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Thermal transformations of organic compounds of divalent sulfur

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Abstract. Published data on thermolysis of organic compounds of divalent sulfur and on thermal synthesis involving these compounds are summarised. The bibliography includes 201 references.

I. Introduction

Among the great variety of the ways of formation and chemical transformations of organic compounds of divalent sulfur, the thermal reactions, *i.e.*, the processes which occur at elevated temperatures in the absence of catalysts or promoters, take a special place. Such reactions proceeding in the earth's crust over millions of years have led to the formation of sulfur-bearing components of combustible fossils.

Mankind has dealt with the thermal reactions of sulfurous compounds from time immemorial, whenever a sulfur-containing material of organic origin is subjected to thermal treatment.

All combustible fossils, *viz.*, oil, bituminous and brown coals, oil-shales and natural gas, contain some amount of sulfur compounds. Therefore, high-temperature reactions of formation and thermal transformations of organosulfur compounds accompany virtually all processes of thermal fossil treatment. These are, for instance, the distillation and cracking of high-boiling oil fractions at temperatures from 300 to 800 °C and dry-distillation of bituminous and brown coals, oil-shales and peat at 450 – 1000 °C.

Thermal reactions of organosulfur compounds were studied in the very early stages of the development of chemistry as a science. However, the detailed exploration of these processes was started only in the past century.

The interest in thermal reactions of particular sulfur-containing organic compounds and in high-temperature syntheses involving these compounds is caused by the necessity to solve a number of problems, the most important of which are listed below.

1. The utilisation of sulfur-containig wastes in oil-refining, gas-, coal- and pulp-processing industries.

2. The development of thermal methods for the synthesis of organic and organosulfur compounds which are difficult to obtain alternatively.

3. Mechanistic studies of free-radical thermal reactions of sulfur-containing organic compounds occurring with involvement of free radicals. The development of methods for the generation of thiyl radicals, the evaluation of their reactivities and possible utilisation in high-temperature synthesis.

4. The generation of labile sulfur-containing intermediates, *e.g.*, thioformaldehyde, ethylenethiol, thioketones, sulfines, sulfenes, sulfenic acids, dialkylsilanethiols, *etc.*, using the flash pyrolysis technique and the development of methods for the detection of such intermediates.

The present review is devoted to the thermal transformations of organic compounds of divalent sulfur, except for thiones, and to the latest achievements in the field of high-temperature synthesis involving these compounds. Earlier, only a few papers [1, 2] with a brief survey of the literature on these issues have been published.

II. Thiols

1. Alkanethiols

Pyrolysis of alkanethiols in the gas phase at temperatures above 425 °C yields hydrogen sulfide and alkenes as the major products.[3, 4] The degree of decomposition of alkanethiols increases with an increase in the reaction time and temperature.[5] Aliphatic hydrocarbons do not react with alkanethiols or products of their decomposition. Benzene accelerates thermolysis of alkanethiols, whereas carbon dioxide or hydrogen inhibit this process. Higher homologues of alkanethiols are somewhat less stable than the lower ones. Linear alkanethioles are more stable than their branched isomers,[6] especially at higher temperatures (475 °C).

Hydrogen sulfide, hydrogen and methane are the pyrolysis products of methanethiol.[5] Dialkyl sulfides, thiophene, hydrogen sulfide and elementary sulfur have been found among the thermolysis products of other alkanethiols.[4] The decomposition is catalysed by metal sulfides and inhibited by cyclohexene.[7] Since in both cases the ratio of the surface to the volume of a reactor does not affect the reaction rate,[8] a free-radical chain mechanism for the thermolysis of alkanethiols has been suggested.[6, 9]

$$C_nH_{2n+1}SH \longrightarrow {}^{\bullet}C_nH_{2n+1} + {}^{\bullet}SH\,, \qquad (1)$$

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$$C_nH_{2n+1}SH + {}^{\bullet}SH \longrightarrow H_2S + {}^{\bullet}C_nH_{2n}SH\,, \quad (2)$$

$${}^{\bullet}C_nH_{2n}SH \longrightarrow C_nH_{2n} + {}^{\bullet}SH\,. \quad (3)$$

The main process is accompanied by parallel reactions (4) and (5).

$$C_nH_{2n+1}SH + {}^{\bullet}C_nH_{2n+1} \longrightarrow {}^{\bullet}C_nH_{2n}SH + C_nH_{2n+2}\,, \quad (4)$$

$${}^{\bullet}C_nH_{2n}SH \longrightarrow C_nH_{2n} + {}^{\bullet}SH\,. \quad (5)$$

The thermal decomposition of n- and *sec*-butanethiols in a flow system follows a molecular mechanism involving the synchronous abstraction of hydrogen from the α-carbon atom *via* a cyclic transition state.[10]

$$MeCH_2CH_2CH(H\cdots H)S \longrightarrow H_2S + MeCH_2CH{=}CH_2\,. \quad (6)$$

The decomposition of 1,1-dimethylethanethiol under the same conditions follows a free-radical mechanism.[9]

$$Me_3CSH \longrightarrow Me_3C^{\bullet} + {}^{\bullet}SH\,, \quad (7)$$

$$Me_3CSH + Me_3C^{\bullet} \longrightarrow Me_2(\dot{C}H_2)CSH + Me_3CH\,, \quad (8)$$

$$Me_2(\dot{C}H_2)CSH \longrightarrow Me_2C{=}CH_2 + {}^{\bullet}SH\,. \quad (9)$$

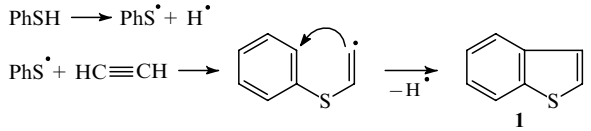
The activation energy for reaction (8) was found to be 7 kcal mol^{-1}. The pyrolysis of isomeric butanethiols in a static system occurs as a homolytic process in accordance with Eqns (1)–(8).[8] The thermal decomposition of cyclohexanethiol at 420–470 °C and under reduced pressure leads to the formation of hydrogen sulfide and cyclohexene.[11] Hydrogen sulfide accelerates this process, while cyclohexene retards it. In the presence of sulfur dioxide or over activated carbon at 425 °C, cyclohexanethiol is converted into benzenethiol.[12] α-Toluenethiol decomposes more readily than the lower alkanethiols yielding hydrogen sulfide and 1,2-diphenylethane.[4–6] Ethanedithiol is converted into thiirane and hydrogen sulfide on heating *in vacuo*.[13]

Most of the data available suggest a free-radical mechanism of alkanethiol decomposition, the initial step of which involves the cleavage of the C–S bond and generation of an $^{\bullet}SH$ radical. The activation energy of this reaction presumably equals the energy of the C–S bond dissociation. Owing to the generation of thiyl radicals, high-temperature reactions of alkanethiols with aryl halides can take place yielding the corresponding arenethiols.[14]

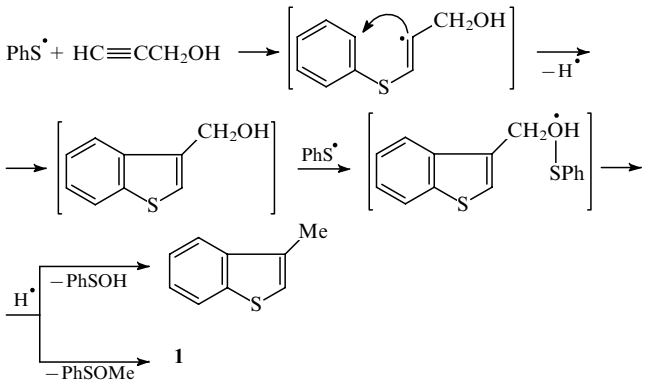
2. Arenethiols

Decomposition of benzenethiol begins at about 200 °C.[15] At 530–600 °C, benzenethiol, its derivatives and naphthalenethiol are converted into the corresponding diaryl sulfides.[16] These reactions are catalysed by copper sulfide, cadmium sulfide and activated carbon; in the presence of these catalysts conversions occur at lower temperatures (300–500 °C).[17,18] The *cis–trans*-isomerisation of the $C_{Ar}S-H$ bond takes place on flash vacuum pyrolysis of benzenethiols at 70–600 °C.[19] Under reduced pressure of ozone, benzenethiol decomposes at 30–125 °C to form oxygen, carbon dioxide, sulfur dioxide and polymeric products depositing on the reactor walls.[20]

Benzenethiol reacts with acetylene at 550–590 °C to give benzo[*b*]thiophene. A similar reaction with propargyl alcohol at 450–630 °C yields benzo[*b*]thiophene (**1**) and 3-methylbenzo[*b*]thiophene. It is supposed that pyrolysis of benzenethiol involves the generation of thiyl radicals, which add to the triple bonds of the substrates.[21]



1



Gas-phase reactions of benzenethiol with chlorobenzene and its *para*-substituted derivatives **2a–d** at 500–600 °C lead to symmetrical (**3a**) and unsymmetrical diaryl sulfides (**3b–d**).[22,23]

$$\underset{\mathbf{2a-d}}{p\text{-}XC_6H_4Cl} + PhSH \longrightarrow \underset{\mathbf{3a-d}}{p\text{-}XC_6H_4SPh} + HCl$$

X = H (**a**), Me (**b**), OMe (**c**), Cl (**d**).

Analogous diaryl sulfides are formed in the gas-phase reactions of *para*-substituted arenethiols with chlorobenzene at 500–620 °C.

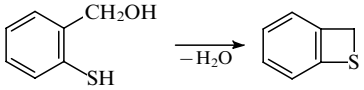
$$p\text{-}XC_6H_4SH + PhCl \longrightarrow p\text{-}XC_6H_4SPh + HCl\,.$$

The Arrhenius rate constants for these reactions have been determined.[23,24]

ñ	k /litre mol^{-1} s^{-1}
H	$3.89\times10^{10}\exp(-149.90/RT)$
Me	$3.48\times10^{9}\exp(-140.20/RT)$
OMe	$4.20\times10^{8}\exp(-116.57/RT)$
Cl	$7.76\times10^{13}\exp(-206.1/RT)$

Benzenethiol reacts in the gas phase at 400–530 °C with 1,2-dichloroethene (a 3:1 mixture of *E*- and *Z*-isomers) to give β-chlorovinyl phenyl sulfide (a 1:1 mixture of *E*- and *Z*-isomers) in 84% yield.[25] The reaction of benzenethiol with β-bromostyrene in the liquid phase at 140–160 °C leads to phenyl β-styryl sulfide.[26] At 125–215 °C, benzenethiol readily reacts with 2- and 4-bromophenols, 1-bromo-2-naphthol, 1-bromonaphthalene and 1-bromoanthracene to form the corresponding aryl phenyl sulfides.[27]

o-Chlorobenzenethiol and *o*-chloromethylbenzenethiol eliminate hydrogen chloride on flash vacuum pyrolysis.[19] At 700 °C in vacuum, hydroxymethylbenzenethiol is converted into benzothiete (**4**).[28]



4 (68%)

When a mixture of toluenethiol and ^{35}S-labelled ditolyl disulfide is heated, isotope exchange between thiyl radicals occurs. This process is accelerated by UV irradiation (Scheme 1). The reaction rate does not depend on the thiol concentration and is determined by the proneness of a disulfide to generate thiyl radicals as a result of S–S bond cleavage.[29]

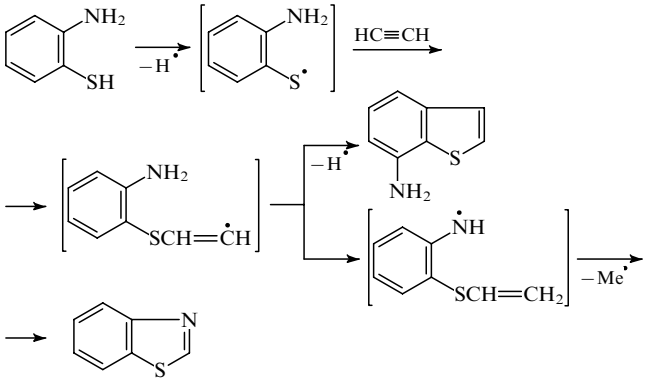
Scheme 1

$$RS^*{-}{*}SR \rightleftharpoons 2\,{}^{\bullet}RS^*,$$

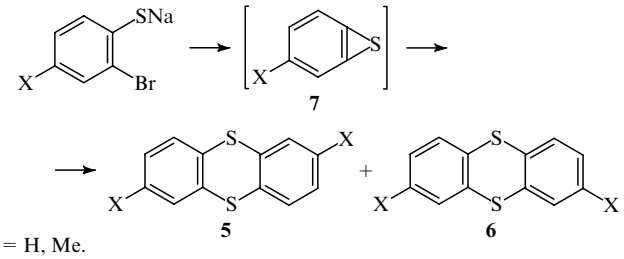
$${}^{\bullet}RS^* + HSR \rightleftharpoons RS^*H + {}^{\bullet}SR,$$

$${}^{\bullet}RS^* + {}^{\bullet}SR \rightleftharpoons RS^*{-}SR.$$

7-Aminobenzo[*b*]thiophene and benzothiazole are the major products in the gas-phase reaction of 2-aminobenzenethiol with acetylene at 450–600 °C. The maximum yields of these products (39% and 41%, respectively) are achieved at 600 °C.[30]

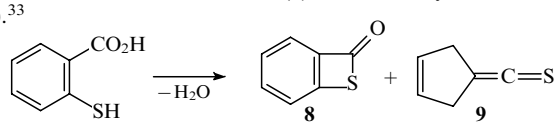


Pyrolysis of sodium 2-bromobenzenethiolate or its derivatives results in thianthrene or a 1:1 mixture of the corresponding isomeric thianthrenes **5** and **6**, thus suggesting the intermediate generation of short-lived thiirene **7**.[31,32]

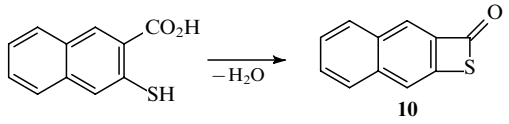


X = H, Me.

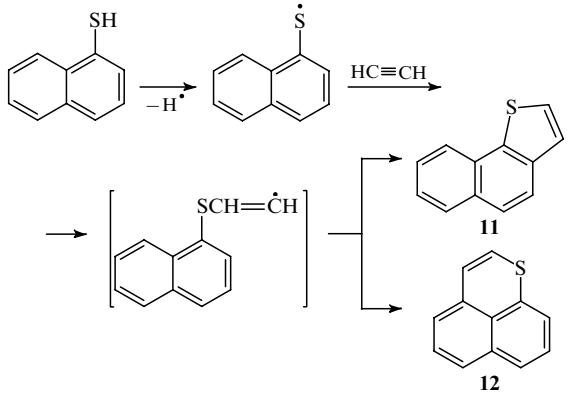
Flash vacuum pyrolysis of 2-mercaptobenzoic acid at 610 °C gives rise to benzothiet-2-one (**8**) and 1,4-dihydrofulvenethione (**9**).[33]



Similarly, 3-mercapto-2-naphthoic acid is converted into naphtho[2,3-*b*]thiet-2-one (**10**) on flash vacuum pyrolysis at 840 °C.[34]

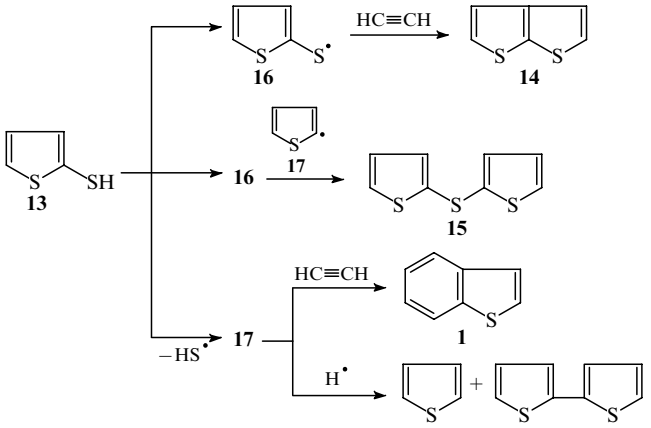


Naphthalene-1-thiol reacts with acetylene at 410–700 °C to form naphtho[1,2-*b*]thiophene (**11**) and 1-thiaphenalene (**12**) in 47% and 60% maximum yields, respectively.[35]

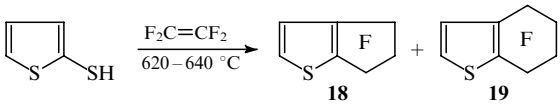


3. Hetarenethiols

The gas-phase reaction of 2-thiophenethiol (**13**) with acetylene at 500–600 °C affords thieno[2,3-*b*]thiophene (**14**) together with bis(2-thienyl) sulfide (**15**), thiophene and benzo[*b*]thiophene.[36] The complex character of transformations of 2-thiophenethiol is caused by the initial cleavage of the S–H and C–S bonds and the generation of radicals **16** and **17**, which either react with acetylene or recombine.



4,4,5,5,6,6-Hexafluorocyclopenta[*b*]thiophene (**18**) is the main co-pyrolysis product of 2-thiophenethiol with tetrafluoroethylene at 620–640 °C; 4,4,5,5,6,6,7,7-octafluorocyclohexa[*b*]thiophene (**19**) is also formed.[37]



The reaction mechanism involves the generation of difluorocarbene from tetrafluoroethylene, the replacement of the thiol group in 2-thiophenethiol by this carbene and the subsequent addition of the C-centered radical thus formed to tetrafluoroethylene. The product **19** is formed due to the elimination of the SH group from the parent thiol and the reaction of thienyl radical with tetrafluoroethylene.

Bromothiophenethiols are unstable and decompose on distillation with elimination of hydrogen bromide and hydrogen sulfide.[38]

III. Sulfides

Thermal decomposition of organic sulfides usually involves cleavage of the C–S bonds. The strength of this bond is different in different compounds. In dialkyl sulfides, either only the 3*p*-orbitals[39] or the hybrid *sp*- and *spd*-orbitals[40,41] are involved in the formation of the C–S σ-bond. The sulfur atom in sulfides can exhibit both electron-donating and electron-withdrawing properties. The latter is true when electron-withdrawing substituents are present in the α-positions to the sulfur atom. In the absence of such substituents the electron-withdrawing properties of the sulfur atom are not so pronounced, since its 3*d*-orbitals in the ground state are diffuse and the energy of their occupation by an electron cannot be compensated by the energy of covalent bond formation. The presence of electron-withdrawing substituents in sulfides favours the localisation of a positive charge on the sulfur atom, thus weakening the C–S bond. The lone electron pairs of the sulfur atoms in sulfides can conjugate with the π-system of a multiple bond or an aromatic ring (contribution of the structures with the $2p\pi-3p\pi$ bond). Owing to this effect, vinyl and aryl sulfides are rather weak electron donors and are characterised by high strengths of their C–S bonds.

1. Dialkyl sulfides and their derivatives

Studies on the pyrolysis of dialkyl sulfides were begun in 1928 with the aim of elucidation of the course of transformations of sulfur-containing components of raw oil and oil products upon refining.[42] It was found that diethyl sulfide decomposes at 500 °C to form considerable amounts of hydrogen sulfide, gaseous hydrocarbons (38 mass %) and ethanethiol (10 mass %).[42,43] Diisopentyl sulfide is much more stable. The products of its pyrolysis at 500 °C contain mostly the recovered diisopentyl sulfide, 3-methylbutane-1-thiol and thiophene derivatives. Among the gaseous products, alkanes (64%), alkenes (30%), hydrogen sulfide and hydrogen (0.5%) have been found. Dibutyl sulfide decomposes at 500 °C rather rapidly to form hydrogen sulfide and thiols; the thermolysis is accelerated in the presence of benzene and decelerated in the presence of n-heptane. In a vacuum, dibutyl sulfide decomposes at 380–410 °C yielding ethylene and polysulfides.[44] Isobutylene, hydrogen sulfide, isobutane, 1,1-dimethylethanethiol and sulfur are the pyrolysis products of di(*tert*-butyl) sulfide in a static system at 25–250 Torr and 360–413 °C. In the presence of cyclohexane, the yield of the thiol is sharply increased, while the yield of hydrogen sulfide is diminished several-fold and sulfur is not formed at all. In a flow system at 446–466 °C, small amounts of ethane, ethylene, propane, propylene and butene are also formed.[45] Thermal stabilities of most dialkyl sulfides both in pure form and in solutions of Surakhansk kerosene (fraction with b.p. 180–200 °C) have been determined.[46]

The decomposition of dialkyl sulfides in the gas phase at 400–800 °C to yield hydrogen sulfide and the corresponding alkenes follows a free-radical mechanism involving the intermediate formation of alkanethiols (Scheme 2).[42,47–49]

Scheme 2

$$R_2(Me)CSC(Me)R_2 \longrightarrow R_2(Me)CS^{\bullet} + R_2(Me)C^{\bullet},$$

$$R_2(Me)CS^{\bullet} \xrightarrow[-R^{\bullet}]{HR} R_2(Me)CSH \xrightarrow[-H_2S]{} R_2C{=}CH_2,$$

$$2\,R_2(Me)C^{\bullet} \longrightarrow R^2(Me)CC(Me)R_2.$$

If the pyrolysis of alkanethiols is carried out in vacuum (0.1 Torr), the yield of hydrogen sulfide is quantitative. Both unsymmetrical dialkyl sulfides and those with branched aliphatic chains are less thermally stable than symmetrical di(n-alkyl) sulfides.

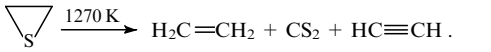
Dialkyl sulfides bearing methyl groups in the β-position are converted into the corresponding alkenes and hydrogen sulfide on flash vacuum pyrolysis at about 1000 K.

$$Me_2S \xrightarrow{1270\,K} H_2C{=}S + H_2S + CH_4 + CS_2,$$

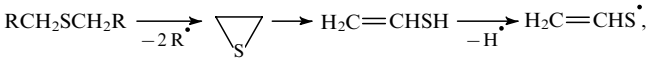
$$EtSMe \xrightarrow{1100\,K} H_2C{=}CH_2 + H_2C{=}S + H_2S + CH_4 + CS_2.$$

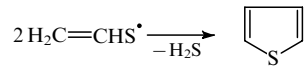
All derivatives with an α-methyl group and thiirane are more thermally stable and decompose at higher temperatures.[50]

Thiirane is the most stable sulfide despite the strain in its molecule. It forms ethylene, acetylene and hydrogen sulfide at 1270 K.[50]

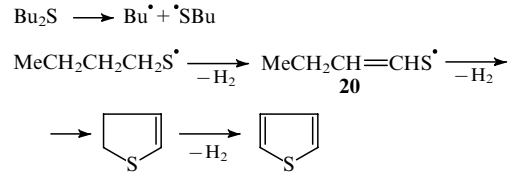


A new reaction pathway in the thermal decomposition of di(n-alkyl) sulfide leading to ethylenethiol and its further conversion into thiophene was found later.[51,52] Most likely, ethylenethiol is generated from dimethyl sulfide and other dialkyl sulfides according to a scheme common for all dialkyl sulfides through the initial formation of thiirane and its subsequent isomerisation.

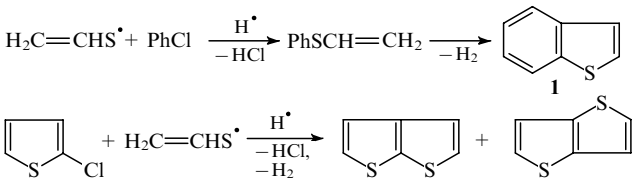




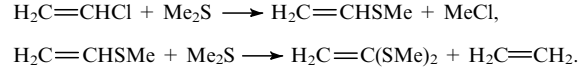
Thiophene is formed from butyl sulfide mostly as the result of an intramolecular cyclisation of the butenethiyl radical **20**.



The gas-phase reactions of dialkyl sulfides with chlorobenzene or 2-chlorothiophene lead to benzo[*b*]thiophene (**1**) and thienothiophenes, respectively.[52–55]



The reaction of dimethyl sulfide with vinyl chloride in the gas phase at 430–450 °C is accompanied by the formation of 1,1-bis(methylthio)ethane in 30% yield.[56]



Thermolysis of aliphatic sulfides in non-polar solvents (heptane, nonane, octane, decalin) under pressure occurs at 140–250 °C. In these reactions, sulfides and thiols can exchange their RS groups in accordance with the Scheme 1. Highest sulfides and lowest thiols have higher exchange rates.[48,57]

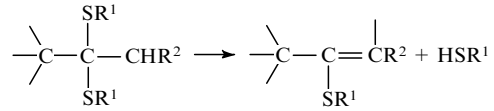
Decomposition of aliphatic sulfides at 300–400 °C in melts of $ZnCl_2-HCl$, $ZnCl_2-LiCl$, $ZnCl_2-SnCl_2$, $SnCl_2-KCl$, $ZnCl_2-KCl-NaCl$, $CuCl-KCl-NaCl$ eutectics leads to a mixture of alkanes, C_2-C_4 alkenes and hydrogen. Complexes of the $(Pr^i_2S)_3(ZnCl_2)_2$ type are formed as intermediate products. In zinc-containing eutectics, sulfides decompose faster to form predominantly alkenes the structures of which correspond to those of the alkyl chains in the starting sulfides. Sulfur is liberated as ZnS, which is then dissolved in the melt.[58]

Thermal decomposition of benzyl methyl sulfide and substituted 1,2-bis(benzylthio)ethanes proceeds according to the Scheme 2.[5,59]

Polyethylene sulfide decomposes at 230 °C to form hydrogen sulfide, ethane and a small amount of ethanethiol. The activation energy for this reaction corresponds to the energy of a homolytic cleavage of the C–S bond in macromolecular chains of polyethylene sulfide.[60]

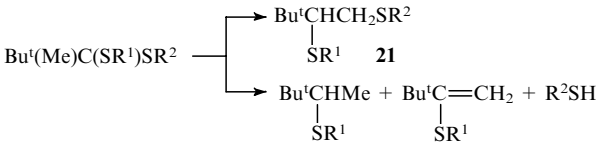
Thermolysis of bis(2-ethoxyethyl) sulfide, 1,1-bis(ethylthio)ethane and 1,3-bis(propylthio)propane involves the initial cleavage of the C–S bonds and occurs in accordance with reactions (1)–(4). The dissociation energies of the C–S bonds in these compounds have been calculated.[61]

Heating of dialkyl dithioacetals to 130 °C results in the elimination of a thiol and the formation of the corresponding vinyl sulfide.[62–64]

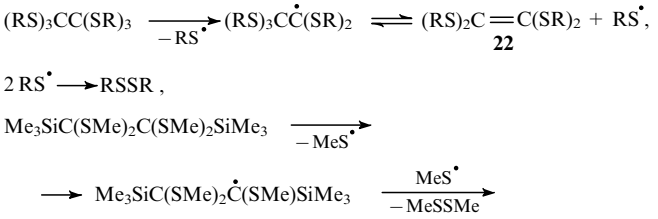


R^1 = Alk, Ar; R^2 = Alk.

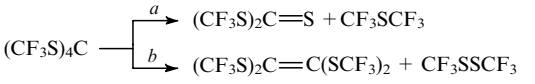
The main process is accompanied by the 1,2-migration of the thiyl group and the formation of the saturated sulfide **21** according the following scheme.[65–68]



Hexakis(alkylthio)- and tetrakis(methylthio)bis(trimethylsilyl)ethanes undergo thermolysis at 110 °C to form the corresponding ethylene derivatives **22** as the result of the alkylthiyl radical elimination.[69]



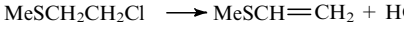
Vacuum pyrolysis of tetrakis(trifluoromethylthio)methane at 400 °C and 1–1.5 Torr leads mainly to bis(trifluoromethyl) trithiocarbonate together with small amounts of bis(trifluoromethyl) sulfide, bis(trifluoromethyl) disulfide and tetrakis(trifluoromethylthio)ethylene. The latter is formed as the major product on pyrolysis of tetrakis(trifluoromethylthio)methane at 400 °C under atmospheric pressure. The reaction mechanism involves the formation of free radicals and carbenes.[70]



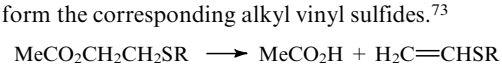
(*a*) 400 °C, 1 Torr; (*b*) 400 °C, 760 Torr.

Hexakis(trifluoromethylthio)ethane undergoes the C–C bond dissociation producing tris(trifluoromethylthio)methyl radicals even at 30 °C.[71]

2-Chloroethyl methyl sulfide eliminates hydrogen chloride at 360–400 °C.[72] The rate of its decomposition at 400 °C is 234-fold higher than that for ethyl chloride or ethylene chlorohydrin.[72]

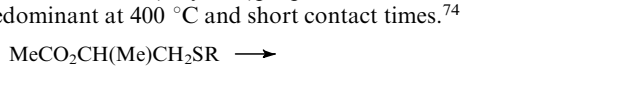


2-Alkylthioethyl acetates eliminate acetic acid at 460–465 °C to form the corresponding alkyl vinyl sulfides.[73]



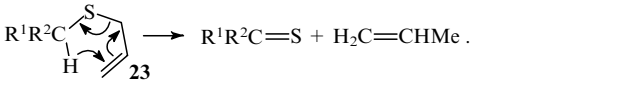
R = Me, Bu^n, Bu^i, Bn.

2-Alkylthio-1-methylethyl acetates are converted into a mixture of 1- and 3-(alkylthio)propenes at 500 °C. 3-Isomers are predominant at 400 °C and short contact times.[74]



Gas-phase thermolysis of alkyl and cycloalkyl allyl sulfides at 400–500 °C is accompanied by a molecular rearrangement involving either four- or six-membered cyclic transition states and leading to the corresponding alkenes and thioaldehyde.[75]

Upon flash pyrolysis at 600–650 °C, allyl sulfides **23** eliminate propene and are converted into the corresponding thiocarbonyl compounds.[76,77]

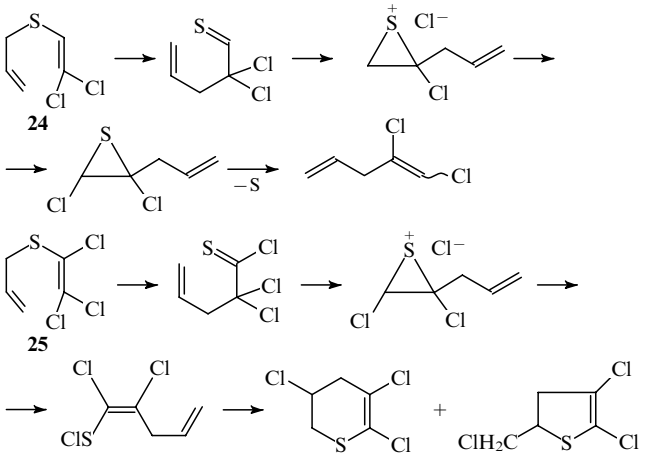


Thioacrolein and thiobenzaldehyde have been found in the pyrolysis products of diallyl and allyl benzyl sulfides.[76,78] 1,3-Bis(allylthio)propane decomposes at 520 °C to form unstable compounds which are rapidly converted into a polymer built of $-S(CH_2)_3S-$ units.[79] The extent of isomerisation of a *cis*-rotamer of methyl vinyl sulfide into the *gauche*-rotamer at 200–600 °C is 20%.[80]

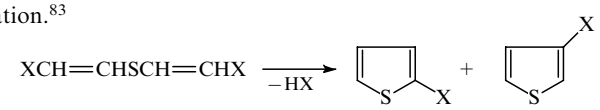
2. Vinyl and ethynyl sulfides

Thermolysis of *tert*-butyl 1-propenyl sulfide at 340–390 °C proceeds tenfold faster than that of di(*tert*-butyl) sulfide and is not inhibited by cyclohexene. Isobutene, isobutane and propenylthiyl trimer are the reaction products.[45]

Heating of allyl 2,2-dichlorovinyl sulfide (**24**) at 160–180 °C and of allyl 1,2,2-trichlorovinyl sulfide (**25**) at 100–120 °C results in unusual rearrangements leading to 1,2-dichloropenta-1,4-diene and a mixture of 2,3-dichloro-5-chloromethyl-4,5-dihydrothiophene and 3,5,6-trichloro-3,4-dihydropyran-2*H*-thione, respectively. The mechanism of the reactions involves a [3,3]-sigmatropic rearrangement and the formation of thiirane intermediates.[81]

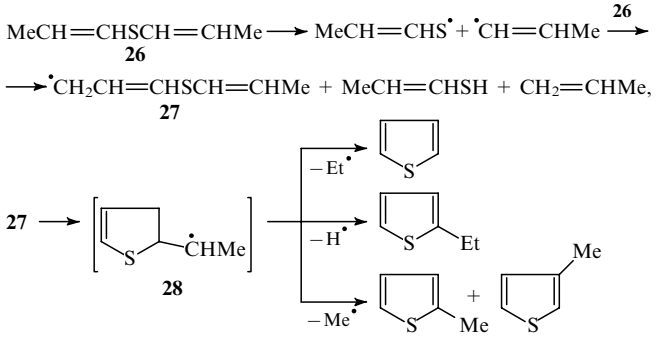


Gas-phase pyrolysis of divinyl sulfide at 450–560 °C gives rise to thiophene in 40% yield.[82] At 440–460 °C, 2-chlorovinyl sulfide is converted into 2- and 3-chlorothiophene predominantly through the involvement of the *trans*-isomer in this heterocyclisation.[83]



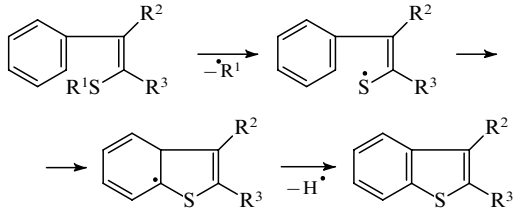
X = H, Cl.

Thermolysis of di(1-propenyl) sulfide (**26**) in the gas phase at 460–540 C leads to propenethiol, thiophene, methylthiophenes and 2-ethylthiophene. Heterocycles are formed as the result of the intramolecular cyclisation of the sulfide, involving the intermediate formation of radicals **27** and **28**.[84]



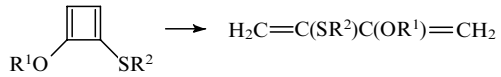
Upon pyrolysis (580 °C) under an atmosphere of nitrogen, alkyl β-styryl sulfides undergo intramolecular heterocyclisation to

give the corresponding benzo[*b*]thiophene derivatives in 50% – 70% yields.[85]



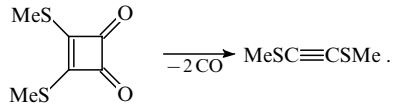
R^1, R^2, R^3 = Alk, Ph.

2-Alkoxy(acyloxy)-3-alkyl(aryl)thiocyclobutadienes are converted into the corresponding dienes on heating to 350 °C as the result of the cleavage of the C(1) – C(4) bond in the rings.[86]



R^1, R^2 = Me, Ph, CO_2Me, 4-ClC_6H_4, 4-$MeOC_6H_4$, COMe.

Pyrolysis of 3,4-bis(methylthio)cyclobutene-1,2-dione at 450 °C leads to the ring opening with the formation of bis(methylthio)acetylene and CO. At 550 °C, hydrogen sulfide and methanethiol are also formed in this reaction.[87]



Allyl and propargyl 1,1-dicyano-2-ethoxyvinyl sulfides undergo the Claisen rearrangement on distillation being converted into the corresponding *O*-ethyl thiocarboxylates **29**.[88]

$(CN)_2C{=}C(OEt)SR \longrightarrow EtOC(S)C(CN)_2R$

29

R = $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$.

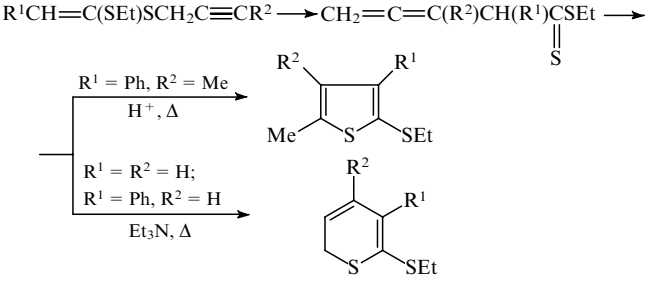
On heating, ketene allyl thioacetals **30** are converted into α-allyl dithiocarboxylates.[89–91]

$XYC{=}C(SR^1)SR^2 \rightleftharpoons XYC(R^2)C(S)SR^1$

30

X, Y = CO_2Me, CO_2Et, CN, Ac, Bz *etc.*; R^1 = All, Alk; R^2 = All.

Ketene allenyl thioacetals undergo the Claisen rearrangement on heating to 80 – 100 °C to form ethyl acetylenedithiocarboxylates, while ketene ethynyl thioacetals are converted at 100 – 140 °C into dithiocarboxylates containing the allene fragment.[92,93] In some cases, the latter undergo partial or complete heterocyclisation on distillation to form 2*H*-thiopyrans or substituted thiophenes.



Vacuum pyrolysis of *tert*-butynyl ethynyl sulfide at 500 °C results in the formation of thioketene (**31**), which is more stable than its tautomers, *viz*., thiirane and ethylthiol.[94]

$HC{\equiv}CSBu^t \longrightarrow [HC{\equiv}CS^{\bullet} + {}^{\bullet}Bu^t] \longrightarrow$

$\longrightarrow [HC{\equiv}CSH \rightleftharpoons H_2C{=}C{=}S] + H_2C{=}CMe_2$.

31

On heating to 250 °C, dibenzyl sulfide is converted into stilbene with liberation of hydrogen sulfide. The latter partly reduces stilbene to toluene. This produces sulfur which reacts with stilbene to give tetraphenylthiophene.[95]

3. Aryl and hetaryl sulfides

Pyrolysis of a mixture of methyl phenyl sulfide and toluene vapours at 600 °C leads to methane, benzenethiol and dibenzyl. This free-radical reaction was proved to follow a monomolecular mechanism.[96]

$PhSMe \longrightarrow PhS^{\bullet} + Me^{\bullet}$,

$PhS^{\bullet} + PhMe \longrightarrow PhSH + PhC^{\bullet}H_2$,

$Me^{\bullet} + PhMe \longrightarrow CH_4 + PhC^{\bullet}H_2$,

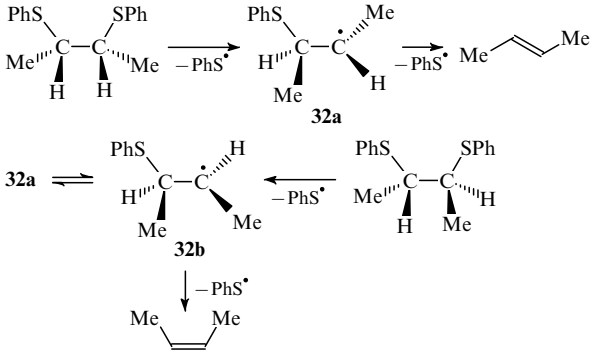
$2\,PhC^{\bullet}H_2 \longrightarrow PhCH_2CH_2Ph$.

The kinetics of the thermal decomposition of methyl phenyl sulfide and benzyl methyl sulfide at low pressure was studied, and the dissociation energies of the PhS – Me and $PhCH_2$ – SMe bonds were found to be 67.5 and 59.4 kcal mol^{-1}, respectively.[97] The enthalpies of the formation of radicals $MeS^{\bullet}$ and $PhS^{\bullet}$ are 34.2 and 56.8 kcal mol^{-1}, respectively.[97]

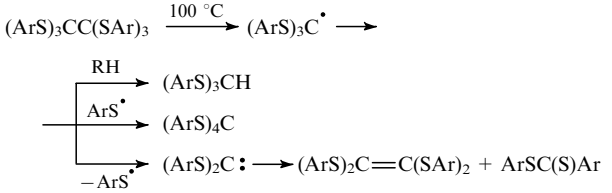
Heating of benzyl phenyl sulfide to 250 – 270 °C leads to a mixture of liquid and gaseous products, *viz*., toluene, 1,2-diphenylethane, biphenyl, diphenylmethane, stilbene, benzenethiol, tetraphenylthiophene, benzaldehyde, hydrogen sulfide and carbon dioxide. The yield of benzenethiol reaches 31%.[98]

Flash pyrolysis of benzyl phenyl sulfide in vacuum at 800 °C results in the formation of 1,2-diphenylethane and diphenyl disulfide, which are the recombination products of benzyl and phenthiyl radicals, respectively.[99]

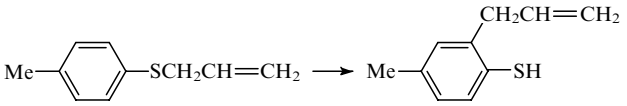
1,2-Bis(phenylthio)ethane and its derivatives decompose at 350 °C to form benzenethiol, diphenyl disulfide and the corresponding alkene. The reaction occurs stereospecifically as a *trans*-elimination. Radicals **32a** and **32b** are converted into the corresponding butenes much more rapidly than they isomerise.[100]



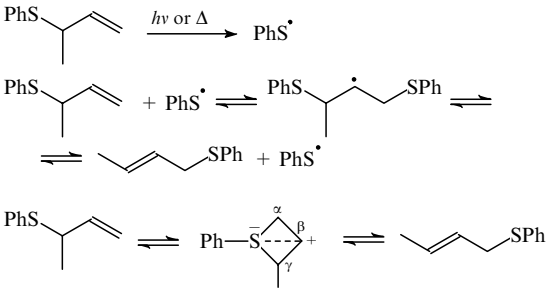
Decomposition of hexakis(phenylthio)ethane begins at 100 °C to generate tris(phenylthio)methyl radicals detectable by EPR spectroscopy.[101–104] The cleavage of the C – C bond in hexakis(phenylthio)ethane is mostly caused by steric factors (repulsion of the ArS substituents). The disproportionation of the $(ArS)_3C^{\bullet}$ radicals is responsible for the formation of the major reaction products.[101]



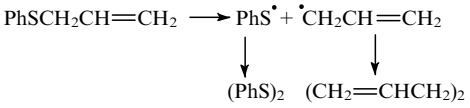
On heating to 200 °C, allyl aryl sulfides undergo the thio-Claisen rearrangement.[105]



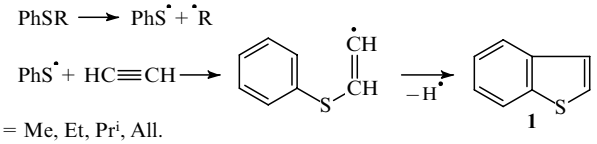
Allyl 2-benzofuryl and allyl 2-benzothienyl sulfides behave similarly on heating. In the latter case, the rearrangement product undergoes further heterocyclisation.[106,107] The thioallyl rearrangement usually precedes the thio-Claisen rearrangement in allyl aryl sulfides. Mechanisms involving the intermediacy of free radicals or a four-membered transition state have been considered for these rearrangements.[108]



On flash vacuum pyrolysis, allyl phenyl sulfide undergoes initial cleavage of its C–SPh bond resulting in the formation of phenthiyl and allyl radicals and their subsequent dimerisation.[50]



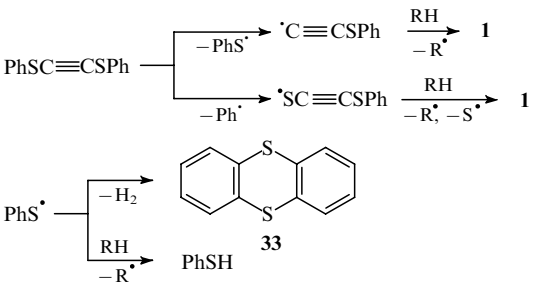
The gas-phase reactions of alkyl phenyl and allyl phenyl sulfides with acetylene at 480–600 °C occur selectively yielding benzo[*b*]thiophene (**1**) as the addition product of phenthiyl radicals to the triple bond of acetylene.[109]



R = Me, Et, Pr^i, All.

Benzothiophene (**1**) was obtained in the highest yield starting from allyl phenyl sulfide, and this reaction occurs at lower temperature. At 600 °C, vinyl phenyl sulfide undergoes an intramolecular cyclisation to form benzothiophene.[110]

Pyrolysis of bis(phenylthio)acetylene at 560 °C leads to diphenyl sulfide, benzenethiol, thianthrene (**33**) and benzothiophene (**1**). The reaction involves the generation and subsequent transformations of phenyl and phenylthioethynylthiyl radicals.[111] In the presence of chlorobenzene, diphenyl sulfide is formed upon its reaction with phenthiyl radicals.



Diaryl sulfides differ from other diorganyl sulfides in that they possess rather strong C–S bonds. These sulfides are usually stable at 400–600 °C, while at higher temperature they undergo intramolecular cyclisations. Thus at 700–750 °C, diphenyl sulfide, phenyl *o*-tolyl sulfide and 2-hydroxyphenyl phenyl sulfide are converted into dibenzothiophene, thioxanthene and 4-hydroxydibenzothiophene, respectively.[112] Dithienyl sulfide is less stable: it decomposes at 500–600 °C to give thiophene, isomeric thiophenethiols and bithienyls and also isomerises into 2,3-dithienyl sulfide. These conversions result from the addition of thiyl radicals to the double bonds of thiophene and to the sulfur atom of sulfides.[113]

4. Sulfenyl halides and sulfonium salts

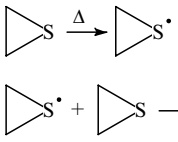
Heating of alkanesulfenyl chlorides to 100 °C affords alkyl chlorides in low yield.[114] Flash pyrolysis of methanesulfenyl chloride at 590 °C leads to thioformaldehyde.[115] Benzenesulfenyl chloride decomposes at 100 °C to form chlorobenzene, diphenyl disulfide and sulfur monochloride. At 90 °C, 4-methyl- and 4-methoxy-benzenesulfenyl chlorides eliminate sulfur to yield the corresponding *para*-substituted chlorobenzenes.[114]

Phenyldiarylsulfonium halides undergo complete thermolysis at 250 °C yielding a mixture of aryl halides and diaryl sulfides containing all possible combinations of the aryl substituents in their molecules. A pair 2,5-$Me_2C_6H_3X$ and 4-MeC_6H_4SPh is formed in the highest yield upon pyrolysis of (2,5-dimethylphenyl)(phenyl)(*p*-tolyl)sulfonium chloride.[116]

5. Cyclic sulfides

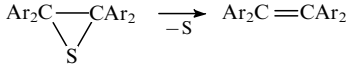
Thiirane (ethylene sulfide) is the simplest three-membered cyclic sulfide with a thermodynamically unfavourable three-centre dipolar atomic system which is, however, stabilised by the efficient involvement of the non-bonding orbitals of the heteroatom into the frontal interactions.[117] A characteristic feature of thiirane and its derivatives is their capacity to split the sulfur atom off yielding the corresponding alkene. The conditions required for this reaction, which can sometimes occur at temperatures below 0 °C, depend on the nature of substituents in the thiirane ring. As usual, the substituents exerting the –E-effect and many π-donating systems facilitate the desulfuration.

Thiirane itself decomposes completely in the gas phase at 250 °C into ethylene and elementary sulfur. This is a first-order homolytic reaction the activation energy of which is 40.2 kcal mol^{-1}. Since this value is lower than the enthalpies of the direct elimination of the sulfur atom from the thiirane ring or of the cleavage of this ring, both these processes can be ruled out from mechanistic considerations. A reaction mechanism involving the intermediacy of the excited thiirane has been suggested.[118,119]



This mechanism is supported by the complete stereospecificity of the low-temperature thermolysis of *cis*- and *trans*-2,3-dimethylthiiranes.[118]

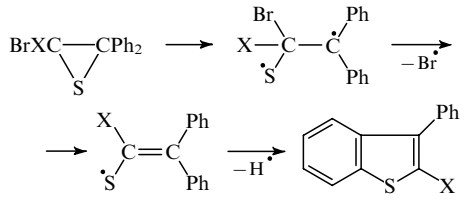
Gas-phase pyrolysis of thiirane at 500–600 °C results in the formation of hydrogen sulfide, ethylenethiol, thiophene, benzothiophene and hydrocarbons C_1–C_4 (Ref. 120). Alkyl-, cycloalkyl-, 2-aryl- and 2,3-diaryl-thiiranes eliminate sulfur on distillation or moderate heating.[121–124] Only tetraarylthiiranes decompose at higher temperature (180–215 °C) to form tetraarylethylenes.[125,126]



Ar = Ph, 4-$MeOC_6H_4$, 4-BrC_6H_4, 4-$Me_2NC_6H_4$ *etc.*

3,3-Dichloro-2,2-diphenylthiirane undergoes a similar reaction.[127]

Thermal transformations of 3-bromo- and 3,3-dibromo-2,2-diphenylthiiranes are accompanied by intramolecular cyclisations of the initially generated thiyl radicals without elimination of sulfur.[127]

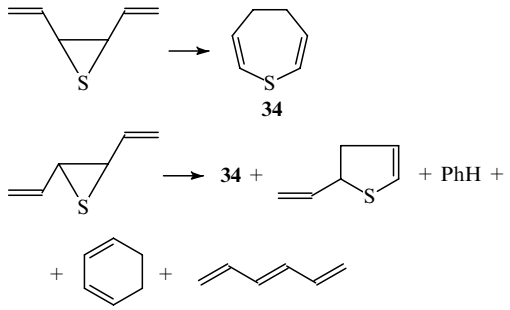


X = H, Br.

3-Chloro-2,2-diphenyl-3-X-thiiranes also cyclise into the corresponding benzothiophenes on heating.[128, 129]

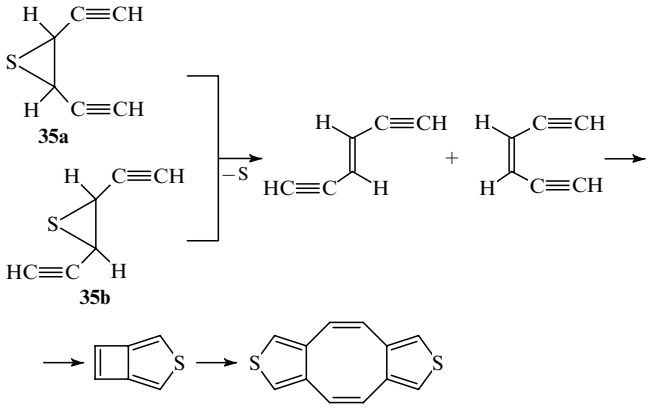
Tetrafluorothiirane is distinguished by its high thermal stability. Its partial conversion into difluorothioformaldehyde, tetrafluoroethylene and a number of other products takes place only at 430 °C.[130]

On thermolysis at 340 °C, *cis*- and *trans*-divinylthiiranes undergo the Cope rearrangement into 4,5-dihydrothiepane (**34**).[131]



Dihydrothiophene, thiophene and *cis*- and *trans*-1-phenylbutadienes are the thermolysis products of *cis*- and *trans*-2-vinyl-3-phenylthiiranes at 360–400 °C.[131] When the concentration of thiirane is relatively high, a bimolecular mechanism predominates.[132] With a decrease in the concentration of thiirane in the reaction, monomolecular desulfurisation becomes the main process.

Pyrolysis of *cis*- (**35a**) and *trans*-2,3-diethynylthiiranes (**35b**) in a solution (toluene-d_8, 100 °C) yields only sulfur-free alkenes. If the pyrolysis of *cis*-isomer **35a** is carried out in a flow system, thienocyclobutadiene is formed in 6% yield along with alkenes. This diene dimerises on standing in benzene solution.



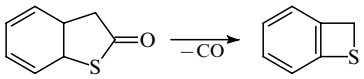
Thus, the data presented here show that in the thermal decomposition of thiirane and its derivatives at temperatures up to 200–350 °C the elimination of sulfur is the main process. The isomerisation of the thiirane ring into an ethylenethiol form is observed only for bromine-substituted diphenylthiiranes. Divinylthiiranes also undergo intramolecular rearrangements. The high-temperature (up to 1000 °C) thermolysis of thiiranes results mostly in the cleavage of the C–S bond in the thiirane ring and its partial isomerisation into ethylenethiol rather than in elimination of sulfur. Unstable biradicals and thiyl radicals thereby formed undergo further decomposition into hydrogen sulfide, hydrocarbons and thiophene.[120]

Four-membered sulfur-containing heterocycles are rather unstable. Thietane (trimethylene sulfide) decomposes on heating to 95 °C. Its thermal destruction in vacuum (250 °C, 10 Torr) leads to an oily polymer and small amounts of hydrogen sulfide, ethylene, ethane, propene and propane.[117, 131] Thioformaldehyde is the product of the flash pyrolysis of thietane at 1000 °C.[133] Photolysis of thietane, 3-ethyl-2-propylthietane and 3-methylthietane in the gas phase, solution and glassy matrices was shown[134] to involve the cleavage of the C–S bonds and the formation of 1,4-biradicals. Derivatives of thiete (thiacyclobutene) undergo polymerisation even at room temperature. They are relatively stable only in solution.[135]

Five-membered sulfur-containing heterocycles are more stable. Thiolane is stable below 450 °C. The extent of its decomposition at 500 °C is 10% and that at 550 °C is 60%; the products formed include thiophene, hydrogen sulfide and hydrocarbons. 1-Thiaindan decomposes at 450 °C into hydrogen sulfide and thiols.[136]

Thermal decomposition of 2,5-dihydrothiophene at 600 °C leads to thiophene and hydrogen in the ratio of 1 : 1 along with hydrogen sulfide and polymeric products. Hydrogen is liberated in this reaction synchronously with other products.[119, 137]

Benzo[b]thiophen-2(3*H*)-one is converted into benzothiete on flash vacuum pyrolysis (700 °C, 0.05 Torr).[138]



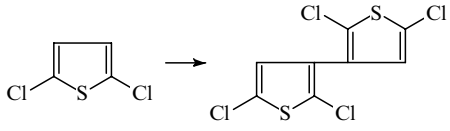
(98%)

2,3-Dihydrothiophene-2,3-diones and their analogues eliminate CO on flash vacuum pyrolysis to form the corresponding thietones.[139]

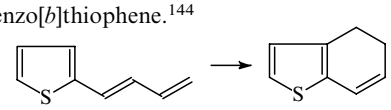
Thiophene is stable up to 800 °C, while at 850 °C it decomposes to give a mixture of isomeric bithienyls, benzothiophene, phenylthiophene (7%–8% overall yield) and gaseous products.[140] In a flow-recycling system, the yields of isomeric bithienyls, benzothiophene and phenylthiophene are 30%, 20% and 10%, respectively. Hydrogen sulfide accelerates the thermal transformation of thiophene into isomeric bithienyls, among which 2,3′- and 3,3′-isomers predominate (95% total yield).[141]

Hydrogen sulfide, thiophene and benzene are the main pyrolysis products of 2-methylthiophene at 825 °C. Aromatic compounds are formed in this reaction as the result of condensations of intermediate radicals and carbenes.[142]

2,3-Dichlorothiophene undergoes the condensation into tetrachloro-3,3′-bithienyl at 560–570 °C.[143]

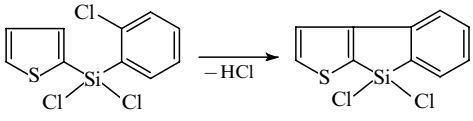


Vacuum pyrolysis of 1-(2-thienyl)buta-1,3-diene at 525–575 °C and 0.1–1.0 Torr leads to 4,5-dihydrobenzo[*b*]thiophene.[144]

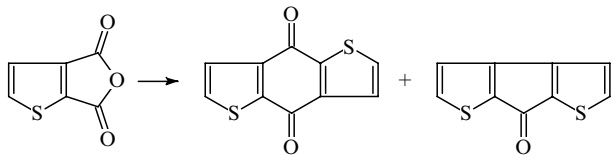


(70%)

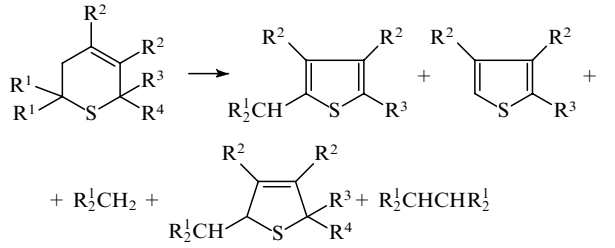
2-Chlorophenyl(2-thienyl)dichlorosilane undergoes heterocyclisation at 480–700 °C.[145]



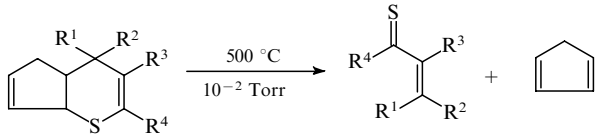
Vacuum thermolysis of thiophene-2,3-dicarboxylic anhydride at 500 °C (1–5 Torr) in a flow system leads to annelated thiophenes, which can be considered as analogues of anthraquinone and fluorenone.[146]



Six-membered sulfur-containing heterocycles are less stable than thiophene and its derivatives. Under an argon atmosphere, dihydro-2*H*-thiopyrans undergo rearrangements into the corresponding thiophenes and dihydrothiophene on heating to 260 °C.[147]

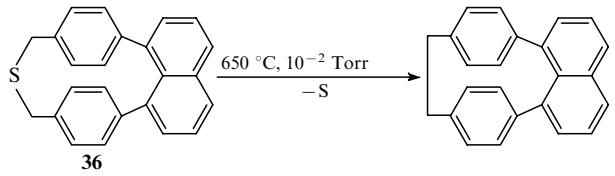


Fused dihydro-2*H*-thiopyrans undergo a retro-Diels–Alder reaction on flash vacuum pyrolysis.[148]



Tetrasubstituted 4-thiapyrones rearrange into the corresponding 2-thiapyrones on heating to 200–250 °C.[149]

On flash vacuum pyrolysis, the polynuclear cyclic sulfide **36** eliminates the sulfur atom to form a cyclophane-like hydrocarbon.[150]

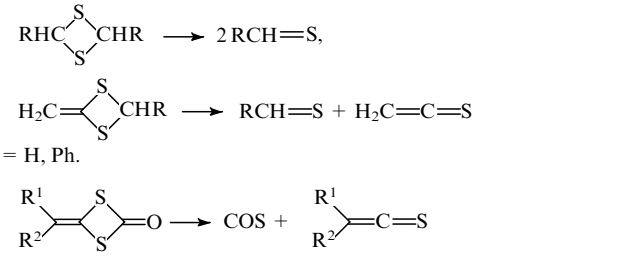


36

Benzothiophene and dibenzothiophene are fairly stable in the gas phase. Both the aromatic and thiophene rings are hydrogenated in the reaction of benzothiophene with atomic hydrogen at 150 °C. At 560 °C, only the thiophene ring is hydrogenated providing vinyl phenyl sulfide.[151, 152] Octachloro-2,3-dihydrobenzothiophene is converted into hexachlorobenzothiophene at 200–250 °C.[153]

Dibenzothiophene does not decompose up to 900 °C. Thianthrene decomposes partially at 550 °C to form dibenzothiophene and benzene. Due to the high stability of these heterocycles, not all sulfur from cyclic sulfides is lost on pyrolysis of coals.[154]

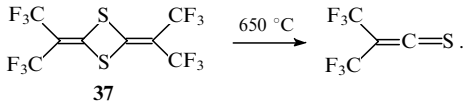
The direction of the gas-phase thermolysis of dithiacycloalkanes and alkenes depends on the nature of the heterocycle. The vacuum thermolysis of 1,3-dithianes[77] and -dithietanes[155, 156] at 300–750 °C leads to their cleavage into starting monomers, *viz.*, thioaldehydes and thioketenes.



R = H, Ph.

R^1 = CN: R^2 = CN, COMe, COOEt.

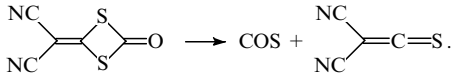
Bis(trifluoromethyl) thioketene is obtained on pyrolysis of its dimer **37** at 650 °C; it can be stored in a sealed tube for several months.[157] Hydrogen sulfide, tetrakis(trifluoromethyl)allene and perfluoroisobutylene are the other products of this reaction.



37

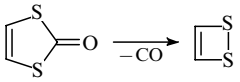
Thioketenes were characterised by photoelectron spectroscopy (PES) and isolated in the form of dimers or adducts of 1,3-dipolar cycloaddition reactions.

Dicyanothioketene is formed in the vacuum pyrolysis of 2-(4-oxo-1,3-dithietane-2-ylidene)malononitrile (470 °C, 0.05 Torr). However, this thioketene appeared to be extremely unstable and was characterised only by PES.[158]



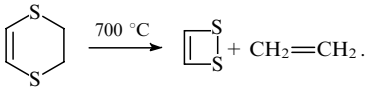
Dithiaspirocycloalkanes with five- and six-membered rings undergo pyrolysis at 600 °C to give cyclopentanethione or cyclohexanethione.[159] Ethylenedithioketal of quadricyclanone undergoes extensive fragmentation at 200 °C to form benzene and hydrogen sulfide.[160]

On flash pyrolysis, 1,3-dithiol-2-one (**38**) and its derivatives lose CO to give the corresponding dithietes.[161]

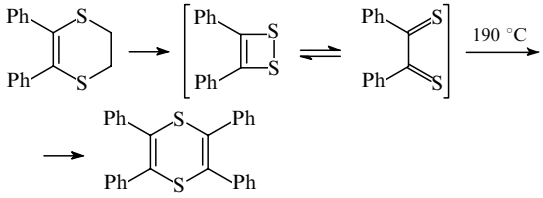


38

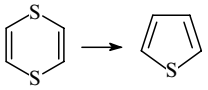
Dithiete and ethylene are formed in the flash vacuum pyrolysis of 2,3-dihydrodithiine at 700 °C.[161]



Flash pyrolysis of 1,2-diphenyl-5,6-dihydro-1,4-dithiine at 720 °C (0.1 Torr) involves the elimination of ethylene and leads to polymers which are converted into tetraphenyldithiine on heating in decalin.[162] 1,2-Dithietes or α-dithiones are presumably the intermediate products in these reactions.

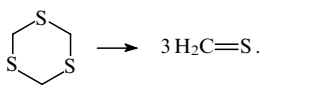


The main direction in the flash vacuum thermolysis of 1,4-dithiines at 700 °C involves the extrusion of sulfur and the formation of thiophene.[161]



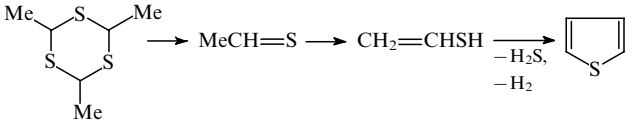
Substituted 1,4-dithiines eliminate sulfur even on heating to only 200 °C.[163–165]

1,3,5-Trithiane and its derivatives decompose to the starting monomers on pyrolysis. Thus thioformaldehyde is formed from trithiane at 600 °C in vacuum.[166, 167]

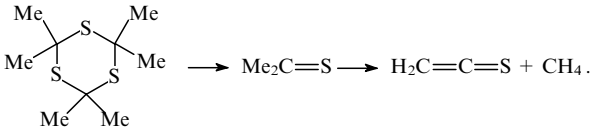


Pyrolysis of 2,4,6-trimethyl-1,3,5-trithiane at 600 °C in vacuum leads to monomeric thioacetaldehyde, which has a lifetime of

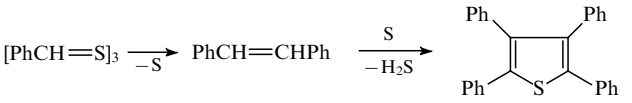
10 s;[166, 167] at 450–600 °C and normal pressure; ethylenethiol and thiophene are formed. Thiophene is obtained as the result of the initial isomerisation of thioacetaldehyde and subsequent intermolecular condensation of ethylenethiol.[168]



Vacuum pyrolysis of hexamethyltrithiane at 500 °C leads to thioacetone, while at 900 °C it yields thioketene, which results from the thermal decomposition of thioacetone.[169] Under ordinary conditions, monomeric thioacetone is stable for only a few minutes.



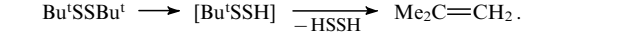
The fact that thiobenzaldehyde trimer and high-molecular-mass thiobenzaldehyde polymer decompose at 150 °C producing sulfur and stilbene from which tetraphenylthiophene is formed at 250 °C was established back in the past century.[170, 171]



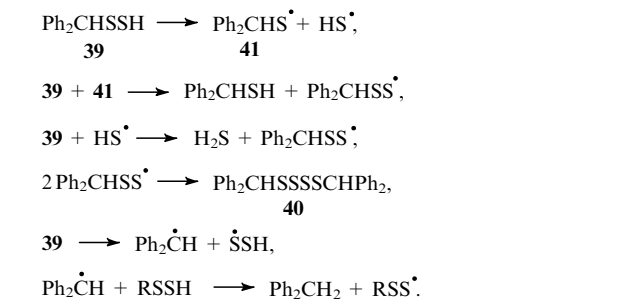
Heating of thioacetophenone trimer with rapid distillation of the thermolysis products yields monomeric thioacetophenone. The latter, as well as its trimer, is converted into 2,4-diphenylthiophene, stilbene and ethylbenzene on heating.[172]

IV. Hydrodisulfides

Hydrodisulfides (RSSH) are unstable compounds and are often formed as intermediates in the thermolysis of organic disulfides. Thus the thermal decomposition of di(*tert*-butyl) disulfide apparently results in the initial formation of *tert*-butyl hydrodisulfide, which then rapidly decomposes into isobutene and H_2S_2.[173]



Diphenylmethyl dihydrodisulfide (**39**) decomposes at 120 °C to form diphenylmethane, bis(diphenylmethyl) tetrasulfide (**40**) and hydrogen sulfide. The reaction involves the initial generation of thiyl radicals **41**, which further react with the starting hydrodisulfide according to a free-radical chain mechanism.[174]



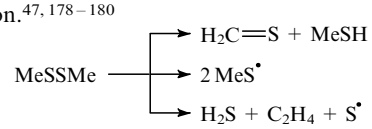
V. Disulfides

Organic disulfides are less stable than the corresponding sulfides and therefore readily undergo diverse transformations and react with organic compounds under the liquid- and gas-phase thermolysis conditions.

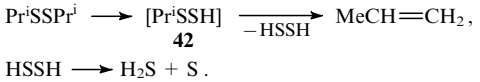
1. Dialkyl disulfides

Decomposition of dialkyl disulfides begins at temperatures approximately 200–250 °C lower than those required for the thermolysis of the corresponding sulfides.[45] Temperatures at which dialkyl disulfides decompose completely were determined by PES and decrease with an increase in the length and the branching of an alkyl chain in disulfides (from 1100 K for Me_2S_2 to 690 K for $Bu^t_2S_2$).[50]

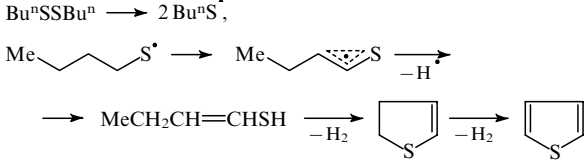
The corresponding thiols, alkyl sulfides, hydrogen sulfide, saturated and unsaturated hydrocarbons are the main products in the gas-phase pyrolysis of dialkyl disulfides at 500 °C. Also, a small amount of thiophene is formed.[49] At higher temperatures (580–610 °C), carbon disulfide is the major liquid product (23.5% yield) in the pyrolysis of dimethyl disulfide. From diethyl disulfide under the same conditions, carbon disulfide is formed in only 9.5% yield.[175] Flash vacuum pyrolysis of dimethyl disulfide at 300–700 °C leads to methanethiol and thioformaldehyde, while at 900 °C it mainly yields carbon disulfide.[77, 176] The addition of methanethiol to the reaction does not affect its rate, whereas hydrogen sulfide substantially accelerates the pyrolysis of dimethyl disulfide.[177] Thioformaldehyde and methanethiol were detected and characterised by PES. Both molecular and radical mechanisms are assumed to be responsible for their formation.[47, 178–180]



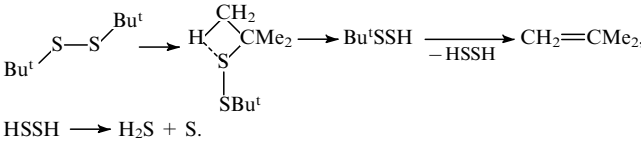
The reactions of thiyl radicals with the starting disulfide lead to its complete decomposition. Vacuum pyrolysis of diethyl disulfide occurs in a similar way.[178] Flash pyrolysis of diisopropyl disulfide presumably occurs through the stage of formation of isopropyl hydrodisulfide (**42**), since more stable propane-2-thiol was not found among the pyrolysis products.[50]



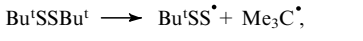
A liquid product obtained upon gas-phase pyrolysis of di(n-butyl) disulfide at 500–550 °C represents pure thiophene (40%–60% yield). Gaseous hydrocarbons C_1–C_4 and hydrogen sulfide are the other products.[181] The reaction mechanism involves the thermal generation of butylthiyl radicals and their intramolecular cyclisation into dihydrothiophene with its further dehydrogenation.[137, 182]



Gas-phase pyrolysis of di(*tert*-butyl) disulfide at 330–400 °C in both a flow and a static systems (60–212 Torr) leads to isobutene and *tert*-butyl hydrosulfide. The latter then decomposes into sulfur and hydrogen sulfide on the reactor walls.[183]



Carbon disulfide, hydrogen sulfide, acetylene and methane are formed at 1127 °C.[45] Since the C–S bond in di(*tert*-butyl) disulfide is weaker than the S–S bond, thiyl radicals are not formed. The initial cleavage of the C–S bond can only induce a short chain process



$$Bu^tSS^{\bullet} + Bu^tSSBu^t \longrightarrow Bu^tSSH + Bu^tSSCMe_2\dot{C}H_2,$$

$$Bu^tSSCMe_2\dot{C}H_2 \longrightarrow Bu^tSS^{\bullet} + CH_2{=}CMe_2,$$

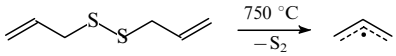
$$2\,Me_3C^{\bullet} \longrightarrow CH_2{=}CMe_2 + CHMe_3.$$

The formation of isobutane (5% and 13% yields in a flow and a static systems, respectively) confirms this scheme.[45]

Thermal decomposition of bis(diphenylmethyl) disulfide at 150–200 °C leads to thiobenzophenone, diphenylmethane and sulfur. The reaction rate is increased with an increase in temperature.[184]

$$Ph_2CHSSCHPh_2 \longrightarrow Ph_2CH_2 + Ph_2C{=}S + S.$$

Diallyl disulfide eliminates sulfur on flash pyrolysis. The allyl radical formed in this reaction was isolated in an argon matrix and characterised by UV, IR and EPR spectroscopy.[185]



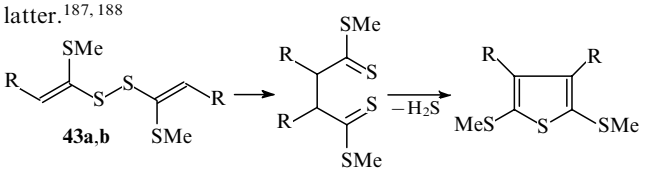
Bis(triphenylmethyl) polysulfides decompose on refluxing in benzene to form hexaphenylethane and sulfur. The thermal stability of $Ph_3CS_nCPh_3$ is decreased with the change in n as follows: 1 > 3 > 4 > 2 (Ref. 186)

$$Ph_3CS_nCPh_3 \longrightarrow 2\,Ph_3C^{\bullet} + S_n,$$

$$2\,Ph_3C^{\bullet} \rightleftharpoons Ph_3CCPh_3.$$

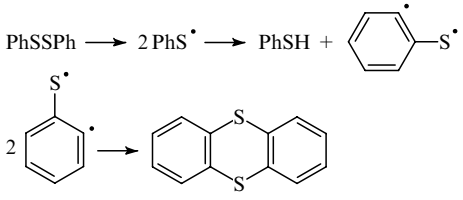
2. Unsaturated, aromatic and heteroaromatic disulfides

Bis(1-methylthiopropenyl) (**43a**) or bis(1-methylthio-2-phenylvinyl) disulfides (**43b**) cyclise into tetra-substituted thiophenes at 100–200 °C. The reactions involve a [3,3]-sigmatropic Cope rearrangement of compounds **43a**,**b** into the corresponding dithio esters **44a**,**b** and the elimination of hydrogen sulfide from the latter.[187, 188]



R = Me (**a**), Ph (**b**).

Benzenethiol and thianthrene are formed from diphenyl disulfide on heating to 260–300 °C in an inert atmosphere. This reaction follows a free-radical mechanism.[189]



Analogous products are formed in the thermolysis of bis(4-methylphenyl) disulfide. The formation of phenthiyl radicals in the vacuum pyrolysis of diphenyl and 2,2′-dinaphthyl disulfides (400–700 °C) was proved by EPR spectroscopy (in a liquid nitrogen matrix).[190]

Thermolysis of diphenyl disulfide at 180–250 °C in an atmosphere of hydrogen sulfide leads to benzenethiol and diphenyl sulfide. The maximum yield of benzenethiol (52%) is achieved at 180 °C, while diphenyl sulfide is the major reaction product (82%) at 250 °C. Benzenethiol and diphenyl sulfide result from two parallel reactions.[191]

$$PhSSPh \longrightarrow 2\,PhS^{\bullet},$$

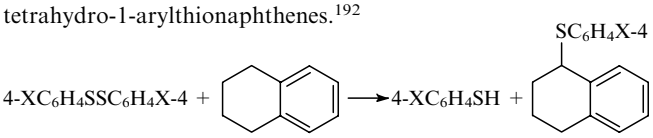
$$PhS^{\bullet} + H_2S \longrightarrow PhSH + HS^{\bullet},$$

$$PhSSPh \longrightarrow PhSPh + S,$$

$$S + H_2S \rightleftharpoons 2\,HS^{\bullet}.$$

The liberation of sulfur in the thermolysis of diphenyl disulfide predominates at high temperatures and is apparently induced by hydrogen sulfide.

Thermolysis of diaryl disulfides in refluxing tetralin results in the formation of the corresponding arenethiols and 1,2,3,4-tetrahydro-1-arylthionaphthenes.[192]



X = Cl, OMe, Me.

The following reaction mechanism has been suggested [192]

$$ArSSAr \xrightarrow{k_1} 2\,ArS^{\bullet},$$

$$ArS^{\bullet} + RH \xrightarrow{k_2} ArSH + R^{\bullet},$$

$$ArS^{\bullet} + R^{\bullet} \xrightarrow{k_3} ArSR,$$

$$R^{\bullet} + R^{\bullet} \xrightarrow{k_4} \text{products},$$

$$ArS^{\bullet} + ArSSAr \underset{}{\overset{k_5}{\rightleftharpoons}} ArS^{\bullet} + \text{products},$$

$$R^{\bullet} + ArSSAr \xrightarrow{k_6} ArS^{\bullet} + \text{products}$$

RH is tetralin, $R^{\bullet}$ is a radical derived from tetralin.

The reaction is induced by arylthiyl radicals generated on the thermal dissociation of the S–S bond in diaryl disulfides. The arylthiyl radicals abstract the α-hydrogen from tetralin producing tetralinyl radicals, which react either with thiyl or other tetralinyl radicals. Based on the results of kinetic and UV studies, an assumption that arylthiyl radicals are π-radicals has been put forward.[192]

Diphenyl disulfides with substituents in the *para*-positions of the benzene rings decompose more rapidly. The order in the change in the reaction rates depending on the nature of substituents (MeO > Cl ≃ Me > H) correlates with the stability of the respective thiyl radicals. The latter is increased with the strengthening of the resonance interaction between the substituent and the benzene ring.

Di(2-thienyl) disulfide eliminates sulfur to form di(2-thienyl) sulfide on heating to 130–180 °C in an atmosphere of hydrogen sulfide.[193]

3. Thermal reactions involving disulfides

Thiyl radicals generated on thermal decomposition of dialkyl disulfides can substitute the halogen atom at the sp^2-hybridised carbon atom and add to the triple bond of acetylene and its derivatives. These reactions predominantly yield heterocyclic compounds of the thiophene series.

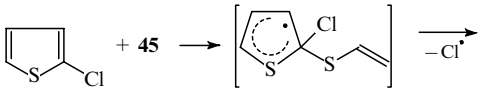
The gas-phase reaction of 2-chlorothiophene with diethyl polysulfides at 560 °C leads to a 4:1 mixture of thieno[2,3-*b*]thiophene (**46**) and thieno[3,2-*b*]thiophene (**47**) (in up to 33% overall yield). Thieno[2,3-*b*]thiophene is formed as the result of the addition of vinylthiyl radicals **45** generated from diethyl polysulfides to 2-chlorothiophene and subsequent heterocyclisation [55]

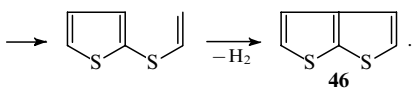
$$EtSSEt \longrightarrow 2\,EtS^{\bullet},$$

$$EtS^{\bullet} + EtSSEt \longrightarrow EtSH + Me\dot{C}HSSEt,$$

$$Me\dot{C}HSSEt \longrightarrow EtSH + CH_2{=}CHS^{\bullet},$$

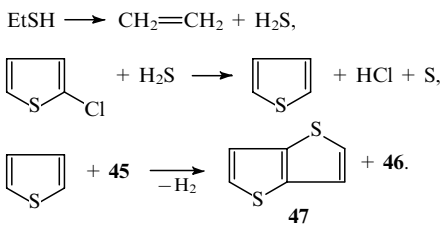
45





46

Both isomeric thienothiophenes are formed in parallel addition reactions of vinylthiyl radicals to thiophene. The latter is obtained on reduction of 2-chlorothiophene with hydrogen sulfide



47

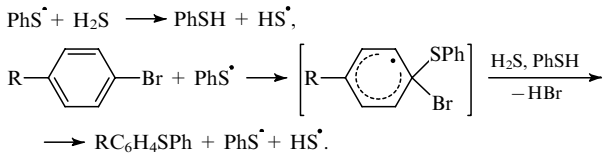
Chlorobenezene reacts with dialkyl disulfides in the gas phase in a similar way.[194]

Aryl bromides effectively react with a diphenyl disulfide–hydrogen sulfide system at 125–240 °C to form aryl phenyl sulfides (49%–84% yields).[195] The reactions occur at a lower temperature if a π-donating substituent is present in the benzene ring of aryl bromides.

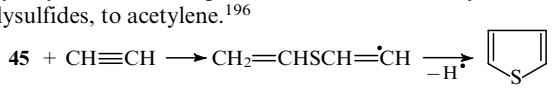
$$2\,ArBr + PhSSPh \xrightarrow{H_2S} 2\,ArSPh + 2\,HBr + S$$

Ar = Ph, 2-HOC_6H_4, 4-HOC_6H_4, 4-EtC_6H_4, 4-CNC_6H_4, 1-naphthyl, 2-hydroxy-1-naphthyl.

Phenthiyl radicals generated from diphenyl disulfide substitute the bromine atom in aryl bromides, thus inducing the reactions. These radicals are generated again in the reaction chain propagation stage, playing also a role as hydrogen atom acceptors from hydrogen sulfide.[195]



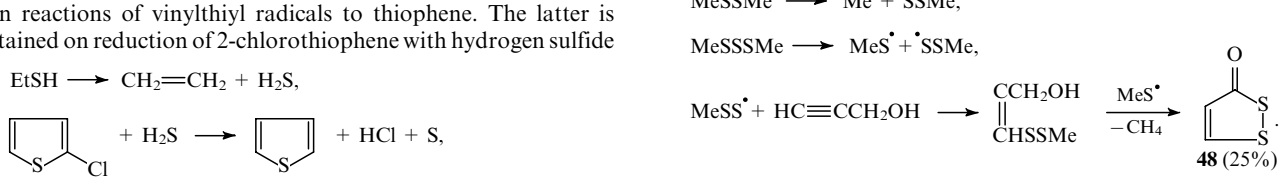
Dialkyl polysulfides react with acetylene in the gas phase at 470–520 °C to form thiophene (up to 60% yield) and isomeric thienothiophenes. Thiophene arises as the addition product of vinylthiyl radicals **45**, generated on the thermolysis of dialkyl polysulfides, to acetylene.[196]



Isomeric thienothiophenes **46** and **47** are formed due to the addition of vinylthiyl radicals **45** to thiophene. The so-called 'disulfide oil' representing a mixture of dimethyl, diethyl and ethyl methyl disulfides can be used instead of diethyl disulfide in the reaction with acetylene. On pyrolysis, all these disulfides generate vinylthiyl radicals **45**, which then are trapped by acetylene.[175] However, the yield of thiophene in this case is lower than that obtained from pure diethyl disulfide.[197] If a mixture of diethyl disulfide and diethyl selenide is used in the reaction with acetylene, the yield of thiophene is increased up to 92%.[198]

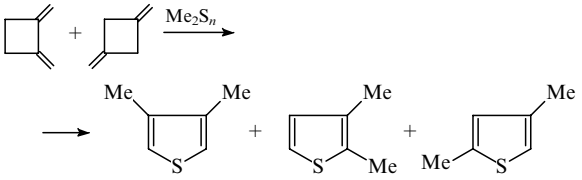
The reaction of 2-chlorothiophene with a diethyl disulfide–acetylene system at 650–700 °C leads to thiophene and thieno[2,3-*b*]thiophene (**46**).[199] Thiophene results from the reaction of acetylene with the vinylthiyl radicals **45**. Thieno[2,3-*b*]thiophene (**46**) is formed due to the reaction of acetylene with 2-thienylthiyl radicals **16** generated *in situ* from 2-chlorothiophene and hydrogen sulfide (the thermolysis product of diethyl disulfide). Acetylene is a more efficient scavenger of thiyl radicals than 2-chlorothiophene; its addition suppresses the competing reaction leading to di(2-thienyl) sulfide.[199]

The gas-phase reaction of dimethyl di- or trisulfide with propargyl alcohol at 500 °C leads to 1,2-dithiol-3-one (**48**).[200] In this reaction, propargyl alcohol acts as a scavenger of MeSS$^{\bullet}$ radicals



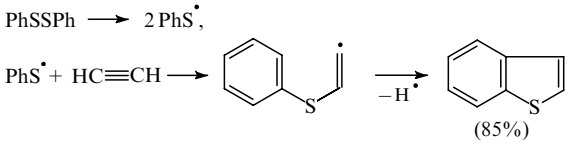
48 (25%)

Dimethylthiophenes (a mixture of 3,4-, 2,3- and 2,4-isomers) are the main products in the gas-phase reaction of dimethyl di- or trisulfide with a mixture of 1,2- and 1,3-dimethylenecyclobutanes at 450–500 °C.[201] The reaction involves cyclobutane ring-opening by methylthiyl radicals.



n = 2, 3.

Benzo[*b*]thiophene is selectively formed in the gas-phase reaction of diphenyl disulfide with acetylene at 500 °C.[21]



(85%)

In the gas phase, acetylene reacts with 1,1-dinaphthyl disulfide in the same way as it does with naphthalene-1-thiol (see Section II.2).[35]

VI. Conclusion

Thus, as can be seen from the data presented here, the thermal reactions of organic compounds of divalent sulfur produce both thiyl radicals and such highly reactive intermediates as thioformaldehyde and its homologues, ethylenethiol, thioketene, *etc*.

Further transformations of these intermediates and their reactions with thiyl radicals and organic additives result in a great variety of the products obtained on thermolysis and pyrolysis of sulfur-containing organic compounds. Many of these processes are highly selective and can be used for the synthesis of compounds inaccessible by other methods.

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