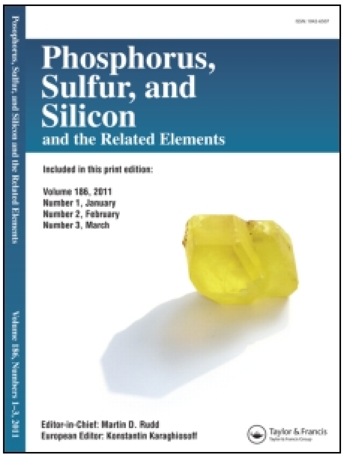

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

High Temperature Reactions of Thiyl Radicals

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To cite this Article Voronkov, M. G. and Deryagina, E. N.(1991) 'High Temperature Reactions of Thiyl Radicals', Phosphorus, Sulfur, and Silicon and the Related Elements, 58: 1, 151 — 178

To link to this Article: DOI: 10.1080/10426509108040630

URL: http://dx.doi.org/10.1080/10426509108040630

Phosphorus, Sulfur, and Silicon, 1991, Vol. 58, pp. 151-178
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HIGH TEMPERATURE REACTIONS OF THIYL RADICALS

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Abstract Some results of the exemination of the reactivity of thiyl radicals in thermal processes, which allow the synthesis of organic compounds of sulfur other types of compounds, have been summarized for the first time.

INTRODUCTION

Thiyl (sulfur-centered) free radicals are short-living reactive sulfur-containing intermediates $RS^\cdot$ in which the sulfur atom has an unpaired electron. They are involved in numerous chemical reactions, including various industrial and natural processes with participation of organic sulfur compounds; therefore they are of great practical and theoretical interest.

The stability of thiyl radicals is stimulated by the degree of unpaired electron delocalization[1]. The stability can quantitatively be evaluated by electron spectroscopy and electron spin resonance.

The thiyl radicals which have the lone electron pair on the radical center are, judging by their reactivity, electrophilic. The relative stability of thiyl radicals can be characterized by the energy of the highest molecular orbital with one electron[2].

In this paper the thermal methods for generating thiyl radicals from simplest sources, such as hydrogen sulphide and its derivatives, as well as methods of high temperature synthesis by use of thiyl radicals are discussed. During the latest fifteen years extensive investigations of the high temperature reactions of thiyl radicals with organic compounds have been carried out. They show, in particular, hydrogen sulfide to be the most available and promising source of thiyl radicals which further initiate diverse thermal and organic reactions[3].

THERMOLYSIS OF HYDROGEN SULFIDE

When heated, hydrogen sulfide decomposes into elemental hydrogen and sulfur[4]. This process starts at 360-400° [5] and becomes appreciable at 1300-1600° [6]. At 700°, only 0.0003% of H_2S decomposes[7] whereas at 930°, the amount of decomposed hydrogen sulfide is 15-20% [8] and 83% at 1700° [7].
Investigation of the shock-wave induced thermal destruction of hydrogen sulfide in low concentrations in argon has revealed the first most energy-consuming stage to be dissociation into free radicals involving argon molecules

$$H_2S + Ar \xrightarrow{2400\ -3500\ C^{o}} HS^{\cdot} + H^{\cdot} + Ar$$

The energy of activation of the reaction is 92[7] or 74 kcal/mole[9] which is close to that of the bond in the molecule of hydrogen sulfide: 98.3[10], 95.0[11], 81.2[12], 92.0 kcal/mole[13].
Ingibition of the thermolysis with nitrogen oxide and initiation with atomic hydrogen indicates a free radical mechanism of this process. A significant role in the homolytic decomposition of hydrogen sulfide is played by the exothermal reaction of hydrogen sulfide with atomic hydrogen, which occurs at a high rate. It is this reaction that initiates the decomposition of hydrogen sulfide into elements at the stage of the generation of sulfhydryl radicals[14]:

$$H_2S \longrightarrow H^{\cdot} + HS^{\cdot} \quad -92 \text{ kcal/mole}$$

$$H_2S + H^{\cdot} \longrightarrow HS^{\cdot} + H_2 \quad +12.6 \text{ kcal/mole}$$

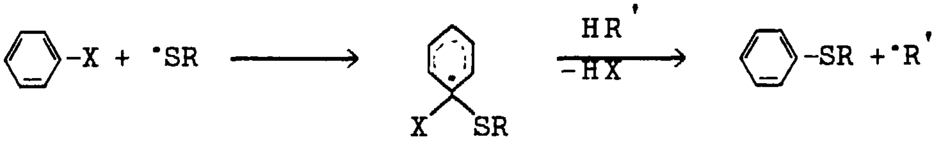
$$2\,HS^{\cdot} \longrightarrow H_2S + S \quad +9 \text{ kcal/mole}$$

$$H_2S + S_2 \longrightarrow H_2 + S_2 \quad +30.7 \text{ kcal/mole}$$

This reaction is responsible the low energy of activation (37 kcal/mole) of the thermolysis of undiluted hydrogen sulfide at 400-1000° [15].

GAS-PHASE REACTION OF HYDROGEN SULFIDE WITH HALOAROMATIC AND HETEROAROMATIC COMPOUNDS

The thermal reaction of hydrogen sulfide with chloro- and bromosubstituted aromatic and unsaturated hydrocabons and their derivatives have been studied in more detail. These available organic compounds differ by high thermal stability[16] and low reactivity in nucleophilic thiylation[17]. However, the thermal reaction of ipso-substitution of the halogen atom in the aromatic ring by sulfhydryl, aryl or vinyl thiyl radicals is facilitated by the electrophilic of thiyl radicals, the increased electronic density on the C_{sp^2}- X bond (X = Cl, Br), the possibility of the formation of intermediate radical-adduct stabilized with the participation of the aromatic ring π-system, as well as by the removal of the halogen atom as a thermally stable hydrogen halide[18].



X= Cl, Br; R= H, vinyl, aryl

These reactions were carried out in a conventional flowing system (hollow quartz tube) which models the size and conditions of the gradientless reactor.

The gas-phase reaction of hydrogen sulfide with chlorobenzene starts at 550° and becomes vigorous at 600-700° (chlorobenzene conversion 40-50%), yielding thiophenol, diphenyl sulfide and benzene. Their ratio depends much on the reaction temperature. The yield of thiophenol and diphenyl sulfide reaches maximum within a narrow temperature range of 600-620° above which a considerable increase in the rate of benzene formation is observed. Partially in the same temperature range, the cyclization of diphenyl sulfide into dibenzothiophene takes place[19-20]. Excess hydrogen sulfide or chlorobenzene increases the yield of thiophenol or diphenylsulfide, respectively[21-23]. Kinetic curves characterize the reaction of chlorobenzene with hydrogen sulfide as a complex process involving successive-parallel irreversible reactions. Chlorobenzene is converted to diphenyl sulfide via an intermediate formation of thiophenol, and is simultaneously reduced to benzene[22]:

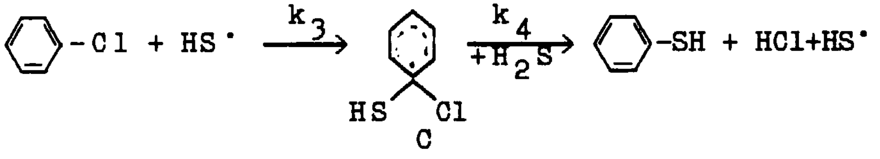
$$C_6H_5Cl + H_2S \xrightarrow{k_1} C_6H_5SH + HCl \qquad (1)$$

$$C_6H_5Cl + C_6H_5SH \xrightarrow{k_2} C_6H_5SC_6H_5 + HCl \qquad (2)$$

$$C_6H_5Cl + H_2S \longrightarrow C_6H_6 + HCl + S \qquad (3)$$

The reaction conditions leading to the maximal yield of thiophenol, are optimized by the method of mathematical planning of the experiment[21]. The yield of C_6H_5SH reaches 30% based on the initial compound, and 90% based on chlorobenzene reacted at 600-620°, molar ratio H_2S: C_6H_5Cl 3:1, exposure time 38-48 s.

Since the thermolysis of chlorobenzene involving the rupture of the C-Cl bond at 600° has not yet started, while the dissociation of hydrogen sulfide to form thiyl radicals is in full progress, the mechanism of thiophenol and diphenyl sulfide formation may be presented on the basis of kinetic data by the following schemes[24]:



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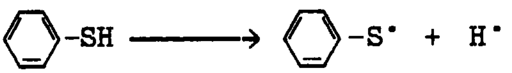

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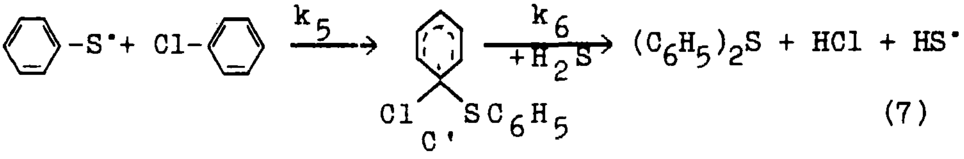


(7)

According to these schemes, the ipso-substitution of the chlorine atom in the aromatic ring by thiyl radicals follows a bimolecular chain mechanism. The thiyl radicals are generated presumably at the stages of chain transfer. The slowest stages are those of the formation of radical-adduct (reaction (4) and (7)), the latter evidently being the limiting stage, since the concentration of phenylthiyl radicals is always lower than that of sulfhydryl radicals. This scheme is supported by the fact that in the gaseous phase alkylchlorides are only reduced, but not thiylated with hydrogen sulfide. Under the conditions studied, benzene also fails to react with hydrogen sulfide.

The Arrhenius expressions of the rate constants of the formation of thiophenol (k_1) and diphenyl sulfide (k_2) by reactions (1)-(2) and the results of the direct reaction of thiophenol with chlorobenzene (k_2') are written as follows[24]:

$$k_1 = 10^{5.15\pm0.9} \mathrm{esp}[(-27.7\pm0.37)\ \mathrm{kcal/mole/RT}]\ \mathrm{s}^{-1}$$

$$k_2 = 10^{8.30\pm0.14} \mathrm{esp}[(-29.0\pm0.6)\ \mathrm{kcal/mole/RT}]\ 1\ \mathrm{mole}\ \mathrm{s}^{-1}$$

$$k_2' = 10^{10.17\pm0.63} \mathrm{esp}[(-33.6\pm3.0)\ \mathrm{kcal/mole/RT}]\ 1\ \mathrm{mole}\ \mathrm{s}^{-1}$$

The energies of activation of reactions (1)-(2) are close. This shows that the critical contribution to the energy of activation in all these cases is that from hybridization of the carbon atom of the C-Cl bond in chlorobenzene in the processes of the formation of an activated complex (C or C') with the thiyl radicals. The low entropies of activation indicate a bimolecular mechanism of thiophenol and diphenyl sulfide formation. The rate constant of diphenyl sulfide formation in the chlorobenzene - thiophenol system, k_2', is approximately 5 times as high as in the chlorobenzene - hydrogen sulfide system.

Expression (8) for the k_2 constant obtained by comparison of functional identities of differential equations describing the real process of chlorobenzene thiylation (reaction (1)-(2)) and its mechanism (reaction (4)-(7)) indicates that this value includes the rate constant of the limiting stage (formation of the active C' complex) and is dependent upon the ratio of phenylthiyl radical and thiophenol concentrations:

$$k_2 = \frac{k_5 [C_6H_5S^\bullet]}{[C_6H_5SH]} \qquad (8)$$

The k_2 value increases upon direct interaction between chlorobenzene and thiophenol in the absence of hydrogen sulfide. Excess hydrogen sulfide facilitates reaction (6) due to which the concentration of thiophenol (denominatior in expression (8)) increases and the rate constant of diphenyl sulfide formation (k_2) decreases. As a result, the selectivity of thiophenol synthesis, according to scheme shown in reaction (1) becomes higher.

The initiators and inhibitors of free-radical reactions affect correspondingly the rate and direction of the reaction of hydrogen sulfide with chlorobenzene. Phenol and cyclohexane slow this reaction by decreasing two-fold the conversion of chlorobenzene[22]. Chloromethanes, which generate free radicals and carbenes during thermolysis[25], accelerate the reaction of thiophenol formation, seemingly due to a supplementary initiation of the chain decomposition of hydrogen sulfide[26]. Enlargement of the reaction zone surface reduces the conversion of chlorobenzene without changing the kinetic regularities of the reaction of the latter with hydrogen sulfide, which indicates that the reaction occurs in full volume. However, when the reactor's walls are involved, generation and annihilation of the thiyl radicals may take place[22].

Therefore, that the material the reactor is made up of, affects much the rate of reactions (1) and (2). With the same contact time, the conversion of chlorobenzene in a steel reactor is approximately 30% higher than that in a quartz reactor. In this case, the reaction products ratio is changed in favour of thiophenol and benzene[27]. Evidently, the steel reactor's walls are involved in the formation of $HS^{\bullet}$ and $C_6H_5^{\bullet}$ radicals due to the catalysis of hydrogen sulfide and chlorobenzene thermolysis by use of nickel and chromium sulfides and polysulfides formed on the H_2S-induced passivation of the reaction surface[28]. In a copper reactor, hydrogen sulfide fails to react with chlorobenzene.

By analogy with chlorobenzene, in the gaseous phase, only its para-substituted derivatives, $4\text{-}XC_6H_4Cl$ react with hydrogen sulfide. In this case, the formation of corresponding thiol, $4\text{-}XC_6H_4SH$, and sulfide, $4\text{-}X(C_6H_4)_2S$ is indicative of ipso-substitution of the chlorine atom by thiyl radicals and supports the mechanism of reactions (4)-(7)[29]:

$$4\text{-}XC_6H_4Cl + H_2S \longrightarrow 4\text{-}XC_6H_4SH + HCl \qquad (9)$$

$$4\text{-}XC_6H_4Cl + 4\text{-}XC_6H_4SH \longrightarrow 4\text{-}XC_6H_4SC_6H_4X\text{-}4 + HCl \qquad (10)$$

$$4\text{-}XC_6H_4Cl + H_2S \longrightarrow 4\text{-}XC_6H_5 + HCl + S \qquad (11)$$

$$X = H,\ Cl,\ OH,\ CH_3,\ CF_3$$

Pentafluorochlorobenzene also reacts with hydrogen sulfide in a way analogous to the schemes shown in reactions (9)-(11) to form C_6F_5SH and $(C_6F_5)_2S$. The optimal temperature of the formation of thiol and sulfide is determined by the nature of substituent X in chlorobenzene and by the nature of the benzene ring in C_6F_5Cl. It drops with increasing C-Cl capacity for homolytic dissociation. The order of increasing conversion of the chloro derivative coinsides with an increase in the electronic density on the chlorine atom. Accordingly, in the reaction with H_2S, the conversion of 4-XC_6H_4Cl and C_6F_5Cl and the physicochemical parameters of the C-Cl bond change in the following order of variation in X or the nature of the ring (C_6F_5):

Conversion	F_5 <	OH <	Cl <	CF_3 <	H <	CH_3
Q (Cl)	-	-0,16	-	0,15	-0,17	-0,17
^{35}Cl NQR	39.4	34.9	34.8	34.7	34.65	34.5
$C^{13}(C_1)$	-	-8.74	-1.71	3.88	0.00	-3.21
$C_1(\pi)$	-	-0.04	-	3.03	0.00	-0.02

The thiylation products ratio (RSH/R_2S) depends much on the reactivity of the intermediate thiol. This ratio correlates with the electronic structure and reactivity of 4-XC_6H_4SH and C_6H_4SH and increases in the following order of variation in X or the nature of the ring (C_6F_5):

$$Cl < CH_3 < H < CF_3 < OH < F_5$$

The reactivity of these thiols is mainly determined by the degree of HOMO localization on the sulfur atom as other parameters of the electronic structure (ionization potential and the charge on the sulfur atom) do not depend much on the nature of substituent X or the benzene ring.

The degree of HOMO localization correlates only with the resonance component of substituent X, thus increasing with the decrease in their π-donor ability. The thiol/sulfide ratio correlates in a symbath way with the value of HOMO localization on the thiol sulfur atom, thus decreasing when the π-donor properties of substituent X increase.

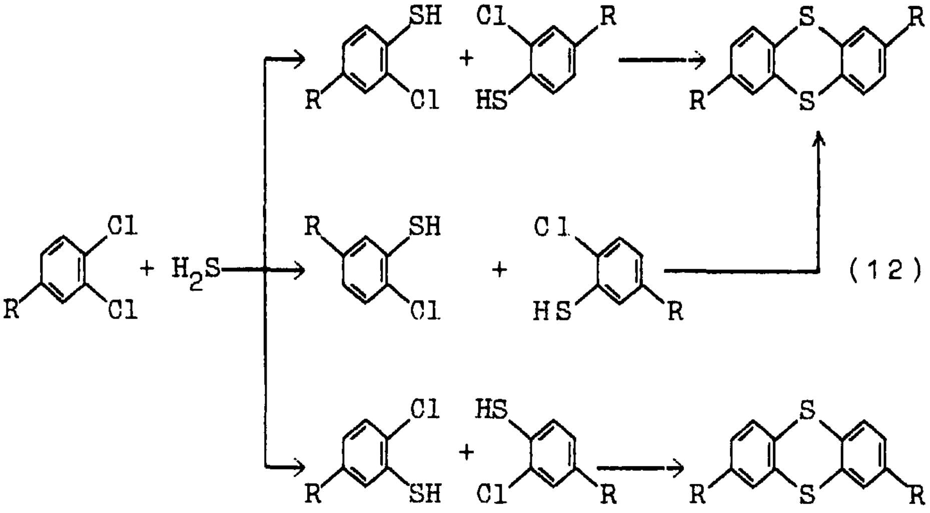
Thus, the π-acceptor substituent X in thiol 4-XC_6H_4SH

reduces its reactivity in the reaction with the initial chloro derivative (scheme shown in reaction (10)), whereas π-donor properties increase the reactivity. In terms of free-radical mechanism of reactions (9) and (10), the formation of the aryl thiyl radical to participate in the second step of reaction (7) under the conditions of competing reaction with H_2S (eq.(6)), is determined by the stabilization ability of this radical. The unpaired electron distribution in $4\text{-}XC_6H_5S^{\bullet}$ is believed to be similar to the HOMO distribution in $4\text{-}XC_6H_4SH$.

Therefore, the π-donor substituents stabilize and the π-acceptor substituents destabilize the thiyl radicals, which, in turn are generated at a lower rate and, in the latter case,further react, presumably with hydrogen sulfide of scheme (6), rather than with the initial chloro derivative of scheme (7). These regularities are not the case for 4-hydroxythiophenol,evidently due to the autoinhibition of the free-radical process. By increasing the dehydration activity of $4\text{-}XC_6H_4S^{\bullet}$ the π-acceptor substituents X promote the highly selective formation of thiol $4\text{-}C_6H_4SH$ according to scheme shown in reaction (9), the starting chloride conversion being low. The highest selectivity is observed in the of C_6H_5SH.

Ortho-substituted chlorobenzenes react with hydrogen sulfide in the gaseous phase in a different way than does the para-substituted isomer. The main product of 2-chlorotoluene or chloromesytylene thiylation is the corresponding thiol (scheme shown in reaction (1)) since the steric effect of the ortho-methyl group hinders the interaction of the 2-methylphenyl thiyl or mesytyl thiyl radical at the stage of sulfide formation according to scheme shown in reaction (7)[30].

In the reaction with hydrogen sulfide, 1,2-dichloro- or 1,2,4-trichlorobenzene correspondingly forms thianthrene or dichlorothiantrenes according to scheme shown in reaction (12)[31]:



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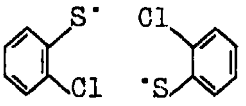
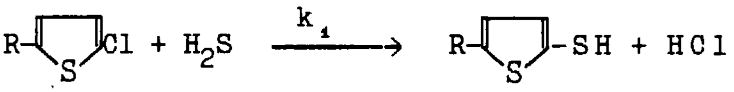


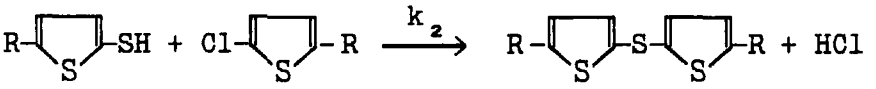
The formation of the above thianthrenes seems to be caused by a fast intramolecular cyclization of ortho-chloro substituted phenyl thiyl radicals.

Unlike para-chlorophenol, its ortho-isomer reacts with hydrogen sulfide more efficiently with a more selective formation of 2-hydroxythiophenol[32].

The reaction of hydrogen sulfides with 2-chlorothiophene, to give thiophenethiol and bis(2-thienyl) sulfide, occurs at lower temperatures (500-540°) than with chlorobenzene[33]:



(13)



(14)

R= H, Cl, C_2H_5

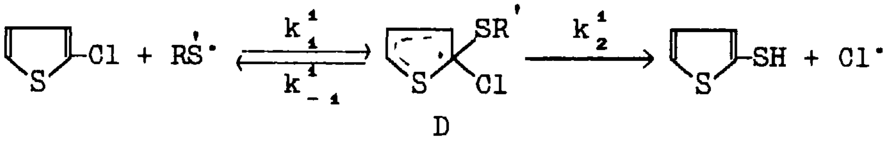
Here, reaction (14) leading to the sulfide, proceeds at a higher rate than with chlorobenzene (reaction (2)).

The Arrhenius expressions of the rate constants k_1 and k_2, describing the formation of 2-thiophenethiol and bis(2-thienyl) sulfide, have been derived.

$$k_1 = 10^{14.2 \pm 0.4} \exp[(-52.0 \pm 3.4 \text{ kcal/mole}) \cdot 10^3/RT] \text{ s}^{-1}$$

$$k_2 = 10^{13.8 \pm 0.2} \exp[(-55,7 \pm 2,9 \text{ kcal/mole}) \cdot 10^3/RT] \text{ l mole}^{-1} \cdot \text{s}^{-1}$$

The high energies of activation of the two reaction stages and the preexponential multiplier value indicate a monomolecular reaction mechanism. In contrast to the reaction of chlorobenzene with hydrogen sulfide, this can be due to a faster attack of thiyl radicals HS• and RS• on the polarized double bonds of the thiophene ring and a greater stability of the activated D complex which slowly decomposes at the limiting stage according to the scheme shown in reaction (15)[34]:


(15)

R' = H, R

By the schemes shown in reactions (13) and (14), the thiol from 5-ethyl-2-chlorothiophene is formed in a somewhat higher yield and the thiol from 2,5-dichlorothiophene and in a lower yield than that from 2-chlorothiophene. In the absence of hydrogen sulfide, 2,5-dichlorothiophene is dehydrodimerized into tetrachloro-3,3'-dithienyl at 570°[35].

The reaction of hydrogen sulfide with bromobenzene starts at 500°, i.e., 50° lower than with chlorobenzene. At various the temperatures studied, the conversion of bromobenzene is higher than that of chlorobenzene, the products of the reaction with hydrogen sulfide being similar.

However, the product ratios and yields are different[36]. The reactions of hydrogen sulfide with bromobenzene and its substituted derivatives give mainly the corresponding sulfides.

Condensed aromatic hydrocarbon bromo derivatives (naphthalene, anthracene, phenanthrene) react with hydrogen sulfide even in the liquid phase at 150-250° to form only the corresponding sulfides[37].

Iodobenzene reacts with hydrogen sulfide at as low as 480-500° to be converted mainly to diphenyl sulfide and benzene with a small amount of thiophenol and diphenyl disulfide. In the reaction of benzene halides with hydrogen sulfide the best temperature for the formation of thiophenol and diphenyl sulfide drops with increasing halogen atomic number: Cl (600-620°) > Br (550- 580°) > I (400-500°). The conversion of halo derivatives increases and the thiol/sulfide ratio decreases in the same order. This order of the change in halogen mobility is consistent with the change in the strength of the C-X bond in benzene halides and is characteristic of radical reactions[38].

Fluorobenzene fails to react with hydrogen sulfide even at 700°. Above this temperature, the former is partially converted to a mixture of mono- and difluorodiphenyls.

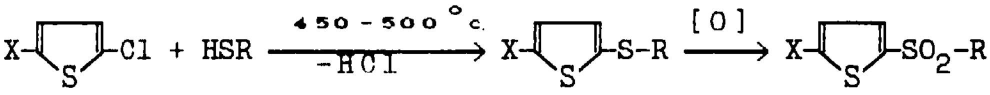
GAS-PHASE REACTION OF THIOPHENOL WITH HALO AROMATICS AND HALO HETERO AROMATICS

Thiophenol reacts with halo derivatives of the aromatic series at 400-600° first to form unsymmetric aromatic sulfides according, to the general scheme[39]:

$$C_6H_5SH + RX \longrightarrow C_6H_5SR + HX \qquad (16)$$

R = Aryl, thienyl, naphtyl; X = Cl, Br

Reaction (16) is favored by excess halo derivatives and the lowest temperature. An increase in the temperature and concentration of thiophenol accelerates the reduction of halo derivatives, exchange and cyclization reactions of diaryl sulfides and thiyl radicals. The reaction of thiophenol with ortho-substituted benzene halides involves the formation of sulfur-containing heterocyclic compounds: thioxanthene has been isolated in the reaction of thiophenol with 2-chlorotoluene[40], thianthrene in the reaction with ortho-dihalobenzenes and 4-oxydibenzothiophene in the reaction with ortho-chlorophenol[41]. Many unsymmetrical aryl thienyl sulfides (yield 44-76%) were prepared for the first time by the reaction of aromatic thiols with 2-chlorothiophene and 5-substituted chlorothiophene[42]:



X= H, C_2H_5, Cl

R= C_6H_5, $4-H_3C-C_6H_4$, $1-C_{10}H_7$

GAS-PHASE REACTION OF ALKANE THIOLS, DIALKYL SULFIDES AND POLYSULFIDES WITH ARYL HALIDES

Readily available alkanethiols, dialkyl sulfides and polysulfides or their mixtures may be used as the source of thiyl radicals in the reactions with aryl halides. In the gas phase they decompose to form hydrogen sulfide and olefins by a free-radical mechanism via the intermediate generation of thiyl radicals[43]:

$$CH_3CH_2SCH_2CH_3 \longrightarrow CH_3CH_2S^{\bullet} + CH_3CH_2$$

$$\xrightarrow{RH} CH_3CH_2SH + R^{\bullet}$$

$$CH_3CH_2SH \longrightarrow CH_3\dot{C}H_2 + HS^{\bullet}$$

$$CH_3CH_2SH + HS^{\bullet} \longrightarrow CH_3\dot{C}HSH + H_2S$$

$$CH_3\dot{C}HSH \longrightarrow CH_2{=}CH_2 + HS^{\bullet}$$

$$CH_3CH_2SH + CH_3\dot{C}H_2 \longrightarrow CH_3\dot{C}HSH + CH_3CH_3$$

$$\underset{\displaystyle H\cdots SH}{CH_3CH_2CH{-}{-}{-}CH_2} \longrightarrow H_2S + C_4H_8$$

$D_{C_2H_5SH}$ C-S 63.5 kcal/mole

D_{H_2S} S-H ~ 90 kcal/mole

The high temperature reactions of alkane thiols, dialkyl sulfides and disulfides with benzene, thiophene, and naphthalene chloro derivatives give the same thiylation products those with hydrogen sulfide[44-46] which seems to indicate a single mechanism for these reactions involving radicals according to the schemes shown in reaction (4-7):

$$\begin{array}{l} R{-}S{-}H \\ R{-}S_n{-}R \\ n = 1,2 \end{array} \rightarrow + R'Cl \xrightarrow{600-630^{\circ}C} R'SH + R'SR' \qquad (17)$$

R = alkyl

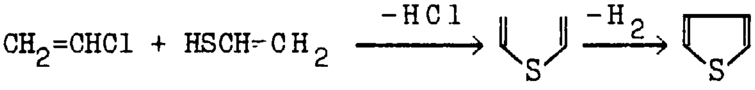
R'= C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}ClC_6H_4$, $2\text{-}ClC_6H_4$, $4\text{-}CF_3\text{-}C_6H_4$, C_6F_5, $(Cl_2)C_6H_3$, 2-thienyl, 1-naphtyl

The reaction of alkanethiols with arylhalides are distinguished by the higher selectivity of the formation of thiol R'SH (reaction 17). It is likely that the limiting stage of the formation of sulfide R'SR' is inhibited by the alkenes.

REACTION OF HYDROGEN SULFIDE, THIOLS, DIALKYL SULFIDES AND DIALKYL POLYSULFIDES WICH ALKEN HALIDES

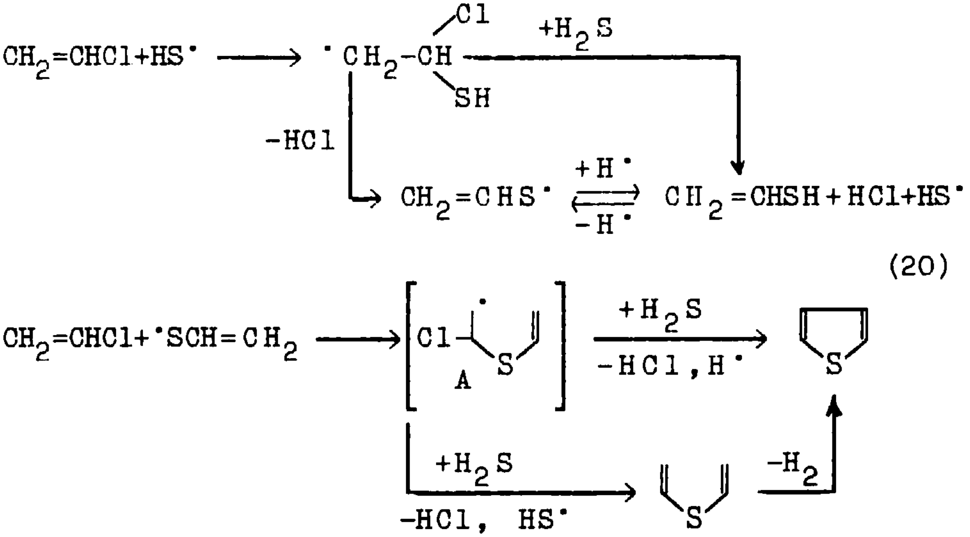
At 400-550°, hydrogen sulfide is condensed with haloalkenes. The simplest of these, vinyl chloride, reacts with hydrogen sulfide at 530-550° to form vinyl thiol and thiophene. With excess hydrogen sulfide, vinyl thiol presents the major reaction product (60% yield), whilst with excess vinyl chloride, thiophene is mainly formed (60-80% yield)[47]:

$$CH_2{=}CHCl + H_2S \longrightarrow CH_2{=}CHSH + HCl \qquad (18)$$


(19)

On passing out of the gaseous phase, vinyl thiol was stabilized by cooling to -70°, and after a quick defrosting, it was subjected to analysis[48].

In reactions (18) and (19) the thiyl radicals add at the double bond of the halo olefin to the carbon atom attached to the halogen atom. This leads to the ipso-substitution of the latter according to scheme (20):


(20)

Vinyl thiol, the primary product of reaction (20), thermally generates the vinyl thiyl radical which further initiates chain thiylation of vinyl chloride. Thiophene may be the product of cyclization of radical-adduct A or divinyl sulfide. Reaction (20) is also confirmed by the fact that neither ethylene nor acetylene react with hydrogen sulfide under analogous conditions, and by the direction of the reaction of dichloroethylenes with hydrogen sulfide and its organic derivatives.

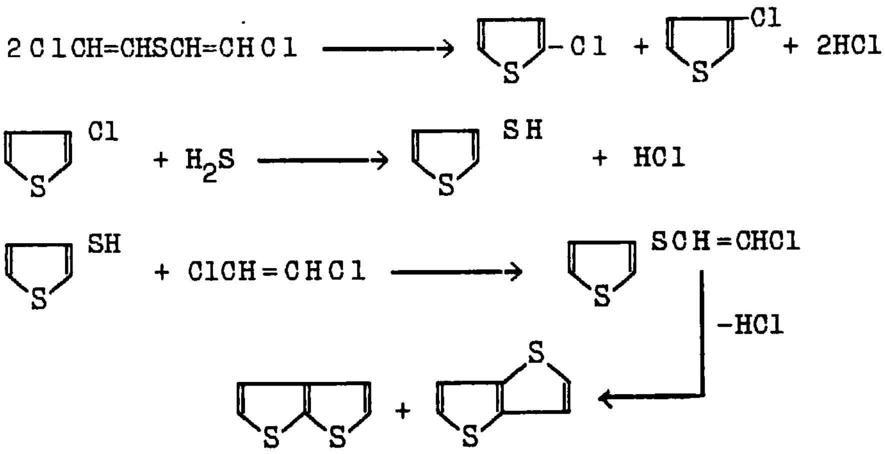
Unlike vinyl chloride, vinyl bromide reacts with hydrogen sulfide at 450-500° to form only vinyl thiol in accordance with scheme shown in reaction (18) independently of the reaction conditions[49]. This may be due to the inhibiting effect of hydrogen bromide released in the reaction course. Being a stronger hydrogen-donor than hydrogen sulfide, hydrogen bromide reacts very quickly with the vinyl thiyl radical, the latter does not take part in reaction (20) which yields thiophene.

The reaction of dichloroethylenes with hydrogen sulfide proceeds mainly by schemes shown in reactions (18-20). In this case, a mixture of organic sulfur compounds is formed due to secondary transformations of labile intermediates.

The interaction of 1,2-dichloroethylene with hydrogen sulfide is illustrated by scheme (21) which may explain the formation of all the reaction products observed[50]:

$$\mathrm{ClCH{=}CHCl + H_2S \longrightarrow ClCH{=}CHSH^{\bullet} + HCl}$$

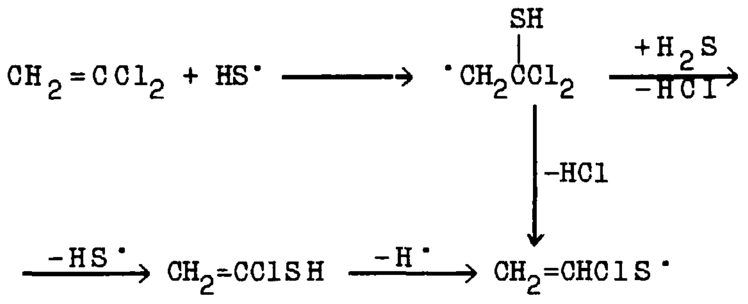
$$\mathrm{ClCH{=}CHSH + ClCH{=}CHCl \longrightarrow ClCH{=}CHSCH{=}CHCl + HCl}$$



(21)

Excess 1,2-dichloroethylene promotes the predominant formation of 2- and 3-chlorothiophene in yields amounting to 30-35%.

According to the schemes analogous to that in (21), 1,1-dichloroethylene and hydrogen sulfide at 470° form a mixture of 2- and 3-chlorothiophene, thiophene, 2- and 3-thiophenethiol, thienothiophenes and vinyl sulfides[51]. However, the sulfides formed contain the chlorine atom in the β-, rather than in the α-position to the sulfur atom. This shows that the α-chlorovinyl thiol wich generates the α-chloro vinyl thiyl radical responsible for the formation of all further reaction products, to be the primary product of the reaction of 1,1-dicholoroethilene with hydrogen sulfide:



$$CH_2{=}CCl_2 + HS^{\bullet} \longrightarrow {}^{\bullet}CH_2\overset{SH}{C}Cl_2 \xrightarrow[-HCl]{+H_2S}$$

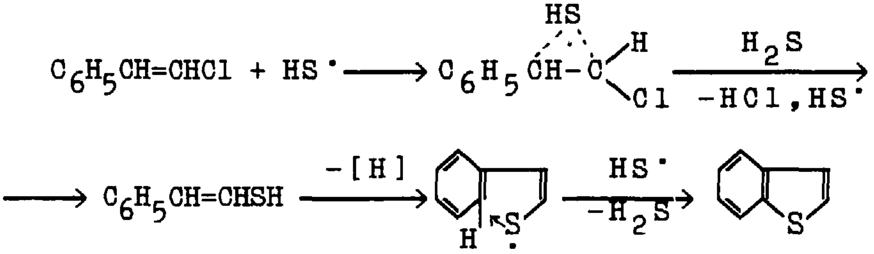
$$\xrightarrow{-HS^{\bullet}} CH_2{=}CClSH \xrightarrow{-H^{\bullet}} CH_2{=}CHClS^{\bullet}$$

$$ {}^{\bullet}CH_2\overset{SH}{C}Cl_2 \xrightarrow{-HCl} CH_2{=}CHClS^{\bullet}$$

In this case, strong evidence is provided for the regio direction of the thermal addition of thiyl radicals to alkene halides, and namely, to the carbon atom attached to the halogen atom.

Trichloroethylene in the gas phase does not form any sulfur-containing compounds with hydrogen sulfide. The reaction of tetrachloroethylene with hydrogen sulfide[52] at 450° leads to tetrachlorothiophene (in 75% yield), however, it proceeds more slowly than with other chloroolefins having polarized multiple bonds[53].

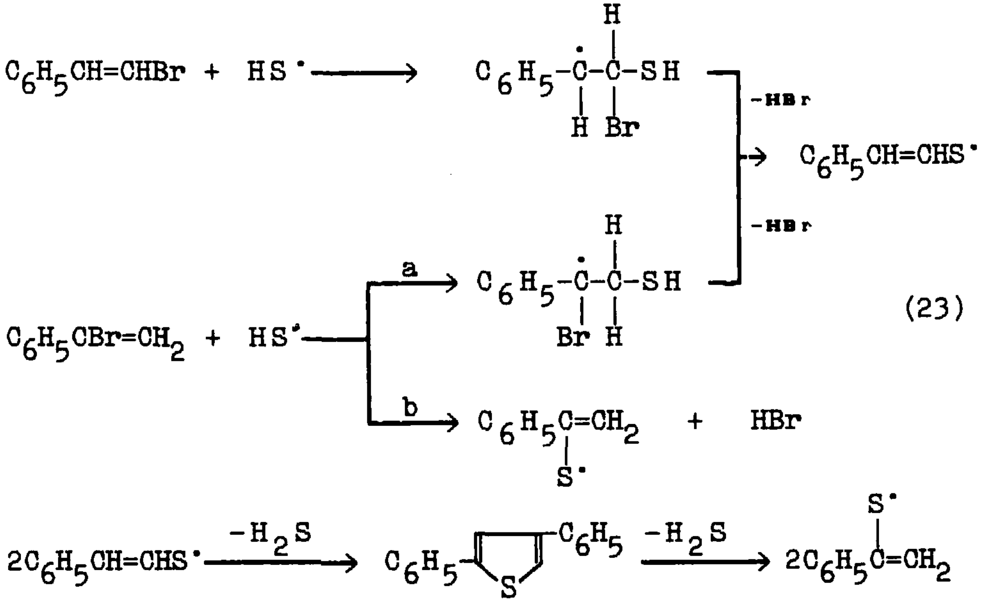
Benzo[b]thiophene (85% yield) is practically the only product of the reaction of β-chlorostyrene with hydrogen sulfide at 600°. The initially formed β-phenyl vinyl thiol readily generates the β-phenyl vinyl thiyl radical (stabilized by the ring-multiple bond π,π-conjugation), which undergoes a very fast intramolecular condensation to benzothiophene[54-55]:



(22)

Instead of chlorostyrene, its gas-phase precursor, α,β-dichloroethylbenzene, is involved in reaction (22) where lower alkanethiols are used instead of hydrogen sulfide.

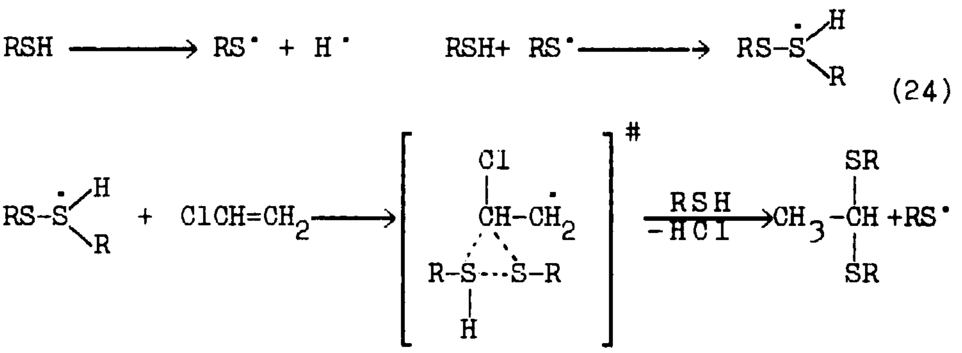
In the liquid phase, boiling β-chlorostyrene fails to react with hydrogen sulfide. However, both α- and β-bromostyrenes react with hydrogen sulfide in the liquid phase as low as 150-170° to form mainly 2,4-diphenylthiophene (37% yield). In the liquid phase the phenyl vinyl thiyl radicals seem to undergo only intermolecular condensation which gives the same product as reaction (23) (due to the cage effect and a fairly high concentration of radicals at the moment of formation)[56]:



(23)

In the gaseous phase, benzothiophene is formed in 76% yield from β-bromostyrene and hydrogen sulfide and in 9% from α-bromostyrene. In the latter case, partial generation of β-phenyl vinyl thiyl radical takes place, however this trend of the HS• radical attack on the halo olefin molecule is achieved to only a very small extent even in this case when the radical adduct of the benzyl type is formed (scheme 23, reaction 'b' is more preferable than reaction 'a').

Organic derivatives of hydrogen sulfide (thiols, dialkyl sulfides and disulfides) react with alkene halides in both gaseous and liquid phase. The reactions of the above derivatives with vinyl chloride at 400° give 1,1-bis(alkylthio)ethenes (in 10-30% yield) formed due to a preliminary thermal condensation of the alkyl thiyl radicals with the initial sulfur-containing reagent according to the scheme shown in reaction (24)[57]:



(24)

No intermediate formation of alkyl vinyl sulfides occurs in this case, since the thermal addition of alkane thiols under similar conditions leads to the normal anti-Markovnikov adducts. Also, no thermal isomerization of the latter to isomeric thioacetals is observed :

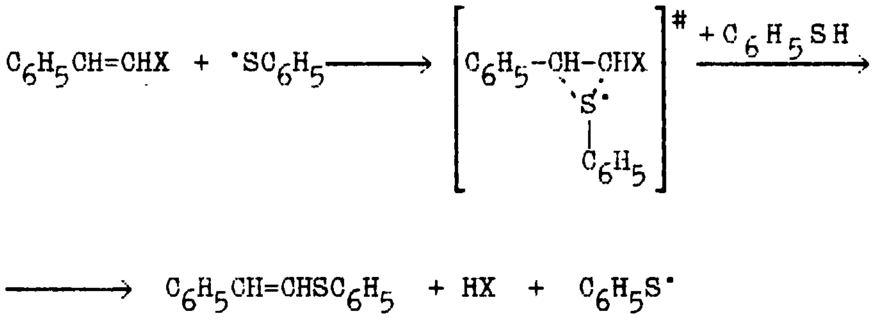
$$RSH + CH_2{=}CHSR \longrightarrow RSCH_2\text{-}CH_2SR$$

The gas-phase reaction of vinyl chloride with aromatic thiols and 2-thiophenethiol leads to the corresponding aryl vinyl sulfides or 2-thienyl vinyl sulfide, respectively. The reaction selectivity is facilitated by excess chloro derivative[58]:

$$RSH + ClCH{=}CH_2 \xrightarrow{350-450^{\circ}C} \underset{60-90\%}{RS-CH{=}CH_2} + HCl$$

$$R = C_6H_5,\ 4\text{-}CH_3C_6H_4,\ 3\text{-}CH_3C_6H_4,\ 1\text{-}C_{10}H_7,\ 2\text{-}C_4H_3S$$

The aromatic thiols and 2-thiophenthiol react with β-chloro and β-bromo styrene in the liquid phase as low as 80-160° to give 1-phenyl-2-aryl or (2-thienyl)thioethanes, respectively (70-95% yield)[59]:



$$C_6H_5CH{=}CHX + {}^{\bullet}SC_6H_5 \longrightarrow \left[C_6H_5-CH-\underset{\underset{C_6H_5}{|}}{\dot{S}^{\bullet}}\!\!\cdots CHX \right]^{\#} \xrightarrow{+C_6H_5SH} \qquad (25)$$

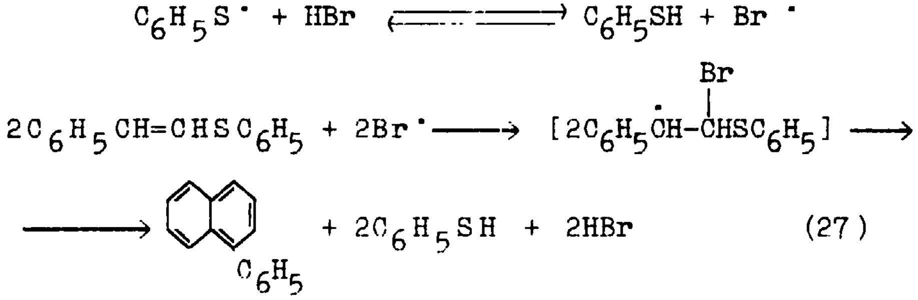
$$\longrightarrow C_6H_5CH{=}CHSC_6H_5 + HX + C_6H_5S^{\bullet}$$

Reaction (25) starts as low as 80° and proceeds effectively at 140-160°.

At 80-100° reaction (25) involves only the trans isomer of β-halostyrenes whereas at 140-160° the two isomers are involved. The reaction is highly stereospecific, probably due to the β-phenylthio group. In this case, a less strained transition state arises from the β-halostyrene trans isomer (26)[60]:

(26)

Thiophenol reacts with β-bromostyrene more slowly than with β-chlorostyrene owing to the inhibiting effect of hydrogen bromide which acts as a trap of thiyl radicals and initiates decomposition of the sulfide formed according to the scheme shown in reaction (27):



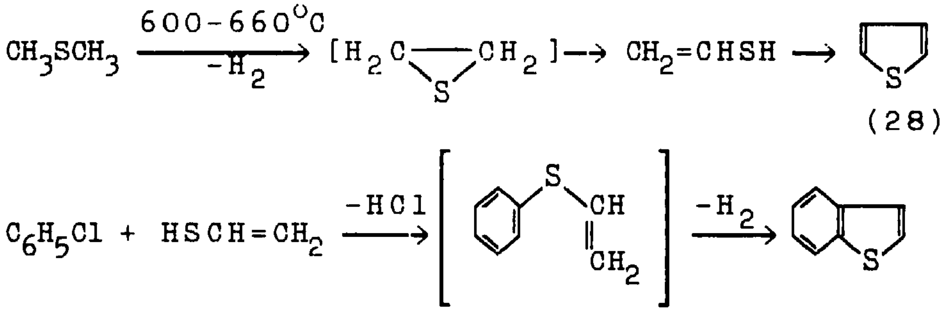
(27)

In particular, 1-phenyl-2-(naphthylthio)ethene and 1-phenyl-2(thienylthio)ethene have been prepared by reaction (25).

THERMAL SYNTHESIS OF THIOPHENE AND THIOPHENE DERIVATIVES

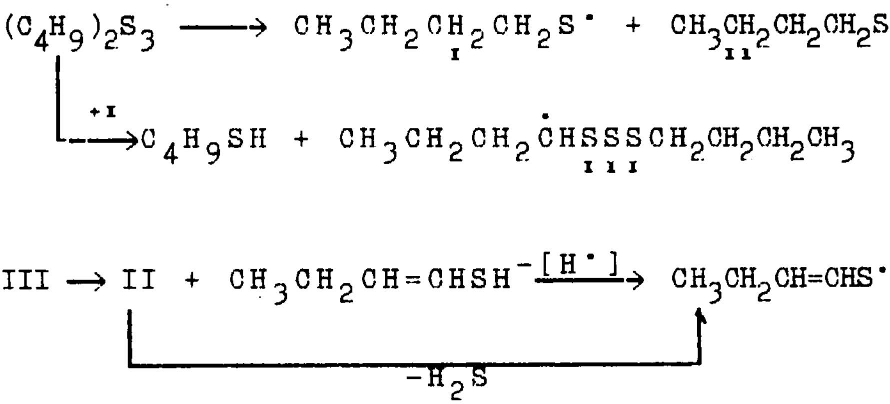
The reaction of thermal conversions of the thiyl radicals generated from diverse organic compounds of sulfur made it possiblle to develop different synthetic routes to thiophene, benzothiophene, dibenzothiophene, thianthrene, thioxanthene, and other sulfur-containing heterocycles. All these methods are based on thermal cyclizations and condensations of various types of α,β-unsaturated thiyl radicals[61].

The thiophenes are the products of the thermolysis of dialkyl sulfides which decompose by a single mechanism involving a stage of vinyl thiol generetion. The vinyl thiyl radical formed from the latter, is subjected to intermoleoular condensation to thiophene according to the scheme shown in reaction (28)[62-63], for example:



(28)

Thiophene is also formed upon the pyrolysis of vinyl sulfides and dialkyl polysulfides[64-65]. In this case, dibutyl polysulfides $(C_4H_9)_2S_n$ are subjected to the most selective thermolysis to thiophene[65]:



$$(C_4H_9)_2S_3 \longrightarrow \underset{I}{CH_3CH_2CH_2CH_2S^\bullet} + \underset{II}{CH_3CH_2CH_2CH_2S_2^\bullet}$$

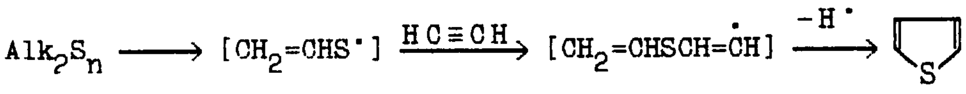
$$(C_4H_9)_2S_3 \xrightarrow{+I} C_4H_9SH + \underset{III}{CH_3CH_2CH_2\dot{C}HSSSCH_2CH_2CH_2CH_3} \qquad (29)$$

$$III \longrightarrow II + CH_3CH_2CH=CHSH \xrightarrow{-[H^\bullet]} CH_3CH_2CH=CHS^\bullet$$

$$II \xrightarrow{-H_2S} CH_3CH_2CH=CHS^\bullet$$

With n = 3, the maximum yield of thiophene attains 43% at 500-520°. According to scheme (29), it is the molecule of trisulfide that provides the richest source of buthenyl thiyl radicals which further undergo cyclization to thiophene[64].

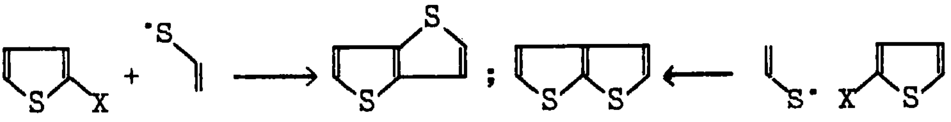
Acetylene is an effective trap of vinyl thiyl radicals. At 470-520,° its cothermolysis with lower dialkyl polysulfides leads to thiophene[66]:



$$Alk_2S_n \longrightarrow [CH_2=CHS^\bullet] \xrightarrow{HC\equiv CH} [CH_2=CHSCH=\dot{C}H] \xrightarrow{-H^\bullet}$$

62%

In this case, along with thiophene, two isomeric thienothiophenes are formed, seemingly due to the interaction of the vinyl thiyl radical with the thiophene ring (1:1 ratio):

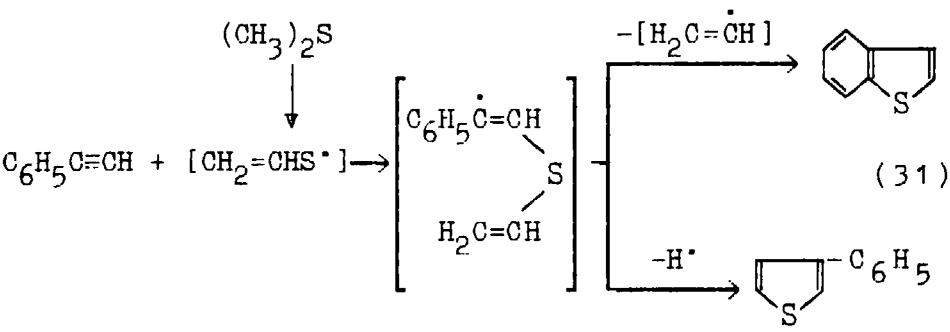


X= H, Cl

(30)

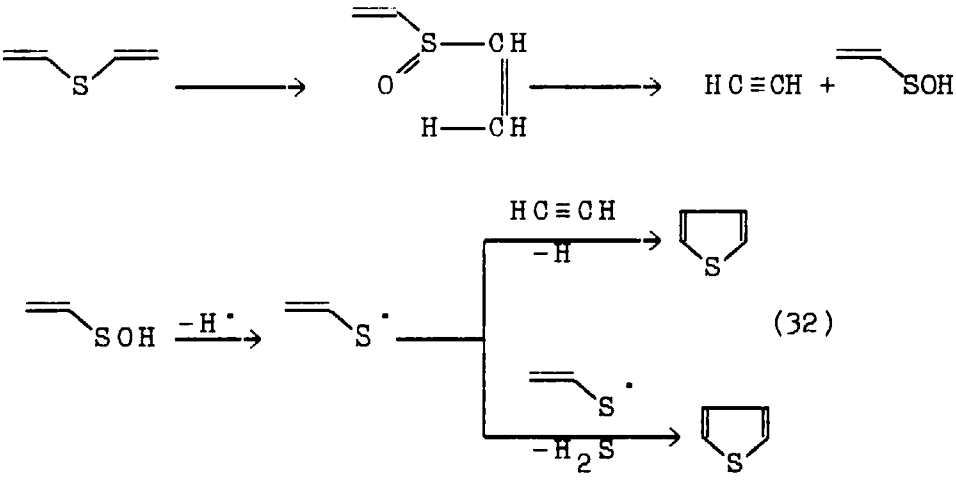
The cothermolysis of 2-chlorothiophene with a mixture of diethyl polysulfides also shown by scheme in reaction (30), forms a mixture of isomeric thienothiophenes; however, in this case the [2,3-b]-isomer prevails[67]. This provides evidence for the predominant attack of the thiyl radical on the sp^2-hybridized carbon atom attached to the halogen atom.

The cothermolysis of phenylacetylene with dimethyl sulfide at 450-500° leads to 3-phenylthiophene and benzo[b]thiophene according to the scheme shown reaction (31)[68]:



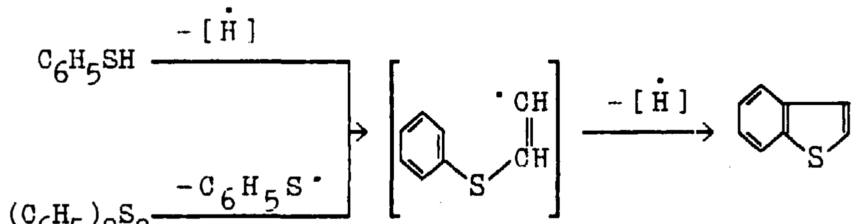
(31)

The main product of the gas-phase thermolysis of divinyl sulfoxide is represented by thiophene, the maximum yield of which is achieved at 400° [69]. The scheme of reaction (32) involves the mechanism proceeding through a stage of vinyl thiyl radical generation:

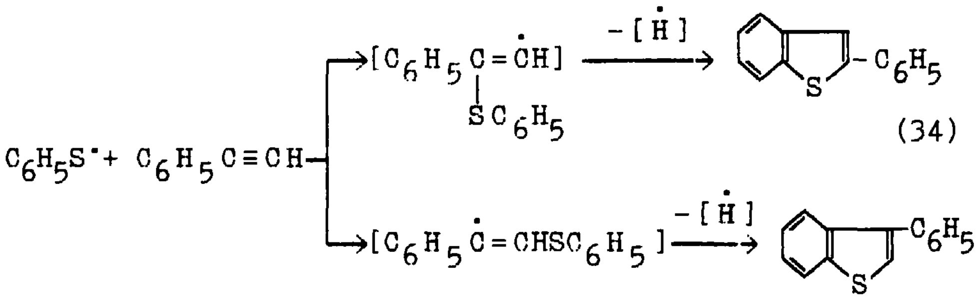


(32)

Thiophenol reacts with acetylene at 550-590° whereas diphenyl disulfide at 500° with a selective formation of benzo[b]thiophene. The products of the reaction of phenylacetylene with diphenyl disulfide are 2- and 3-phenylbenzo[b]thiophenes in a 1:1.5 ratio. The schemes of the mechanism of reactions (33-34) involve the stages of generation and addition of phenyl thiyl radicals[70]:



(33)



(34)

CONCLUSION

In studying the thermal generation and reactivity of thiyl radicals the following regularities have been found:

1. The $HS^{\cdot}$, $CH_2=CHS^{\cdot}$ and $ArS^{\cdot}$ radicals, generated from hydrogen sulfide and its organic derivatives, are readily involved in the reaction of ipso-substitution of the halogen atom attached to the sp^2-hybridized carbon atom.

2. The alkyl thiyl radicals are not prone to conversions of this type. However, they are thermally condensed with alkanethiols, dialkyl sulfides and dialkyl disulfides to the corresponding sulfuranyl radicals $R\dot{S}_nR_2$. In the gas phase the latter are fixed with halo olefins to form dithioacetals.

3. In the gas phase, the vinyl thiyl radicals undergo intra- or intermolecular cyclization to heterocyclic compounds of the thiophene or benzothiophene series.

4. Acetylene and phenylacetylene act as effective trapping agents of thiyl radicals. In the gas phase the sulfhydryl radicals HS˙ do not react with alkynes, alkenes or arenes, but add readily to the multiple bonds of alkene and arene halides.

The above regularities of the thermal reaction of thiyl radicals with organic compounds are of great importance for elucidating the mechanism of the formation of sulfur-containing components of oils, coals, shales and gases as well as the products of their thermal processing.

Numerous synthetic routes to diverse organic sulfur compounds have been developed on the basis of the above reaction of thiyl radicals. Many of these methods can be performed on a large scale by use of available intermediate products and sulfur-containing wastes of petrochemical, coalchemical, chemical, gas and pulp-and-paper industry.

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