since products formed from the α-methylstyrene did not overlap with the aziridines IV and V.

Preparation of 4-Carbethoxamino-2-methylpentene-2 (VIII). A solution of 1.5 g (0.005 mole) of the N-carbethoxy-2-amino-3-iodo-4-methylpentane (from *trans*-4-methylpentene-2) and 2.5 g (0.025 mole) of triethylamine in 50 ml of absolute ethanol was stirred at room temperature for 3 hr, poured into water, and extracted with ether. From the washed ether solution, a residue was obtained that yielded VIII by gas chromatography on column B (145°). It was identified by its infrared, nmr, and mass spectra. The infrared spectrum showed N–H at 3450 (sharp) and 3350 (broad), carbonyl at 1715 cm^{-1}. The nmr spectrum showed the ethoxy CH$_3$ at δ 1.22 (t), ethoxy CH$_2$ at 4.10 (q); CH$_3$ at 1.17 (d), CH$_3$ groups at C-2 1.72 and 1.74; N–C–H at 4.0–4.7 (m); olefinic C–H and N–H at 4.7–5.2 (m); all with the proper integrals. The parent peak in the mass spectrum was, as expected, at m/e 171; ratio (M + 1)/M

10.4% (calcd for C$_9$H$_{17}$NO$_2$: 10.6%); base peak at m/e 156, corresponding to the loss of a methyl to give EtOOC–NH–CH–CH=C(CH$_3$)$_2$ for this latter peak, the ratio of (M + 1)/M was found as 8.5% (calcd for C$_8$H$_{14}$NO$_2$: 9.3%).

Analysis for 4-Carbethoxamino-2-methylpentene-2 (VIII). A reaction mixture from a run with 1.5% olefin concentration (*cis*-olefin) was analyzed for VIII on column B. A trace of material with the retention time of VIII was noted; its peak area was 2.4% of that of the combined aziridines, IV + V.

Disproportionation of Organic Polysulfides

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Abstract: The thermal decomposition of dimethyl tetrasulfide and trisulfide at 80° has been followed by the use of nmr spectroscopy. In the first case, dimethyl tri-, tetra-, penta-, and hexasulfides were found in the early stages of the decomposition. In the second case, decomposition was much slower and dimethyl di-, tri-, and tetrasulfides were initially present. Addition of a stable free radical to dimethyl tetrasulfide was found to inhibit the formation of tri- and higher polysulfides. A mechanism for the decomposition of dimethyl tetrasulfide is suggested.

The facile thermal decomposition of organic tetra- and trisulfides has been known for many years. For example, Twiss recorded that diethyl tetrasulfide gives diethyl trisulfide and free sulfur on distillation *in vacuo*;[1] Jones and Reid reported that the same tetrasulfide decomposes to diethyl disulfide and sulfur at 140–150°;[2] Bloomfield found that dicyclohexyl tetrasulfide gives a material of reduced sulfur content and dicyclohexyl hexasulfide when heated at 140–150°;[3] Fuson, *et al.*, found that bis(2-chloroethyl) trisulfide gives a mixture of bis(2-chloroethyl) disulfide, higher sulfides, and sulfur on heating at 145–160°;[4] and Guryanova, *et al.*, showed that when ditolyl trisulfide, in which the central sulfur atom is radioactive, is heated with diethyl trisulfide the latter becomes radioactive through exchange of the central sulfur atoms.[5] Recently we have illustrated the instability of the tetrasulfide linkage in a more quantitative manner with the finding that the dissociation energy of the tetrasulfide linkage in dimethyl tetrasulfide is only about 36 kcal/mole.[6]

Although the lability of the polysulfide linkage has been recognized, systematic studies of the thermal decomposition of organic polysulfides have been hindered by lack of suitable means of analysis. Because the products of decomposition are themselves thermally

unstable, quantitative data based on classical methods of separation are not only difficult to obtain but are also suspect. Recently Grant and Van Wazer have reported that various dimethyl and di-*t*-butyl polysulfides can be distinguished by nmr spectroscopy.[7] Using an analogous procedure we have followed the thermal decomposition of dimethyl tetrasulfide and trisulfide at 80°. Investigations into the mechanism of decomposition were also carried out.

Experimental Section

Reagents. Dimethyl tetrasulfide was prepared as previously reported by us.[6] Dimethyl trisulfide was prepared by an analogous procedure using sulfur dichloride (Matheson Coleman and Bell) distilled immediately before use, bp 57–58°. The trisulfide had bp 56–57° (13 mm) (lit. 59° (12 mm),[8] 54–55° (11 mm),[9] 58–59° (15 mm)[10]); n^{30}D 1.5973 (lit.[10] 1.5972). The yield was 87%.

Anal. Calcd for C$_2$H$_6$S$_3$: C, 18.95; H, 4.78; S, 76.24. Found: C, 18.99; H, 4.75; S, 76.30.

β-(Phenyl nitrogen oxide)-β-methylpentan-δ-one oxime (hereafter called Banfield's free radical) was prepared by the method of Banfield and Tüdös.[11,12] Azobisisobutyronitrile (Du Pont) was used as received.

Procedure. The polysulfide under investigation (0.6 ml) and a small sealed capillary tube containing tetramethylsilane were placed in a precision-bore Pyrex nmr tube to which a standard taper joint had been attached. The tube was then degassed and sealed off under a slight pressure of nitrogen following the method previously

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(2) S. O. Jones and E. E. Reid, *ibid.*, **60**, 2452 (1938).
(3) G. F. Bloomfield, *J. Chem. Soc.*, 1547 (1947).
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(12) F. Tüdös and N. I. Smirnow, *Acta Chim. Acad. Sci. Hung.*, **15**, 389 (1958).

described by us.[6] The tube was heated at 80° in a bath completely protected from light. It was removed at intervals, quenched in liquid nitrogen, and allowed to attain room temperature. The nmr spectrum was taken and the tube returned to the bath.

In the other systems investigated the following materials were used: (a) dimethyl tetrasulfide (1.12 g), Banfield's free radical (0.100 g), carbon tetrachloride (0.8 ml); (b) dimethyl trisulfide (0.668 g), dimethyl tetrasulfide (0.014 g); (c) dimethyl trisulfide (0.75 ml), azobisisobutyronitrile (0.107 g); (d) dimethyl trisulfide (0.25 ml), benzene (0.5 ml); and (e) dimethyl trisulfide (0.25 ml), nitrobenzene (0.5 ml). In each case 0.6 ml of solution was placed in an nmr tube and treated as above.

Nmr Analysis. Grant and Van Wazer[7] found that the position of the methyl resonance in a dimethyl polysulfide was progressively shifted to lower fields as the number of sulfur atoms in the polysulfide increased. In mixtures of polysulfides and in the presence of solvents the positions of the peaks, relative to tetramethylsilane, were variable, depending on the composition of the system. However, the positions of the peaks, relative to each other, were practically constant over a range of systems.

In the present work the peaks obtained from the various reaction mixtures were assigned as due to dimethyl di-, tri-, and tetrasulfides by comparison with positions and separation of the peaks obtained from authentic samples and mixtures thereof. The assignment of peaks to higher sulfides was made on the assumption that the extent of deshielding is a smooth monotonous function of the number of sulfur atoms in the polysulfide.

The difference in chemical shift of polysulfides differing by one sulfur atom was averaged over a selection of spectra obtained. The values obtained are shown in Table I; for comparison values computed from the data of Grant and Van Wazer are also given.

Table I. Differences in Chemical Shifts of Dimethyl Polysulfides

$\Delta S_{3,2}{}^a$	$\Delta S_{4,3}{}^a$	$\Delta S_{5,4}{}^a$	$\Delta S_{6,5}{}^a$	
9.1	5.7	1.7	1.2	This work
8.8	5.6	1.0	1.9	Ref 7

^{a} $\Delta S_{m,n}$ is equal to the chemical shift of the methyl protons in MeS_mMe minus the chemical shift of the methyl protons in MeS_nMe in cps.

The nmr spectra were taken on a Varian A-60 high-resolution spectrometer using a sweep width of 50 cps and a sweep time of 250 sec. Peak areas were determined by machine integration. For each spectrum the area of each peak assigned to a particular polysulfide was expressed as a percentage of the total area due to all the polysulfides present. Since all dimethyl polysulfide molecules contain the same number of hydrogen atoms, this percentage area is equal to the number of molecules of the particular polysulfide present expressed as a percentage of the total number of polysulfide molecules present, i.e., to the molar percentage.

Results

The percentage molar distributions of dimethyl polysulfides in the systems investigated at various time intervals are shown in Tables II–VIII. The quantities given are probably accurate to about ±2. (Several duplicate nmr measurements were made in each case.) In no spectrum obtained was there evidence of monosulfide, and hydrocarbons were not formed since the sum of the peak areas remained constant relative to the peak area given by the tetramethylsilane standard. The constancy of the $CH_3:S$ mole ratio in each system investigated shows that in no case is free sulfur formed in detectable quantity.

Discussion

In an earlier publication[6] we suggested that the primary mode of decomposition of dimethyl tetrasulfide was symmetrical homolytic cleavage of the tetrasulfide linkage. Our present findings are in accord with this suggestion.

Table II. Decomposition of Dimethyl Tetrasulfide at 80°; Percentage Molar Composition of Product

Time, hr	Me_2S_2	Me_2S_3	Me_2S_4	Me_2S_5	Me_2S_6
0	0	3	97	0	0
0.5	0	8	80	10	2
1.0	0	13	72	11	4
2.5	0	20	60	16	4
5.2	0	31	49	13	7
20.1	0	47	30	15	8
43.7	0	49	27	15	9
138.0	Trace	48	26	14	10
393.5	1	49	25	14	11
1828.8	6	46	24	13	11

Table III. Decomposition of Dimethyl Trisulfide at 80°; Percentage Molar Composition of Product

Time, hr	Me_2S_2	Me_2S_3	Me_2S_4	Me_2S_5	Me_2S_6
0	0	100	0	0	0
5.2	1	98	1	0	0
20.1	3	94	3	0	0
64.6	5	89	6	0	0
237.2	13	73	12	2	0
552.3	21	62	14	3	Trace
767.2	21	61	16	2	Trace
1368.6	23	60	14	3	Trace

Table IV. Decomposition of Dimethyl Tetrasulfide at 80° in the Presence of Banfield's Free Radical; Percentage Molar Distribution of Dimethyl Polysulfides in Product

Time, hr	Me_2S_3	Me_2S_4	Me_2S_5	Me_2S_6
0^a	3	97	0	0
1.0	3	97	0	0
2.75	10	82	8	0
5.5	20	62	15	3
18.75	44	36	15	2

^{a} The nmr spectrum was taken before the addition of Banfield's free radical since it was not possible to obtain the spectrum in the presence of the initial concentration of free radical.

Table V. Decomposition of Dimethyl Trisulfide at 80° in the Presence of Added Dimethyl Tetrasulfide; Percentage Molar Composition of Product^a

Time, hr	Me_2S_2	Me_2S_3	Me_2S_4
0	0	98	2
1.0	0	98	2
2.5	0	98	2
7.5	Trace	98	2
18.0	1	97	2
41.5	3	95	2

^{a} No Me_2S_5 or Me_2S_6 were found.

Table VI. Decomposition of Dimethyl Trisulfide at 80° in the Presence of Azobisisobutyronitrile; Percentage Molar Distribution of Dimethyl Polysulfides in Product^a

Time, hr	Me_2S_2	Me_2S_3	Me_2S_4
0	0	100	0
4.0	Trace	97	3

^{a} No Me_2S_5 or Me_2S_6 were found.

Table VII. Decomposition of Dimethyl Trisulfide at 80° in Benzene; Percentage Molar Distribution of Dimethyl Polysulfides in Product[a]

Time, hr	Me_2S_2	Me_2S_3	Me_2S_4
0	0	100	0
24.9	Trace	100	Trace
139.9	2	96	2
638.2	4	90	6
1137.0	5	89	6

[a] No Me_2S_5 or Me_2S_6 were found.

Table VIII. Decomposition of Dimethyl Trisulfide at 80° in Nitrobenzene; Percentage Molar Distribution of Dimethyl Polysulfides in Product[a]

Time, hr	Me_2S_2	Me_2S_3	Me_2S_4
0	0	100	0
24.9	Trace	100	Trace
139.9	1	98	1
638.2	3	94	3
1137.0	4	92	4

[a] No Me_2S_5 or Me_2S_6 were found.

The absence of dimethyl disulfide in the early stages of the decomposition of dimethyl tetrasulfide indicates that only symmetrical cleavage of the tetrasulfide linkage occurs. Unsymmetrical cleavage would give rise to $MeS\cdot$ and $MeS_3\cdot$ radicals. The $MeS\cdot$ radical would be expected to give rise to dimethyl disulfide by coupling or by reaction with a polysulfide molecule. In the decomposition of dimethyl trisulfide, where only unsymmetrical cleavage can occur, dimethyl disulfide is a primary decomposition product.

It has been suggested that $MeS_x\cdot$ radicals, where $x > 1$, can be stabilized by a resonance interaction with the adjacent S atoms.[13,14] The estimated dissociation energy of the S–S bond in polymeric S is about 33 kcal/mole,[15] not very different from the value of the dissociation energy of dimethyl tetrasulfide. This indicates that if such stabilization exists, only two or three sulfur atoms are effective in the delocalization. If more were involved, one would expect a substantially larger difference in the dissociation energy of these two materials.

A crude estimate of the magnitude of the stabilization can be made as follows. The dissociation energy of dimethyl disulfide is known to be about 70 kcal/mole.[16] The difference between this value and the 36 kcal/mole found for the dissociation energy of dimethyl tetrasulfide may be attributed to the stabilization each of the fragments from dimethyl tetrasulfide derives from delocalization. This stabilization is thus $(70-36)/2$ or about 17 kcal/mole. From the arguments given above we would expect that the amount of stabilization available to a fragment such as $MeS_3\cdot$ would not be greater than about 20 kcal/mole. Thus symmetrical cleavage of the tetrasulfide linkage would give two stabilized fragments with roughly 34 kcal/mole of "delocalization" energy. Unsymmetrical cleavage would give an $MeS\cdot$ fragment, which cannot be stabilized, and an

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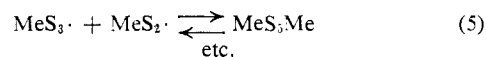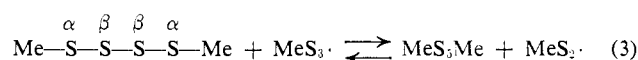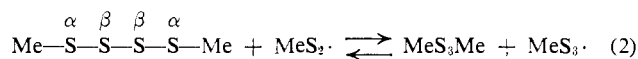(14) G. Gee, F. Fairbrother, and G. T. Merrall, *J. Polymer Sci.*, **16**, 459 (1955).
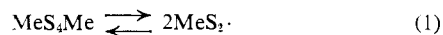(15) D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **78**, 3279 (1956).
(16) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

$MeS_3\cdot$ fragment, which is stabilized to the extent of *ca.* 20 kcal/mole or less. Thus unsymmetrical cleavage would result in the loss of about 14 kcal/mole in stabilization energy in the products and should be very unfavorable.

Table IV shows that the decomposition of dimethyl tetrasulfide is completely suppressed by addition of a free-radical scavenger. From the rate constant for cleavage of the tetrasulfide linkage reported earlier[6] it was possible to compute how long it would take for the scavenger to be consumed. Under our conditions about 47 min should have been required. Most of the scavenger was consumed after 45 min. This could be ascertained by the appearance of a resolvable nmr spectrum at the end of this period. (No resolvable spectrum could be obtained in the presence of the initial amount of free-radical scavenger, owing to the presence of the unpaired electron.) This offers convincing proof that radicals are involved in this decomposition; otherwise it is difficult to envisage a way of removing the unpaired spin. Dimerization of the free-radical scavenger may be ruled out by the observation that no decomposition occurs during the first hour in the presence of the scavenger whereas about 25% of the initial amount of dimethyl tetrasulfide is decomposed in a similar period in the absence of the scavenger. After the free-radical scavenger has been consumed, the decomposition proceeds in virtually identical fashion with that observed in the absence of inhibitor.

We wish to suggest the following mechanism for the decomposition of dimethyl tetrasulfide

$$MeS_4Me \rightleftharpoons 2MeS_2\cdot \qquad (1)$$

$$\overset{\alpha\quad\beta\quad\beta\quad\alpha}{Me-S-S-S-S-Me} + MeS_2\cdot \rightleftharpoons MeS_3Me + MeS_3\cdot \qquad (2)$$

$$\overset{\alpha\quad\beta\quad\beta\quad\alpha}{Me-S-S-S-S-Me} + MeS_3\cdot \rightleftharpoons MeS_5Me + MeS_2\cdot \qquad (3)$$

$$2MeS_3\cdot \rightleftharpoons MeS_6Me \qquad (4)$$

$$MeS_3\cdot + MeS_2\cdot \rightleftharpoons MeS_5Me \qquad (5)$$
etc.

It may be noted that α attack by $MeS_3\cdot$ radicals on dimethyl tetrasulfide results in no new products. The same is true of β attack by $MeS_2\cdot$ radicals on dimethyl tetrasulfide. The higher polysulfides can undergo cleavage at these temperatures and give rise to the same type of reactions as described above for dimethyl tetrasulfide. We also believe that reactions such as

$$MeS_2\cdot + MeS_4Me \longrightarrow MeS_5Me + MeS\cdot \qquad (6)$$
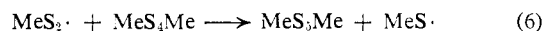
are very unfavorable under our reaction conditions since the $MeS\cdot$ radical would almost certainly give rise to dimethyl disulfide (which was not observed until after long periods of heating).

The greater thermal stability of the trisulfide linkage as compared to the tetrasulfide linkage is apparent from the slower rate of decomposition of dimethyl trisulfide. If this decomposition involves homolytic cleavage, this observation is to be expected from our previous remarks concerning stabilization of the fragments.

An attempt was made to react dimethyl trisulfide with Banfeld's free radical in a manner analogous to that used with the tetrasulfide. However, the slow rate of decomposition and the thermal instability of the free-radical scavenger combined to yield inconclusive results.

Addition of a small amount (2% molar) of dimethyl tetrasulfide to the trisulfide did not accelerate the rate of decomposition of the latter. This indicates that the following reaction does not occur at any appreciable rate.

$$MeS_3Me + MeS_2\cdot \longrightarrow MeS_4Me + MeS\cdot \qquad (7)$$

A similar conclusion follows from consideration of the influence of azobisisobutyronitrile on the decomposition of dimethyl trisulfide. The initial rate of formation of dimethyl tetrasulfide is slightly accelerated, whereas the rate of production of disulfide is unaffected. It is almost certain that the role of the azobisisobutyronitrile is to generate isobutyronitrile radicals which subsequently attack the trisulfide. The following reactions are possible.

$$MeS_3Me + Me_2\dot{C}CN \longrightarrow Me_2(MeS_2)CCN + MeS\cdot \qquad (8)$$

$$MeS_3Me + Me_2\dot{C}CN \longrightarrow Me_2(MeS)CCN + MeS_2\cdot \qquad (9)$$

Reaction 8 may be excluded since the formation of MeS· radicals would almost certainly result in the production of dimethyl disulfide. For the same reason, the MeS$_2$· radicals produced cannot participate in reaction 7 but must undergo recombination to give dimethyl tetrasulfide.

These last two experiments show that the decomposition of dimethyl trisulfide does not occur by a free-radical chain reaction initiated by the fragments of homolytic dissociation. A nonchain radical mechanism is possible and the similarity in the rates of decomposition in the solvents benzene and nitrobenzene is in accordance with this mechanism. However, we feel that our evidence is not sufficient to allow a firm conclusion to be made at the present time.

Preliminary studies in our laboratories have indicated that polysulfenyl radicals, $RS_x\cdot$, where $x > 1$, have substantially different reactivity than sulfenyl radicals, $RS\cdot$.[17] In the past workers have found that non-Markovnikov addition of sulfenyl radicals to olefins is suppressed in the presence of sulfur and polysulfides.[2,3] Such results have been explained in terms of an ionic addition caused by the presence of sulfur. While such explanations are quite reasonable, we suggest that they be viewed with due caution until the reactions of polysulfenyl radicals are more completely understood.

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The Vacuum Ultraviolet Photochemistry of o-Xylene

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Contribution from the Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912. Received December 9, 1966

Abstract: The vapor-phase photolysis of o-xylene has been investigated using light of 1600–2100 A. With the exception of a small amount of benzocyclobutene which is formed by vacuum ultraviolet photolysis, the same products are formed as those produced by irradiation with 2537-A light (toluene, m-xylene, p-xylene, and o-ethyltoluene). This coincidence of products suggests that both photolyses may proceed through a common set of reactive intermediates. Fluorescence measurements, as well as the effect of added inert gases on the reaction, indicate that the first excited singlet and lowest lying triplet states are not suitable choices for such common intermediates. The intermediacy of highly vibrationally excited ground electronic states seems to be most consistent with the available facts. The mechanism of formation of benzocyclobutene has been investigated by deuterium labeling, and found to proceed by the loss of a single hydrogen (or deuterium) atom from each methyl group, rather than loss of molecular hydrogen from one methyl group. The construction of lamps which emit 10^{16} to 10^{17} quanta/sec in the vacuum ultraviolet is described.

The interest in the photochemical reactions of simple, noncondensed, aromatic hydrocarbons has recently been heightened by the reports of Wilzbach and Kaplan[1] of rearrangements to the nonbenzenoid "isomers" under irradiation at the 2537-A mercury line. In the cases where the benzene ring is heavily substituted with bulky groups (e.g., 1,2,4-tri-t-butylbenzene) these isomers are isolable;[1] with smaller groups the intermediacy of the isomers is inferred from the isomerization of labeled compounds.[2] These reactions occur with low quantum efficiencies, typically about 0.01.

(1) K. E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 87, 4004 (1965).
(2) (a) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, ibid., 87, 675 (1965); (b) K. E. Wilzbach and L. Kaplan, ibid., 86, 2307 (1964).

Irradiation with light of wavelengths of less than 2000 A is expected to bring about reactions much more efficiently. This expectation is based on a report[3] that no fluorescence was observed when simple aromatics (benzene, toluene, p-xylene, and mesitylene) were irradiated in the vapor phase at wavelengths corresponding to their second and third absorption bands, approximately 1600–2100 A. It is reasonable that the failure to observe light emission may result from an efficient predissociation path available to the excited molecule.

Since only fragmentary reports of the vacuum ultraviolet photochemistry of aromatics were available, an

(3) C. L. Braun, S. Kato, and S. Lipsky, J. Chem. Phys., 39, 1645 (1963).