containing boron trifluoride etherate (0.2 *M* solution) in about 3 days. The calculated *K* was about 10^2, in contrast to the value of $3\text{-}8 \times 10^2$ for the reactions of 1-propanethiol or 2-acetamidoethanethiol. The value of $3\text{-}8 \times 10^2$ compares favorably with those of $4\text{-}6 \times 10^2$ measured by Johns and Hixon for the reaction of chloral with ethanethiol or 1-butanethiol using a freezing point depression method.[4]

The reaction of chloral with 2-methyl-2-propanethiol also was studied for comparison and gave a *K* of *ca.* 1.5×10^2 in CH_2Cl_2; the spectrum of the α-hydroxy sulfide which resulted had maxima at 3540 and 1055 cm^{-1}. The time of equilibration (*ca.* 2 days) of the neat chloral–thiol mixture appeared to be about double that of the corresponding chloral-1-propanethiol mixture. The reaction of the tertiary thiol $HSC(CH_3)_2CH_2CH_2OH$ with chloral gave a *K* value of 1.3×10^3, the time of equilibration under the conditions used with 2-methyl-2-propanethiol being about 4 hr. The ir spectrum of this α-hydroxy sulfide had maxima at 3520 and 1085 cm^{-1}.

Acetaldehyde.—This did not react in any amount detected with 1-propanethiol, 2-acetamidoethanethiol, or 1-dodecanethiol in CH_2Cl_2 in the absence of acid. In the presence of HCl or boron trifluoride etherate the corresponding mercaptal formed (see footnote *e*, Table I).

Formaldehyde.—Paraldehyde or *s*-trioxane with 1-propanethiol showed no reaction. In the presence of HCl, exothermic conversion into mercaptal occurred.

Benzaldehyde.—In the absence of HCl, slight conversion into an α-hydroxy sulfide occurred, as indicated by diminution in the -CO- absorption at 1700 cm^{-1} and by weak absorptions produced at 3510 and 1100 (1085) cm^{-1}. In the presence of HCl, substantial conversion into the expected mercaptal occurred.

Pentafluorobenzaldehyde.—This gave a reaction similar to that given by benzaldehyde, the spectrum of the mixture in CH_2Cl_2 having absorption maxima of medium intensity at 3575 and 1025 cm^{-1}. However, the calculated *K* was only 5×10^0 (benzaldehyde, 5×10^0). This lower *K* than expected must be due to a cancellation of electronic effects on the aromatic ring.

Registry No.—1-Propanethiol, 107-03-9.

Methanesulfenyl Chloride. V. The Spontaneous Decomposition of Methanesulfenyl Chloride and Methylsulfur Trichloride[1a]

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Methanesulfenyl chloride, CH_3SCl, on standing for a few hours at room temperature begins to decompose into methyl chloride, methyldisulfur chloride, methyl disulfide, methyl trisulfide, and methyl tetrasulfide as major products as indicated by the nmr spectra of decomposition mixtures. Minor peaks in the spectrum correspond to the δ chemical shifts of methyl chloromethyl disulfide and dichloromethyl methyl sulfide. Other products were hydrogen chloride, sulfur dichloride, elementary sulfur, and, in some cases, on long standing an unidentified solid. Methylsulfur trichloride decomposes rapidly when the crystalline solid is heated a few degrees above room temperature. The nmr spectrum of the decomposition mixture indicates that the principal products are chloromethanesulfenyl chloride (*ca.* 60%) and methanesulfenyl chloride (*ca.* 20%). Other products identified by their peaks in the nmr spectrum are methyldisulfur chloride, methyltrisulfur chloride, methyltetrasulfur chloride, bischloromethyl disulfide, and dichloromethanesulfenyl chloride. In addition, hydrogen chloride and sulfur dichloride were also products of the decomposition. Uncertainty exists as to whether the decomposition of CH_3SCl takes place by an ionic or free-radical mechanism. An esr study of the decomposition showed no signals to indicate an appreciable concentration of free radicals. Methyl disulfide, irradiated at liquid nitrogen temperature, produced an esr spectrum with clearly defined signals believed to indicate the $CH_3S\cdot$ radical. This radical appears to be highly reactive and cannot be stabilized on Vycor glass at room temperature. The failure to observe esr signals in decomposing CH_3SCl may possibly be due to the high reactivity of radical intermediates resulting in a low steady state concentration.

Methanesulfenyl chloride, CH_3SCl, and methylsulfur trichloride, CH_3SCl_3, are two highly reactive compounds which, if treated properly, enter into stoichiometric reactions and yield products which can be isolated in high yield.[2,3] If CH_3SCl is allowed to stand a few hours, or if CH_3SCl_3 is warmed only a few degrees above room temperature, however, the compounds undergo profound decompositions, yielding mixtures which defy separation or analysis by conventional means.

Since the two original compounds contain single carbon atoms, most of the decomposition products are capable of yielding sharp singlet peaks in the nmr spectra. Recent experience in our laboratory as well as previous studies by others have shown that nmr affords an excellent means for identifying individual closely related sulfur compounds in complex mixtures.[4,5]

Although there remain a number of uncertainties regarding the identity of some products formed in the decompositions, and the mechanisms by which the products are formed, it seems appropriate to report at this time the products identified. Later work may clarify some of the unsolved questions but the departure of the junior authors and the stinking character of the materials involved discourage further work at the present time.

There are previous reports concerning the instability of these compounds. In his original description of

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[1] (a) Taken in part from the Ph.D. Thesis of R. V. Norton, University of Maine, 1967, and from the M. S. Thesis of R. L. Weichman, University of Maine, 1966. (b) To whom inquiries concerning this paper may be sent. (c) To whom the senior author is indebted for carrying out the esr study of the decomposition of CH_3SCl at Princeton University.

[2] I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).

[3] I. B. Douglass and W. J. Evers, *ibid.*, **29**, 419 (1964), and prior publications.

[4] J. R. Van Wazer and D. Grant, *J. Amer. Chem. Soc.*, **86**, 1450 (1964).

[5] D. Grant and J. R. Van Wazer, *ibid.*, **86**, 3012 (1964).

TABLE I

PRODUCTS OF THE SPONTANEOUS DECOMPOSITION OF METHANESULFENYL CHLORIDE[a]

	Mol %							
Time, days	CH_3SCl	CH_3SSCl	CH_3Cl[b]	CH_3SSCH_3	CH_3SSSCH_3	$CH_3SSSSCH_3$	$ClCH_2SSCH_3$	Cl_2CHSCH_3
0	100	0	0	0	0	0	0	0
1	45	16	5	18	2	4	5	3
2	26	29	5	15	4	6	7	10
7	10	31	6	17	9	9	10	8
10	7	29	5	16	12	11	10	11
17	6	29	5	13	12	14	10	10
38	4	27	4	11	12	21	11	11

[a] Hydrogen-containing components of the liquid fraction. [b] The decomposition was allowed to proceed at atmospheric pressure and most of the methyl chloride escaped from the decomposition mixture.

CH_3SCl, Brintzinger mentioned that, when the compound was allowed to stand or was distilled at ordinary pressure, a high boiling residue was formed.[6] Schneider[7] exposed a 20-g sample of CH_3SCl in a sealed tube to sunlight for 3 days at room temperature. On opening the tube he noted the escape of a large amount of gas which he reported as being hydrogen chloride, but which probably consisted in large part of methyl chloride. Mayer and Frey[8] heated aliphatic sulfenyl chlorides to 100° and found that they readily decomposed to alkyl chlorides.

In an early paper[9] describing methylsulfur trichloride and analogous compounds two principal types of decomposition were noted. One was a reversible decomposition into sulfenyl chloride and chlorine (eq 1).

$$RSCl_3 \rightarrow RSCl + Cl_2 \qquad (1)$$

The other, shown by the alkylsulfur trichlorides, involved the splitting out of hydrogen chloride with the formation of an α-chloroalkanesulfenyl chloride (eq 2). The present study indicates that the decomposition also follows several other paths.

$$RCH_2SCl_3 \rightarrow HCl + RCHClSCl \qquad (2)$$

In carrying out our study the two compounds were allowed to decompose; samples of the resulting mixtures were diluted with carbon tetrachloride (CCl_4) containing tetramethylsilane (TMS) and subjected to pmr analysis. The δ shifts of the peaks in the resulting spectra were then matched against the δ shifts of known compounds and, when possible, tests were made on the decomposition mixtures to isolate specific compounds or to cause an individual component to react in such a way that its presence could be demonstrated.

The principal products of the decomposition of CH_3SCl proved to be methyl chloride, methyldisulfur chloride (CH_3SSCl), methyl disulfide, methyl trisulfide, and either methyl tetrasulfide or methyltrisulfur chloride. (Methyltrisulfur chloride has a chemical shift identical with that of methyl tetrasulfide but tests on the mixture indicate the presence of the tetrasulfide.) Minor peaks in the pmr spectrum of every decomposition mixture corresponded to the δ values characteristic of methyl chloromethyl disulfide, CH_3SSCH_2Cl, and dichloromethyl methyl sulfide, Cl_2CHSCH_3. In addition to the compounds listed above, hydrogen chloride, sulfur dichloride, elemental sulfur, and an unidentified crystalline solid were products of the decomposition. Table I gives the approximate molar composition of samples which had decomposed for varying lengths of time. Heating accelerated the decomposition but irradiation seemed to have no accelerating effect and pmr spectra of irradiated and nonirradiated samples were essentially identical at comparable time intervals.

The decomposition of CH_3SCl_3 is a rapid, self-catalyzed reaction. When a sample of the dry solid, spread out in an inclined test tube, is gently heated through the glass at one edge, the decomposition begins at the point heated and spreads through the mass like fire spreading through a field of dry grass. Condensation of the volatile products and recombination with the liquid residue gave a mixture, the pmr spectrum of which revealed the presence of methyl chloride, chloromethanesulfenyl chloride, methanesulfenyl chloride, dichloromethanesulfenyl chloride, methyldisulfur chloride, methyltrisulfur chloride, methyltetrasulfur chloride, and bischloromethyl disulfide. Hydrogen chloride and sulfur dichloride were also products of the decomposition. Table II shows the approximate relative abundance of the components in decomposition mixtures as determined by integration of their pmr spectra.

TABLE II

DECOMPOSITION PRODUCTS OF METHYLSULFUR TRICHLORIDE

	Mol %		
Compound formed	Dry solid	Dry solid	In CCl_4
$ClCH_2SCl$	55.6	61.0	60.3
CH_3SCl	20.4	14.6	17.2
CH_3S_2Cl	0.0	3.3	0.8
CH_3S_3Cl	8.4	8.9	2.9
CH_3S_4Cl	2.3	2.4	14.4
Cl_2CHSCl	6.8	6.3	
$(ClCH_2S)_2$	4.5	3.5	1.4
CH_3Cl	1.6	0.0	2.9
HCl	+	+	+
SCl_2	?	?	+

At the present time there is no firm basis for formulating a mechanism for these decompositions. Our previous studies of the reaction of methanesulfenyl chloride have emphasized its tendency to react by an ionic mechanism.[3] On the other hand, Grant and Van Wazer[5] explained in terms of free radicals the complicated equilibria and "scrambling of parts" which

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(6) H. Brintzinger, K. Pfannstiel, H. Koddebusch, and K. E. Kling, *Chem. Ber.*, **83**, 87 (1950).

(7) E. Schneider, *ibid.*, **84**, 911 (1951).

(8) R. Mayer and H. J. Frey, *Angew. Chem.*, **76**, (20), 861 (1964).

(9) I. B. Douglass, K. R. Brower, and F. T. Martin, *J. Amer. Chem. Soc.*, **74**, 5770 (1952).

result when sulfur chlorides react with methyl sulfide and methyl disulfide but referred to "initial complex formation." Several other recent publications have discussed free-radical reactions of sulfenyl chlorides.[10] One can readily explain the formation of the decomposition products identified in this study in terms of radical reactions. On the other hand, more difficulty is experienced in outlining ionic steps which would yield the products found.

With the assistance of Mr. Robert B. Clarkson in the chemistry laboratory at Princeton University, an attempt was made to determine whether fresh or decomposing samples of CH_3SCl would give an electron spin resonance spectrum which would indicate the presence of free radicals. No such signals were observed, indicating that, if radicals are formed, they react so rapidly that the concentration at any one time is too low to produce an esr signal. Evidence for highly reactive radicals, believed to be $CH_3S\cdot$, was obtained by irradiating, at liquid nitrogen temperature, methyl disulfide adsorbed on Vycor glass. An esr spectrum of the sample showed a strong signal with partially refined hyperfine structure. The hyperfine structure disappeared when deuteriomethyl disulfide was put through the procedure. The $CH_3S\cdot$ signal slowly decayed at liquid nitrogen temperature and completely disappeared when the sample was warmed to room temperature and immediately cooled again to liquid nitrogen temperature. The observed radical, in contrast to the methyl radical, cannot be stabilized on Vycor at room temperature. The failure to observe esr signals during the decomposition of CH_3SCl may possibly be attributed to the inability of the Vycor glass to stabilize a radical intermediate.

In our attempts to confirm the identity of components in the decomposition mixture and to clarify the reactions by which they might be formed, some previously unreported aspects of organosulfur chemistry were observed. When CH_3SCl was allowed to react with sulfur dichloride a complex mixture resulted containing CH_3SCl, CH_3S_2Cl, CH_3S_3Cl, and CH_3S_4Cl. These results along with others reported below are analogous to those reported by Van Wazer and Grant for other systems.[4,5]

TABLE III

PMR CHEMICAL SHIFTS OF SOME ORGANOSULFUR COMPOUNDS

	CH_3S-	$ClCH_2S$-	Cl_2CHS-
CH_3SCH_3	2.08		
$ClCH_2SCH_3$	2.28	4.68	
$ClCH_2SCH_2Cl$		4.86	
Cl_2CHSCH_3	2.47		6.75
Cl_2CHSCH_2Cl		4.86	6.85
$Cl_2CHSCHCl_2$			6.75
Cl_3CSCH_3	2.66		
Cl_3CSCH_2Cl		5.10	
$Cl_3CSCHCl_2$			7.05
CH_3SSCH_3	2.41		
CH_3SSCH_2Cl	2.60	4.78	
$ClCH_2SSCH_2Cl$		4.84	
CH_3SSSCH_3	2.56		
$CH_3SSSSCH_3$	2.66		
CH_3SCl	2.91		
CH_3SSCl	2.75		
CH_3SSSCl	2.65		
$CH_3SSSSCl$	2.51		
$ClCH_2SCl$		5.08	
Cl_2CHSCl			6.83

The reactions of sulfur dichloride and sulfur monochloride with mercaptans have long been employed to prepare alkyl and aryl trisulfides and tetrasulfides.[11] The present study has shown that in preparing methyl tetrasulfide the order in which the reactants are mixed is important in determining the products formed. Addition of the sulfur monochloride to methyl mercaptan at low temperature gives pure methyl tetrasulfide. Reverse addition, however, of mercaptan to the sulfur monochloride gives a mixture of methylpolysulfur chlorides and methyl polysulfides.

The pmr spectra of a number of organosulfur compounds were examined in an attempt to identify the peaks in the pmr spectrum of the decomposition mixtures. Table III consolidates this data. The δ values for the protons in the methylpolysulfur chlorides do not agree with those previously reported.[4,5] The values for corresponding protons among the chloro derivatives of methyl sulfide appear to be influenced by factors other than simple inductive effects.

Experimental Section

Pmr spectra were obtained by the use of a Varian Associates Model A-60 nmr spectrometer. In each case a 10% solution of the compound or mixture to be tested was prepared in Spectro-Grade carbon tetrachloride containing 1% of tetramethylsilane. At frequent intervals the calibration of the instrument was checked with a sealed tube containing a solution of 1% chloroform and 1% tetramethylsilane in carbon tetrachloride.

Decomposition of Methanesulfenyl Chloride (I).—I was prepared according to the method previously described.[3] It was purified by distillation through an 11-in., glass helix packed column under reduced pressure (boiling below 0° at 10 mm) and condensed in a receiver cooled in Dry Ice. The product, after storing overnight at −78°, showed only a single pmr peak at δ 2.91 downfield from tetramethylsilane.

In first carrying out the decompositions, two 20.64-g (0.25 mol) samples were placed in separate identical Pyrex flasks. Each flask was fitted with a port for removing liquid samples, a manometer to indicate pressure development and an outlet connected through a stopcock to a Dry Ice trap which in turn was connected through a drying tube to a flask containing a measured amount of standard alkali. One flask was illuminated several hours daily with a 274-W General Electric sun lamp and the other was wrapped in black cloth and placed in a dark cupboard. Both flasks were flushed with dry nitrogen at the start of the experiment and were kept at room temperature. At appropriate intervals small samples of the decomposition mixtures were removed with a capillary syringe for pmr analysis.

At the beginning of the experiment the manometer indicated a fairly rapid generation of gas which made it necessary to open the stopcock several times during the first 2 hr. Thereafter it was left open.

After 24 hr the color of the liquid was less red and the pmr spectrum, in addition to the peak at δ 2.91 for CH_3SCl, showed five major peaks at 2.40, 2.55, 2.65, and 2.77 and four minor peaks at 2.47, 2.60, 4.79, and 6.74. All of these peaks persisted to the end of the experiment and no new peaks developed. Table I shows the approximate composition in mole per cent of the liquid withdrawn at the various time intervals.

After 10 days, withdrawn samples were no longer completely

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(10) J. F. Harris, Jr., *J. Org. Chem.*, **31**, 931 (1966), and references therein.

(11) A. Schöberl and A. Wagner in "Houben-Weil, Methoden der Organischen Chemie," Vol. 9, 4th ed, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1955, p 87.

miscible with carbon tetrachloride and precipitated a white solid when diluted. After the seventeenth day crystals appeared in the mother liquor. At the end of 38 days 2.79 g of solid had accumulated in the flask exposed to light and 1.53 g in the one kept in the dark. This was the only detectable difference in the two experiments.

The solid was colorless, insoluble in acetone, carbon tetrachloride, ether, and hexane and melted sharply at 74–75°. It reacted in water to give an acidic solution containing chloride ions. On standing in a loosely stoppered test tube the solid slowly liquefied but appeared to be stable indefinitely when excluded from moisture. Analysis indicated a composition which could not be interpreted in terms of definite composition. Some samples of CH_3SCl, allowed to stand undisturbed for as long as 2 months, failed to precipitate any solid.

Identification of Products from CH_3SCl.—The volatile condensate from the cold trap, after being vaporized through an alkaline solution and dried, gave an infrared (ir) spectrum identical with that of authentic methyl chloride. The pmr spectrum showed a single peak at δ 3.00 also identical with that of methyl chloride.

The peaks in the pmr spectrum of the decomposition mixture at δ 2.41, 2.56, and 2.66 were attributed to methyl disulfide, methyl trisulfide, and methyl tetrasulfide. A freshly distilled sample of methyl disulfide showed a single peak at δ 2.41. A sample of methyl trisulfide, prepared by adding sulfur dichloride to liquefied methyl mercaptan, showed a principal peak at δ 2.56. Likewise, a sample of methyl tetrasulfide, prepared by adding sulfur monochloride to liquefied methyl mercaptan at −20° showed a principal peak at δ 2.66. An old sample of methyl tetrasulfide, showing by its pmr spectrum that it contained all the lower methyl polysulfides, was injected into a gas–liquid chromatograph (110°) column packed with 20% Apiezon J on 60/80 mesh Chromosorb W. The retention times for methyl di-, tri-, and tetrasulfides were found to be 0.8, 3.8, and 19.4 min, respectively. A similar amount of the decomposition mixture showed components with identical retention times.

Methyldisulfur chloride, CH_3SSCl, is believed to be the decomposition product responsible for the pmr peak at δ 2.77. An authentic sample of this compound was prepared by the method of Böhme and von Ham[12] through the reaction of sulfuryl chloride with methyl trisulfide. The pmr spectrum of this reaction mixture showed peaks at δ 2.91 for methanesulfenyl chloride and at 2.77 for methyldisulfur chloride.

The four unidentified peaks remaining were considered as possibly resulting from chloro derivatives of dimethyl sulfide or dimethyl disulfide. All of the chloro derivatives of methyl sulfide were prepared by the methods reported by Truce, Birum, and McBee.[13] The properties of all these compounds, except $\alpha,\alpha,\alpha',\alpha'$-tetrachlorodimethyl sulfide, agree well with those reported by the previous workers. The latter compound, in spite of repeated close fractionation through a 4-ft helix-packed column could not be separated from the $\alpha,\alpha,\alpha,\alpha'$-tetrachloro isomer. In the mixtures, however, the pmr spectra of the two compounds could be readily identified. One of the chloro derivatives of dimethyl sulfide, dichloromethyl methyl sulfide (CH_3SCHCl_2), had pmr δ shifts which coincided with two of the minor unknown peaks in the spectrum of the decomposition mixture. The other two minor unidentified peaks are believed to indicate the presence of chloromethyl methyl disulfide. An impure sample of this compound was prepared by the reaction of chloromethanesulfenyl chloride (containing some I) with methyl mercaptan. A pmr spectrum of the reaction product showed a peak at δ 2.41 characteristic of methyl disulfide and two major peaks at 2.60 for CH_3SSCH_2Cl and at 4.79 for CH_3SSCH_2Cl, having peak areas integrating 3:2.

The amount of hydrogen chloride formed during the decomposition, while not determined precisely, was not large. Titration of the alkaline solution in the absorption train described above indicated that only 0.03 equiv of alkali had been neutralized during the decomposition of 0.25 mol of I. Some hydrogen chloride, however, was lost when the system was periodically opened and some remained dissolved in the original decomposition mixture and in the cold trap condensate.

In an effort to identify elemental sulfur and sulfur dichloride among the decomposition products, a portion of a decomposition mixture was treated with phenol, steam distilled, and acetylated. On chromatographing a chloroform solution of the acetylated mixture on silica gel there was obtained a small sample of elemental sulfur with mp 116–117°, unchanged on admixture with flowers of sulfur which had been recrystallized from chloroform. There was also obtained a small quantity of bis (*p*ce-atoxyphenyl) sulfide with mp 94–94.5°, unchanged on admixture with an authentic sample,[14] prepared by the reaction of sulfur dichloride with phenol followed by acetylation.

Preparation and Decomposition of Methylsulfur Trichloride (II).—A solution of methyl disulfide (4.7 g, 0.05 mol) in 50 ml of anhydrous methylene chloride contained in a large tube was cooled in a Dry Ice–Acetone bath and chlorinated, with frequent shaking, until the red color of methanesulfenyl chloride had disappeared and a greenish yellow color indicated excess chlorine. The solid was then allowed to settle, the supernatant liquid was decanted, and without external cooling the remaining solvent was removed under the reduced pressure of a water pump. The tube containing the fine crystals of CH_3SCl_3 was then connected to a second tube cooled in a Dry Ice–Acetone bath and gently heated to start the decomposition. Occasional cooling of the tube kept the decomposition under control. The liquid residue was finally chilled, combined with the material which had collected in the cold trap, and subjected to pmr analysis. Other preparations were allowed to decompose in the presence of solvent. Table II shows the composition of several decomposition mixtures.

Sulfur dichloride in the reaction product was demonstrated as follows. A carbon tetrachloride solution of the decomposition products from 0.07 mol of CH_3SCl_3 was treated with 5.0 g of freshly distilled phenol and kept at 25° for 1 day. Evaporation of the solution in a rotary evaporator at 50° (14 mm) yielded a gum which was treated with acetyl chloride (10 ml) for 48 hr at 25°. Recrystallization of the gummy product obtained when the residue was poured on ice yielded 100 mg of bis(4-acetoxyphenyl) sulfide with mp 93.5–94° (lit.[14] mp 94°), unchanged on admixture with an authentic sample.

The Reaction of CH_3SCl with Sulfur Dichloride.—Methanesulfenyl chloride (1.0 g, 0.012 mol) was added in one portion to freshly distilled sulfur dichloride (4.5 g, 0.044 mol) contained in a test tube immersed in a 25° bath. An immediate exothermic reaction took place. At various time intervals small samples were removed, diluted to 10% concentration with carbon tetrachloride containing TMS, and analyzed by pmr spectroscopy. Integration of the resulting spectra gave the results shown in Table IV.

Table IV

Products from the Reaction of Methanesulfenyl Chloride[a] with Sulfur Dichloride[b]

Time	Products, mol %			
	CH_3SCl	CH_3S_2Cl	CH_3S_3Cl	CH_3S_4Cl
30 min	64	16	5	16
2 hr	49	25	10	15
24 hr	30	30	23	17
48 hr	28	22	31	19

[a] 0.012 mol. [b] 0.044 mol.

The Reaction between Methyl Mercaptan and Sulfur Monochloride.—Sulfur monochloride (13.5 g, 0.10 mol) was added dropwise over 40–50 min to a stirred solution of methylmercaptan (9.9 g, 0.206 mol) in 45 ml of carbon disulfide at −20°. After holding the pale yellow solution at −20° for 3 hr and storing for 12 hr at 0°, its pmr spectrum showed a single peak at δ 2.66 corresponding to methyl tetrasulfide.

In a second experiment methyl mercaptan (1.12 g, 0.023 mol) was allowed to vaporize slowly into a solution of sulfur monochloride (3.12 g, 0.023 mol) in 25 ml of carbon tetrachloride containing TMS and held at −30°. After the solution was warmed to room temperature, the pmr spectrum indicated that the major

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[12] H. Böhme and G. von Ham, *Ann.*, **617**, 62 (1958).

[13] W. E. Truce, G. H. Birum, and E. T. McBee, *J. Amer. Chem. Soc.*, 74, 3594 (1952).

[14] H. Tassinari, *Gazz. Chim. Ital.*, **17**, 85 (1887).

product was CH_3SSCl along with CH_3SCl, $CH_3S_6CH_3$, $CH_3S_5CH_3$, $CH_3S_4CH_3$, $CH_3S_3CH_3$, and $CH_3S_2CH_3$.

Esr Study of the Decomposition of CH_3SCl.—Preliminary spectra taken on bulk liquid samples at room temperature and at liquid nitrogen temperature gave no esr signals, even when the decomposition was proceeding vigorously. Presuming that the failure to observe the radical intermediate was due to a very short lifetime and low steady-state concentration, it was decided that the reaction be run on Vycor glass, a porous silica glass known to stabilize free radicals, in the hope that the Vycor support would permit the development of a detectable concentration of radical intermediates.

Before attempting to observe a radical intermediate produced by the decomposition of CH_3SCl, a study of the photodissociation products of the parent compound methyl disulfide was made. A small sample of Spectro-Grade methyl disulfide, CH_3SSCH_3, was first degassed by repeatedly freezing the liquid to liquid nitrogen temperature, evacuating the sample, and then allowing the sample to melt under vacuum in a closed vessel. This procedure was repeated until no gas bubbles were observed to evolve in the sample as it melted.

A Vycor glass rod was cleaned in HNO_3, thoroughly washed in water, treated with 30 cm of O_2 at 600° for 15 hr, and evacuated at 500° for 15 hr. Esr spectra of the Vycor glass and sample tube were taken at liquid nitrogen temperature, both before and after 20 min of irradiation with a mercury arc lamp (2537-Å light) at liquid nitrogen temperature, and no signals were observed. Enough CH_3SSCH_3 was then distilled onto the glass to constitute a surface coverage of one-half monolayer. During the distillation process, the Vycor was kept at liquid nitrogen temperature. The sample tube containing the sample then was sealed and allowed to come to room temperature.

Esr spectra of the methyl disulfide on Vycor taken at room temperature and liquid nitrogen temperature disclosed no signals. A sample then was irradiated at room temperature for 10 min intervals with light of 3550-Å wavelengths. No signals were observed even after 1 hr of irradiation. Finally, the sample at liquid nitrogen temperature was irradiated for 10 min with light of 2537-Å wavelength. Esr spectra taken immediately after irradiation and at liquid nitrogen temperature showed a strong signal with partially resolved hyperfine structure. Subsequent spectra at liquid nitrogen temperature showed a slow decay of this signal. Warming to room temperature and immediately cooling again to liquid nitrogen destroyed the signal completely. Two separate runs were made on the preparation and irradiation of methyl disulfide, confirming the reproducibility of the signal observed.

The procedure outlined above was repeated through the distillation of one-half monolayer of CH_3SSCH_3 onto a clean Vycor rod. The sample was allowed to come to room temperature and then cooled to liquid nitrogen temperature. Esr spectra showed no signal present. With the sample at liquid nitrogen temperature on the vacuum line (sealed), a sample of chlorine gas was introduced into the system. The chlorine was frozen into a liquid nitrogen trap and the solid chlorine was evacuated to remove any oxygen present. The chlorine then was warmed to room temperature, and a small amount, less than the amount of methyl disulfide previously adsorbed, was introduced into the sample tube. (Note—an equivalent vapor pressure of 25.3 cm of CH_3SSCH_3 was adsorbed onto the Vycor glass and 20 cm of Cl_2 was introduced in the same way through a volume calibrated cell, resulting in equal volumes of CH_3SSCH_3 at 25.3 cm and Cl_2 at 20 cm being introduced.) The sample then was warmed to Dry Ice–acetone temperature and allowed to stand for 2 hr.

An esr spectrum of the sample taken at liquid nitrogen temperature showed no signal. The sample then was warmed to room temperature for 5 min and cooled to liquid nitrogen temperature; another spectrum was taken. Again no signal was observed. The sample was warmed to room temperature and spectra taken at 20-min intervals for 4 hr. All spectra were observed at liquid nitrogen temperature and several were made at room temperature. No signals were observed. The sample was warmed to 50° for 1 hr and esr spectra were taken. No signals were observed. The sample was allowed to stand at room temperature for 15 hr, after which spectra were taken, then allowed to stand for 48 hr, after which spectra were taken. In no instance were any signals observed over a region of the spectrum between 1.6 gauss and 4 gauss. Over the 3 days in which experiments were performed, the sample was observed to darken in color, from practically colorless at the beginning to dark yellow at the end. At all times, the sample appeared clear and transparent.

The esr signal observed in irradiated methyl disulfide showed an asymmetric signal with four partially resolved hyperfine lines. The intensity ratios of the four lines were approximately 1:3:3:1, giving evidence that the hyperfine field was provided by the three protons on the methyl group. Without detailed consideration of the molecular orbital structure of the proposed radical $CH_3S\cdot$, it is impossible to make a definite assignment. Previous work done on methyl radical, $CH_3\cdot$, on Vycor glass indicates a hyperfine splitting of 23 gauss, and an asymmetry arising from surface effects.[15] Our observed hyperfine splitting of approximately 10 gauss shows that the species responsible for the observed esr signal is not $CH_3\cdot$, but rather some radical whose electron density is concentrated considerably farther from the methyl protons. When the irradiation procedure was repeated using deuteriomethyl disulfide, CD_3SSCD_3, the hyperfine structure of the signal completely disappeared, strengthening the belief that the original signal was due to the $CH_3S\cdot$ radical.

All of the esr spectra cited in this report were made on a Varian X-band spectrometer, using 100-kHz modulation and phase sensitive amplification. The spectrometer has a proven sensitivity to 3×10^{13} absolute number of spins giving a signal-to-noise ratio of 20:1.

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