and HSH are indeed produced in an approximately 2:1:1 ratio as predicted by the mechanism above. It should be noted particularly that no induction period for HS_2H and HSH is predicted or observed in contrast with the case for the decomposition of HS_4H and that the characteristic initial production of HS_5H in the HS_3H decomposition is again not observed or predicted.

Subsequent Equilibration Reactions. Because of the variety of possible reactions it is hardly surprising that after a sufficient reaction time the sulfane distribution is essentially the same whether one starts with H_2S_4 or H_2S_3. In this regard both Figures 1 and 2 are essentially identical beyond 200 hr and differ only in relative positions of lines from 80 hr onward, indicating that a thermodynamic equilibrium distribution among the sulfanes has replaced the initial kinetically differentiated distribution.

Subsequent reactions may include chain-propagation reactions of the type 27 and chain-termination reactions by radical–radical recombination of the type 28.

$$\mathrm{HS}_y\cdot + \mathrm{HS}_x\mathrm{H} \rightarrow \mathrm{HS}_{y+z}\mathrm{H} + \mathrm{HS}_{x-z}\cdot \qquad (27)$$

$$\mathrm{HS}_y\cdot + \mathrm{HS}_{x-z}\cdot \rightarrow \mathrm{HS}_{x+y-z}\mathrm{H} \qquad (28)$$

$$x = 1, 2, 3, \ldots;\ y = 1, 2, 3, \ldots;\ z = 1, 2, 3, \ldots$$

Termination reactions by radical–radical recombination may play an increasingly larger role as the sulfur chain length of the sulfhydryl radicals becomes two or higher. Thus reactions of the type 28 will compete with chain propagation reactions for sulfhydryl radicals, particularly when $y > (x - z)$ (*e.g.*, reactions 12, 13, and 23).

The observed fact that the over-all sulfane concentration decreased with time and that sulfanes ultimately were converted into elemental sulfur and H_2S clearly indicates that sulfanes, in the course of the thermal decomposition, do not truly equilibrate among themselves, but rather achieve an intermediate distribution, while H_2S and elemental sulfur are formed slowly and irreversibly under the prevailing conditions.

At the present stage we may only assume a likely mechanism for the formation of elemental sulfur. The thermal decomposition by S–S cleavage of intermediate sulfanes with a sulfur chain length of ten and above will produce long-chain sulfhydryl radicals, which, by *intramolecular* reaction, may displace S_8 rings by reaction 29. Such a mechanism is similar to that proposed for the depolymerization of polymeric catena sulfur.[9] Reactions which

$$\mathrm{H{-}S{-}S}_x\mathrm{{-}S_8}\cdot \rightarrow \mathrm{S_8}^{\mathrm{R}} + \mathrm{H{-}S{-}S}_x\cdot \qquad (29)$$

$$x = 1, 2, 3, \ldots$$

yield elemental sulfur as the end product cannot be made evident by nmr analysis, but are required in the over-all reaction mechanism.

The Relative Thermal Stabilities of H_2S_3 and H_2S_4

According to arguments used the decomposition of HS_4H should be easier than HS_3H since the initiation reaction

$$\mathrm{HS_4H} \rightleftharpoons 2\mathrm{HS_2}\cdot$$

supposedly occurs more readily than

$$\mathrm{HS_3H} \rightleftharpoons \mathrm{HS}\cdot + \cdot\mathrm{S_3H}$$

Tobolsky[1] certainly found RS_4R to decompose much more readily than RS_3R, but our results suggest that HS_3H disappears faster than HS_4H. It may be that while the HS_4H primary decomposition takes place more readily than HS_3H, the primary radical products of the latter may be more reactive and hence attack the parent HS_3H more readily. If the possibility of hydrogen abstraction by the HS· radical is considered (eq 26), then for each decomposed HS_3H molecule another molecule of HS_3H is converted into a thermodynamically more stable species, namely HSH, which is at least partially removed out of the equilibrium by escaping into the gas phase. If, however, the product formed by the reaction of the primary radicals with the parent sulfane is a daughter sulfane which is not removed out of the equilibrium, this intermediate sulfane subsequently may compete again for sulfhydryl radicals. Therefore, the parent sulfane will at least be partially protected by the daughter sulfanes against attack by sulfhydryl radicals. This might well be the case in the thermal decomposition of HS_4H, which in the initial stage of its decomposition yields the daughter sulfanes HS_3H and HS_5H, which might increase the apparent thermal stability of HS_4H.

The Mixed HS_4H–HS_3H Decomposition

In order to check the validity of the previously proposed reaction mechanism for the thermal decomposition of HS_3H and HS_4H, an attempt will be made to predict the course of the thermal decomposition of a HS_4H–HS_3H mixture. Agreement of the theoretically predicted results with experimental results obtained from the thermal decomposition of an equimolar HS_4H–HS_3H mixture therefore should lend credence to the reaction mechanism outlined above (eq 9–26).

With *both* HS_4H and HS_3H present as starting materials we will have both primary homolysis reactions taking place, *i.e.*

$$\mathrm{HS_4H} \rightleftharpoons 2\mathrm{HS_2}\cdot$$

$$\mathrm{HS_3H} \rightleftharpoons \mathrm{HS}\cdot + \cdot\mathrm{S_2H}$$

In keeping with our previous arguments, however, HS_2· will be the most abundant species. It can now react with both HS_4H and HS_3H starting materials. Reaction with HS_4H will yield products essentially as given by eq 16 and 17. New, however, is the *initial* reaction between HS_2· and HS_3H (see eq 22 and 23). As noted previously eq 22 is an exchange reaction only. If HS_3H decomposition yielding HS· and ·S_2H radicals is important then there will be also the new initial reactions between HS· radicals and HS_4H (see eq 18–21).

Summarizing all reactions of all primary radical products with the mixed starting material other than exchanges, the following reactions might take place.

Sulfur Chain Attack

$$\mathrm{HS_2}\cdot + \mathrm{H{-}S\underset{\uparrow}{-}S{-}S{-}S{-}H} \rightarrow \mathrm{HS_3H} + \mathrm{HS_3}\cdot \qquad (16)$$

$$\mathrm{HS_2}\cdot + \mathrm{H{-}S\underset{\uparrow}{-}S{-}S{-}S{-}H} \rightarrow \mathrm{HS_5H} + \mathrm{HS}\cdot \qquad (17)$$

$$\mathrm{HS_2}\cdot + \mathrm{H{-}S\underset{\uparrow}{-}S{-}S{-}H} \rightarrow \mathrm{HS_4H} + \mathrm{HS}\cdot \qquad (23)$$

$$\mathrm{HS}\cdot + \mathrm{H{-}S{-}S\underset{\uparrow}{-}S{-}S{-}H} \rightarrow \mathrm{HS_3H} + \mathrm{HS_2}\cdot \qquad (18)$$

$$\mathrm{HS}\cdot + \mathrm{H{-}S\underset{\uparrow}{-}S{-}S{-}S{-}H} \rightarrow \mathrm{HS_2H} + \mathrm{HS_3}\cdot \qquad (20)$$

$$\mathrm{HS}\cdot + \mathrm{H{-}S\underset{\uparrow}{-}S{-}S{-}H} \rightarrow \mathrm{HS_2H} + \mathrm{HS_2}\cdot \qquad (24)$$

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[9] W. J. McKnight and A. V. Tobolsky in "Elemental Sulfur," B. Meyer, Ed., Interscience Publishers, New York, N. Y., 1965, Chapter 5.

Hydrogen Abstaction

$$HS\cdot + H\text{-}S\text{-}S\text{-}S\text{-}S\text{-}H \rightarrow HSH + HS_4\cdot \tag{21}$$

$$HS\cdot + H\text{-}S\text{-}S\text{-}S\text{-}H \rightarrow HSH + HS_3\cdot \tag{26}$$

Equations 16 and 23 simply convert one component of the equimolar mixture into the other, and so no significant change in the relative proportions of HS_3H and HS_4H is to be expected. The attack of $HS_2\cdot$ radicals on HS_4H (eq 17) should yield initial small amounts of HS_5H. The fact that $\cdot SH$ radicals may be formed by the primary homolytic scission of HS_3H suggests that *no* induction period for the formation of HSH and HS_2H should be observed, as reactions 20, 21, 24, and 26 may take place immediately from the beginning of the decomposition on. As both HS_3H and HS_4H are equally likely to be attacked by $\cdot SH$ radicals, no change in their relative proportion should result from these reactions.

Figure 3 presents the data on the thermal decomposition of the equimolar mixture of HS_4H and HS_3H. We can therefore compare these experimental observations with the predictions based on the combination of the mechanisms proposed earlier for the decomposition of HS_4H and HS_3H separately.

1. HS_5H is produced initially as predicted by eq 17.
2. No induction period is observed for the production of HS_2H or HSH as was the case in the thermal decomposition of HS_4H. There is an initial rapid production of both of these products as would be predicted from eq 20, 24 and 21, 26. Initially HS_2H and HSH are produced in equimolar amounts again in keeping with the equal relative importance of the pairs of reactions 20, 24 and 21, 26.
3. The relative proportions of HS_3H and HS_4H do not change during the reaction in keeping with the ease of reequilibration as represented by eq 16 and 18.
4. The initial fast buildup of HS_2H to a percentage level considerably greater than that observed in either HS_4H or HS_3H decomposition followed by a decrease in HS_2H concentration reflects the fact that the HS_2H concentration is not reduced by attack of $HS\cdot$ radicals until the concentration of alternative sulfane species, HS_3H and HS_4H, has been significantly reduced. At this point HS_2H will be attacked by $HS\cdot$ radicals to yield HSH and $HS_2\cdot$ radicals. The latter will then feed back into reactions 16, 17, and 23.

In summary, therefore, the thermal decomposition behavior of an equimolar mixture of HS_3H and HS_4H can be predicted on the basis of the mechanisms proposed for the decomposition of the two components. The success of this prediction lends support to the validity of the mechanisms proposed for the HS_3H and HS_4H decomsitions.

Experimental Section

Materials. Solutions (2 *M*) of H_2S_3 and H_2S_4 in CCl_4 were prepared by the reaction of liquid H_2S with SCl_2 and S_2Cl_2 as reported previously.[10] The 2.0 *M* sulfane solutions were then brought to a standard concentration of 0.2 *M*. By combining the required amounts of each 0.2 *M* H_2S_3 and H_2S_4 solution, an equimolar H_2S_3–H_2S_4 mixture was prepared. The purity of the solutions was tested by nmr analysis. Composition of the H_2S_4 solution (mol %): 0 H_2S, 0 H_2S_2, 2 ± 2 H_2S_3, $97 \pm 2\ H_2S_4$, 0 H_2S_5, 3 $H_2S_{\geq 6}$. Composition of the H_2S_3 solution (mol %): 0 H_2S, 0 H_2S_2, $90 \pm 2\ H_2S_3$, 4 ± 2 H_2S_4, 4 H_2S_5, 2 $H_2S_{\geq 6}$. Composition of the equimolar H_2S_3–H_2S_4 mixture (mol %): 0 H_2S, 0 H_2S_2, 46 H_2S_3, 46 H_2S_4, 4 H_2S_5, 4 $H_2S_{\geq 6}$.

Table III. Position of Sulfane Nmr Signals in 0.2 *M* CCl_4 Solution

Sulfane	τ, ppm[a]	Sulfane	τ, ppm[a]
H_2S	9.33	H_2S_4	6.02
H_2S_2	7.40	H_2S_5	5.90
H_2S_3	6.04	$H_2S_{\geq 6}$	5.78–5.75

[a] TMS external reference.

Reactions. The thermal decomposition studies were carried out in evacuated and sealed Pyrex nmr tubes in the absence of oxygen; 0.5 ml each of "pure" H_2S_3, H_2S_4, and the equimolar H_2S_3–H_2S_4 mixture in CCl_4 was deoxygenated by repeated evacuation at −80° and warming to room temperature. The tubes finally were sealed under vacuum. The tubes then were transferred to a thermostated bath at 70.4 ± 0.1°. Nmr analyses were carried out periodically by cooling the tubes to room temperature, running the spectra, and returning the tubes to the thermostated bath.

Analytical Procedure. A Varian A-60 high-resolution nmr spectrometer was used for analysis. The spectrometer was pretuned to TMS before the samples were inserted into the sample probe. The spectra were run at a sweep time of 250 sec using a sweep width of 500 and 100 cps with properly chosen offset setting for the individual sulfane signals on an expanded scale. The sulfane signal positions in 0.2 *M* CCl_4 solution are shown in Table III. The positions of the nmr peaks remained constant within experimental error throughout the course of each experiment. The sulfane distribution was evaluated from the relative areas occupied by each sulfane signal. As the over-all sulfane concentration is relatively low, the errors in the determination of the sulfane distribution are believed to be within ±5% of the values shown in Figures 1–3. It must, however, be pointed out that the H_2S signal is in reponse only to that fraction of H_2S which is dissolved in the liquid phase. The fraction of H_2S in the gaseous phase in equilibrium with the H_2S dissolved in the liquid phase is not detected. Therefore, the values shown for H_2S should be considered to be minimum values. Consequently, the mole per cent values for sulfanes higher than H_2S represent maximum values. In order to establish a common basis for a relative comparison of the individual experiments, care was taken that in the nmr tubes the volume ratio of the liquid phase to the vapor phase was the same for all experiments. At the end of each run the nmr tubes were cooled to −80° and opened and the H_2S was allowed to evaporate. After evaporation of the solvent under vacuum the remaining sulfur was weighed (mp 116–117°). The sulfur recovery was practically 100% on basis of eq 8.

Conclusions

It has been demonstrated that sulfanes in dilute solutions exhibit a remarkable thermal stability with respect to their decomposition into H_2S and elemental sulfur, provided that impurities are vigorously excluded. It has been further demonstrated that sulfanes do not decompose directly into sulfur and H_2S, but rather are interconverted into each other slowly prior to their ultimate decomposition into H_2S and elemental sulfur. The distribution of intermediates clearly differs from any sulfane distribution in hydrogen polysulfide mixtures obtained by the acidification of aqueous sodium polysulfide solutions[10] supporting the view that the sulfane distribution in such mixtures is not a consequence of sulfane equilibration reactions after their formation.

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(10) E. Muller and J. B. Hyne, *Can. J. Chem.*, **46**, 2341 (1968).