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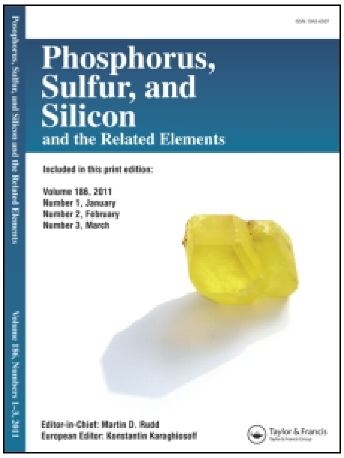

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HIGH TEMPERATURE REACTIONS OF HYDROGEN SULFIDE AND THIOLS WITH ORGANIC COMPOUNDS

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HIGH TEMPERATURE REACTIONS OF HYDROGEN SULFIDE AND THIOLS WITH ORGANIC COMPOUNDS

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The high temperature reaction of hydrogen sulfide with chloro- and bromosubstituted aromatic and heteroaromatic compounds is a convenient method for synthesis of the corresponding thiols and sulfides. The reaction of hydrogen sulfide with *ortho*-dihalosubstituted aromatic compounds may be directed toward the formation of thianthrene or dibenzothiophene and their derivatives. The high temperature reaction of thiophenol with chloro- and bromoderivatives of aromatic and heteroaromatic compounds affords the corresponding mixed sulfides. The reaction with *ortho*-substituted halogen derivatives leads to formation of the sulfur heterocycles of the thianthrene, thioxanthene and dibenzothiophenene series.

The high temperature reaction of hydrogen sulfide with vinyl chloride gives vinylthiol and thiophene. Hydrogen sulfide initiates pyrolytic transformations of thiophene, aniline and benzaldehyde into dithienyls, 5,10-dihydrophenazine and stilbene, respectively. The reaction mechanism has been discussed.

During recent years much attention has been given to high temperature organic reactions occurring selectively and frequently in quite unexpected directions from the point of view of classical organic chemistry.

We have carried out extensive investigations of high temperature reactions of hydrogen sulfide and some thiols with unsaturated, aromatic and heteroaromatic halogen-substituted compounds. The homologue regularities and synthetic possibilities of reactions of the above series of compounds have been studied as well. These investigations have made it possible to develop some new and technologically convenient single-stage methods of synthesis of various unsaturated, aromatic and heteroaromatic sulfur compounds such as vinylthiol, unsubstituted and ring-substituted aromatic and heteroaromatic thiols, sulfides, sulfur-containing heterocyclic compounds of the thiophene, thianthrene, dibenzothiophene and thioxanthene series.

Before our investigations there were only some few patent indications[1,2] that hydrogen sulfide might react with chlorosubstituted aromatic hydrocarbons at 400–700°C to give the corresponding aromatic thiols. However, our attempts to reproduce the synthesis of these compounds under the conditions described in the patent[1] (at 700°C) were unsuccessful. The yields of thiophenols at 400–500°C under the conditions described in Reference 2 proved to be very low (less than 12%), consistent with the patent data. Therefore, a heterogeneous catalytic method [1–3] appears to have been worked out in order to increase the yield of thiophenols from aromatic chloroderivatives and hydrogen sulfide.

We have found that the reaction of hydrogen sulfide and thiols with chloroderivatives of the aromatic and thiophenic series proceeds smoothly at 500–600°C according to a general scheme

$$RX + H_2S \rightarrow RSH + HX \qquad (1)$$

$$2RX + H_2S \rightarrow RSR + 2HX \qquad (2)$$

$$RX + R'SH \rightarrow RSR' + HX \qquad (3)$$

where $X = Cl$; R,R' = aryl, thienyl, etc.

Simultaneously with reactions (1–3), side reactions that reduce chloroderivatives occur

$$RX + R'SH \rightarrow RH + R'X + S \qquad (4)$$

where $R' = H$, aryl.

The reaction rate increases significantly at temperatures above 600°C.

The reaction is carried out in the gaseous phase in a flow or recycling system and requires neither catalyst nor special methods to obtain the reaction products.

High temperature reactions (1–3) are selective (under the best conditions) allowing the corresponding thiophenols or sulfides to be obtained in 50–90% yield.

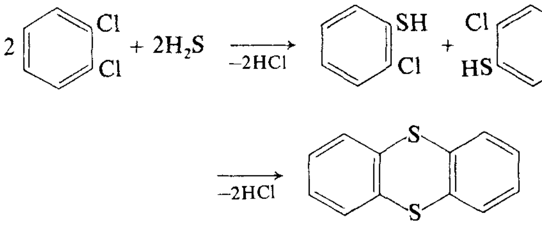
Reaction (1) is selective at a high hydrogen sulfide concentration and a short contact time (less than 30 s) which suppresses further conversion of the thiols.

Thiophenol is the main product of the reaction of chlorobenzene with an excess of hydrogen sulfide according to scheme (1). Its yield amounts to 80–90%. Analogously, the difficult to obtain and little studied thiophene-2-thiol forms readily from 2-chlorothiophene in 70% yield.[4]

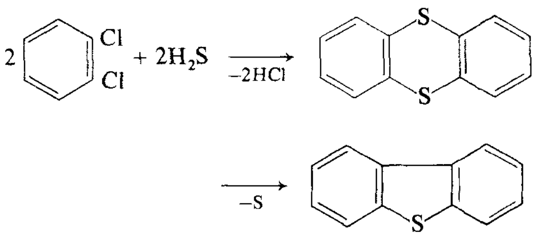
According to scheme (1) exo-substituted thiophenols and thiophenothiols containing various ring substituents such as CH_3, OCH_3, OH, Cl, F, etc. can be obtained from the corresponding chlorobenzene and chlorothiophene derivatives.[5]

The reaction of hydrogen sulfide with an excess of a halogen derivative proceeds according to scheme (2) to give diaryl- and dithienyl sulfides, including those containing various ring substituents (CH_3, OCH_3, Cl, F, etc.).[6]

The reaction of hydrogen sulfide with ortho-substituted chlorobenzene is accompanied by formation of sulfur heterocyclic compounds. Thus, with *ortho*-dichloro- or *ortho*-dibromobenzene, hydrogen sulfide affords thianthrene at 550°C (in 60–70% yield)[7] and dibenzothiophene in 60–70% yield at 600–620°C.[8]



(5)



(6)

According to scheme (5), 2,7-dichlorothianthrene, probably containing 20% of the 2,8-isomer, was obtained from 1,2,4-trichlorobenzene.

In addition to chloroderivatives, bromoderivatives of the aromatic and heteroaromatic series may be used in the reaction with hydrogen sulfide. In this case, especially when polycyclic aromatic hydrocarbons are used, the reaction may be performed in the liquid phase.[9]

The reaction of hydrogen sulfide with bromobenzene and its derivatives proceeds at a higher rate and lower temperatures than that with analogous chloroderivatives to give selectively diarylsulfides according to scheme (2), where X = Br, and is accompanied by lower resin formation.

Conversion of chloroderivatives in the reaction with hydrogen sulfide at high temperatures depends on their structure[10] (Table I). Substituents of both the donor (CH_3, C_2H_5) and withdrawing (Cl) type in position 4 of the aromatic ring or position 5 of the thiophene ring increase conversion of the corresponding chloroderivatives as compared to that of unsubstituted chlorobenzene or chlorothiophene.

1-Chloronaphthalene is also more reactive than chlorobenzene. The introduction of methyl groups into the position *ortho* to the chlorine atom decreases conversion of the chloroderivative (2-chlorotoluene, chloromesitylene) in the reaction with hydrogen sulfide, whereas the introduction of an electron withdrawing substituent such as a chlorine atom, on the contrary, increases it. Electron-donor substituents such as OH, OCH_3, F, independently of their position in the aromatic ring, decrease conversion of the chloroderivative in comparison with that of chlorobenzene. The temperature of the reaction of benzene and thiophene chloroderivatives leading to formation of thiol and sulfide drops as the C—Cl bond polarity decreases, i.e. as the susceptibility to homolytic cleavage increases. This is evidenced from an antibatic dependence of these temperatures on average ^{35}Cl NQR frequencies of the compounds studied (Figure 1). This dependence is not the case for all chlorophenols or 4-chloroanisole which are inhibitors of radical reactions. Pentafluorochlorobenzene also displays an anomalous reactivity relative to hydrogen sulfide.

Under comparable conditions of the reaction with H_2S, the chlorobenzene derivatives bearing donor substituents in the para position of the aromatic ring show a higher thiol–sulfide ratio. A similar picture is observed for 5-substituted 2-chlorothiophenes. In going from chlorobenzene to 1-chloronaphthalene, the thiol–sulfide ratio rises also. The thiol–sulfide ratio of the benzene- or 2-chlorothiophene chloroderivatives containing a withdrawing substituent in the *para*-position or position 5, respectively, decreases as compared to that of unsubstituted chlorobenzene or chlorothiophene. In the reaction of ortho-substituted chlorobenzenes with hydrogen sulfide, the orientation of secondary processes essentially depends on the nature of the substituent. Thus, *ortho*-chlorotoluene reacts with

TABLE I

Conditions and products of the reaction of hydrogen sulfide with chloroderivatives of aromatic and thiophenic series

R	T°C	H_2S:RCl	Contact time, s	RCl conversion %	Yield calculated from the RCl involved, %			RSH:RSR molar ratio
					RSH	RSR	Other products	
C_6H_5	550	2	50	18.5	84.0	2.0	—	42.00
	600	2	50	45.4	43.1	38.6	C_6H_6 5%	1.12
	600	3.5	30	40.0	79.2	4.5	—	16.00
$2\text{-}CH_3C_6H_4$	600	2	50	40.0	68.7	—	Anthracene 6%	—
	600	3	35	20.5	31.0	—	—	—
$3\text{-}CH_3C_6H_4$	600	2	50	43.0	62.5	38.2	—	1.64
$4\text{-}CH_3C_6H_4$	600	2	50	62.5	57.0	27.5	—	2.19
	600	4	30	51.0	87.0	2.8	—	31.40
$3\text{-}Cl,4\text{-}CH_3C_6H_3$	500	2	50	25.0	70.0	23.0	—	2.50
	600	2	50	70.0	28.0	21.0	2,7-Dichloroanthracene 11%	1.30
	600	4	30	45.0	45.5	25.6	—	1.77
$2\text{-}ClC_6H_4$	500	2	50	20.0	29.5	—	Thianthrene 60.5%	—
	500	2	50	66.0	9.0	—	Thianthrene 71.0%	—
$4\text{-}ClC_6H_4$	550	2	50	65.0	1.0	50.0	—	0.02
	580	2	50	75.0	1.5	41.0	C_6H_5Cl 10%	0.04
	580	3	40	70.0	14.5	55.8	C_6H_5Cl 5%	0.26
$3,4\text{-}Cl_2C_6H_3$	500	2	50	35.6	56.0	—	Dichlorothianthrene 26%	—
	550	2	50	68.0	14.6	—	Dichlorothianthrene 45%	—
$2,4,6\text{-}(CH_3)_3C_6H_2$	600	2	50	35.0	61.0	—	—	—
$1\text{-}C_{10}H_7$	600	2	50	81.3	65.7	20.3	Naphthalene 8, 9%	2.80
	600	3	40	77.5	75.5	7.7	—	11.20
Thienyl-2	510	2	50	54.0	16.5	51.8	Thiophene 10%	0.32
Thienyl-2	540	2	50	85.0	10.3	63.5	Thiophene 13%	0.16
5-Ethylthienyl-2	520	2	50	58.5	40.5	23.1	2-Ethylthiophene 10.5%	1.60
5-Chlorothienyl-2	500	4	30	76.0	10.0	40.0	2-Chlorothiophene 25%	0.25
$2\text{-}HOC_6H_4$	520	2	50	43.3	70.0	10.0	—	7.00
$3\text{-}HOC_6H_4$	560	2	50	33.0	80.0	—	—	—
$4\text{-}HOC_6H_4$	560	2	50	41.8	60.0	—	—	—
$4\text{-}CH_3OC_6H_4$	500	2	50	25.0	26.0	—	Phenol 25%	—
C_6F_5	600	2	50	55.0	66.0	25.0	—	2.60

hydrogen sulfide only according to scheme (1) to form *ortho*-thiocresol. Chloromesitylene behaves similarly. 2-Chlorophenol, on the contrary, forms, along with 2-oxythiophenol, the corresponding sulfide though in a low yield. At the same time, 1,2-dichloro- and 1,2,4-trichlorobenzene react with H_2S to transform mainly into thianthrene and dichlorothianthrene according to scheme (5) with minor amounts of 2-chlorothiophenol or 3,4-dichlorothiophenol. The latter do not react with the initial chloroderivative, possibly due to a higher rate of the competitive reaction giving thermally stable heterocyclic compounds.

In reactions (1)–(2) the RSH:RSR molar ratio varies in line with the pK_a value of the thiols formed. The exceptions are all *ortho*-substituted thiophenols as well as oxythiophenols, 4-methoxythiophenol, and pentafluorothiophenol. In these cases, conversion of the initial chloroderivative is also anomalous.

As the temperature of the reactions of all benzene and thiophene chloroderivatives with hydrogen sulfide studied increases, the thiol–sulfide ratio decreases.

Thus, qualitative regularities have been established which allow one to predict to some extent the orientation of the high temperature reaction of

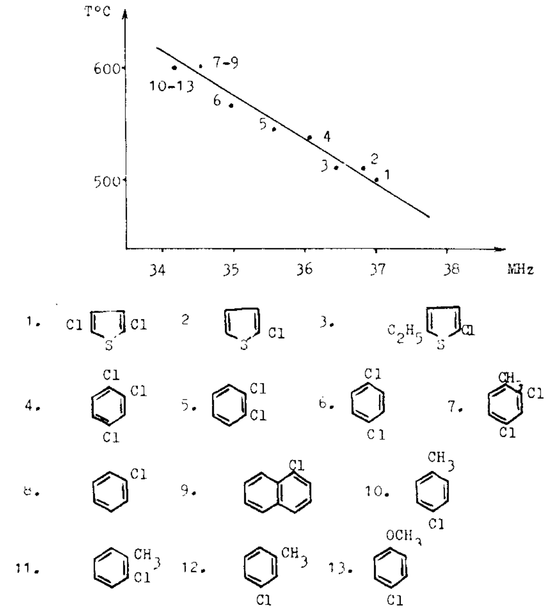


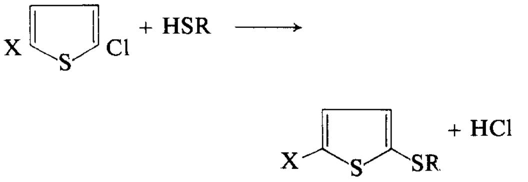
FIGURE 1 Dependence of the temperature of thiol and sulfide formation on average ^{35}Cl NQR frequencies of the initial chloroderivatives.

chloroderivatives of the aromatic and thiophenic series with hydrogen sulfide and to determine the reaction conditions.

One of the intermediate stages of the reaction of hydrogen sulfide with chloroderivatives of the aromatic and thiophenic series at 500–600°C leading to formation of symmetric sulfides is the reaction of thiophenol with initial chloroderivatives. The possibility of such a reaction was first established experimentally by us.

The high temperature reaction of chloroderivatives of the aromatic and thiophenic series with thiophenols according to scheme (3) makes it possible to obtain readily the corresponding mixed sulfides. The reaction selectivity is favored by an excess in the halogen derivative (RCl : RSH $\geqslant$ 2).

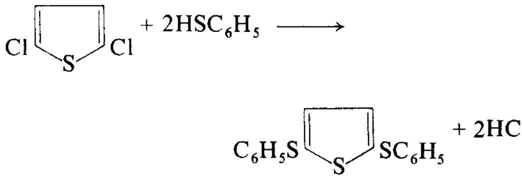
Thus, for example, the reaction of 2-chlorothiophenes with different thiophenols has given previously unknown 2-arylthiophenes in 50–60% yield.[11]



(7)

where X = H, alkyl, Cl, etc.; R = aryl.

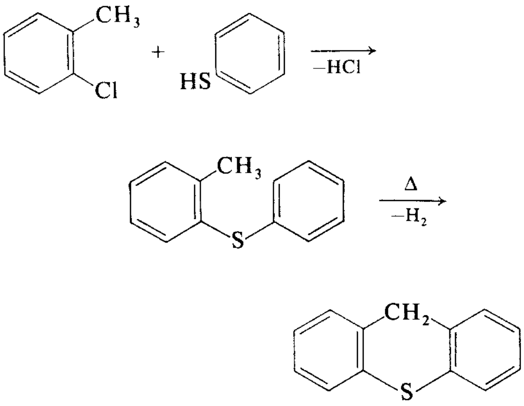
2,5-Diarylthiophenes were obtained from 2,5-dichlorothiophene in 30% yield in a similar way.



(8)

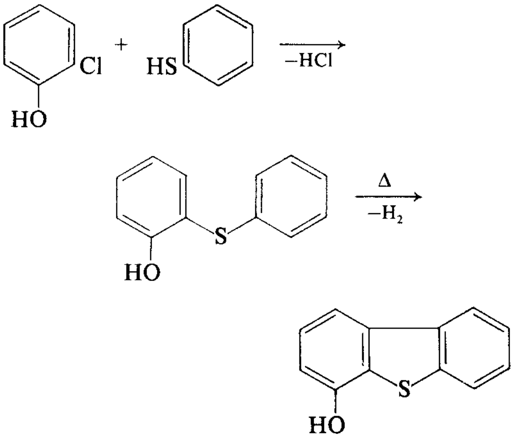
The reaction of thiophenol with some *ortho*-substituted chlorobenzenes yield sulfur-containing heterocyclic compounds (such as thianthrene, thioxanthene, 4-oxydibenzothiophene) which are products of secondary thermal transformation of intermediate unsymmetric aromatic sulfides.

Thus, the reaction of *ortho*-chlorotoluene with thiophenol at 700°C leads to formation of the previously nearly unavailable thioxanthene in 40–50% yield.[12]



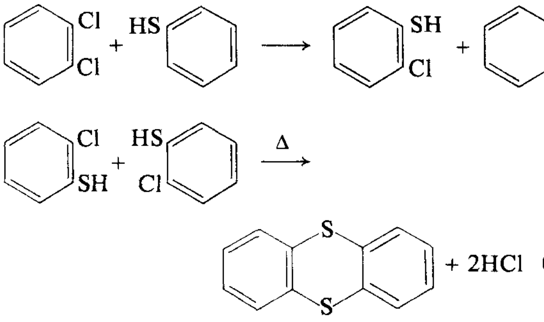
(9)

The high temperature reaction (550°C) of 2-chlorophenol with thiophenol affords 4-oxydibenzothiophene in 30% yield:[13]



(10)

Condensation of *ortho*-dichlorobenzene with an excess of thiophenol at 550°C gives thianthrene whose formation may be explained by the following scheme:[14]



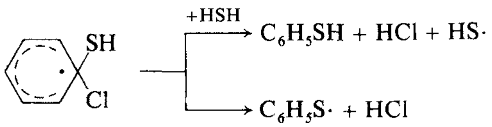
(11)

This scheme is confirmed by formation of dichlorothianthrene from 1,2,4-trichlorobenzene and thiophenol. Thus, the possibility of high temperature exchange between the halogen atoms and the sulfhydryl group attached to the aromatic ring according to general scheme (11) has been established for the first time.

The mechanism of reactions (1) and (2) is most likely based on homolytic substitution of the chlorine atom in the aromatic or heteroaromatic ring by thiyl radicals, ·SH and ·SR formed in pyrolysis of hydrogen sulfide or thiophenol. The mechanism of the high temperature reactions occurring may be represented by the following scheme:

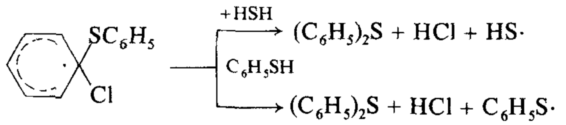
$HSH \rightarrow HS\cdot + H\cdot$

$HS\cdot + C_6H_5Cl \longrightarrow$



$C_6H_5SH \rightarrow C_6H_5S\cdot + H\cdot$

$C_6H_5S\cdot + C_6H_5Cl \longrightarrow$



$H\cdot + HSH \rightarrow H_2 + HS\cdot$ (12)

$H\cdot + C_6H_5SH \rightarrow H_2 + C_6H_5S\cdot$

$C_6H_5S\cdot + C_6H_5SH \rightarrow C_6H_5SC_6H_5 + HS\cdot$

$C_6H_5S\cdot + C_6H_5S\cdot \rightleftarrows C_6H_5SSC_6H_5$

$H\cdot + H\cdot \rightarrow H_2$

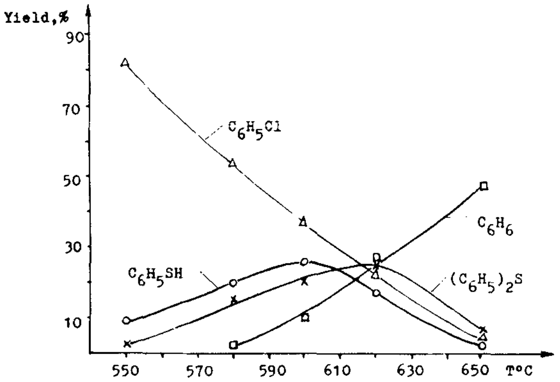


FIGURE 2 Dependence of the product yield in the $H_2S + C_6H_5CL$ reaction on temperature.

The formation of the sigma-complex radical at the stage of chain-transfer is confirmed by the absence of isomeric thiols and sulfides in the reaction products as well as by the *ortho* effect playing an essential role in free-radical substitution. Figures 2 and 3 show the dependence of the yield on the reaction temperature and the initial reactant ratio. A temperature rise from 550 to 650°C at constant contact time influences the yield and ratio of thiophenol, diphenylsulfide and benzene. At temperatures above 620°C the side reduction proceeds faster, thus inhibiting sharply the main process (reaction 1 and 2, Figure 2). This indicates that at temperatures above 620°C hydrogen sulfide may be used to reduce halogen derivatives of the aromatic series. A higher hydrogen sulfide concentration favors selectivity of reaction (1) (Figure 3).

The reaction temperature produces the greatest effect on the yield and ratio of reaction products (Figures 4–5). Within the whole temperature range the thiophenol yield turns out to be maximum at the contact time of 40–50 s and the diphenyl sulfide

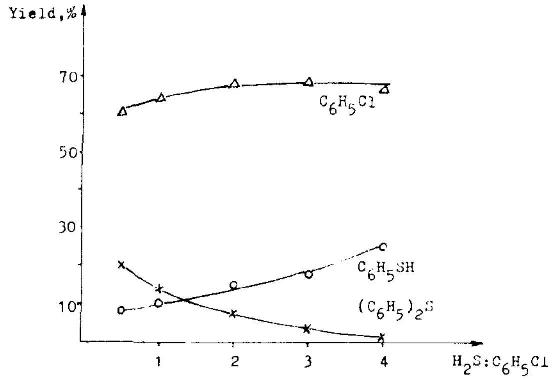


FIGURE 3 Dependence of the product yield in the $H_2S + C_6H_5Cl$ reaction on the initial reactant ratio.

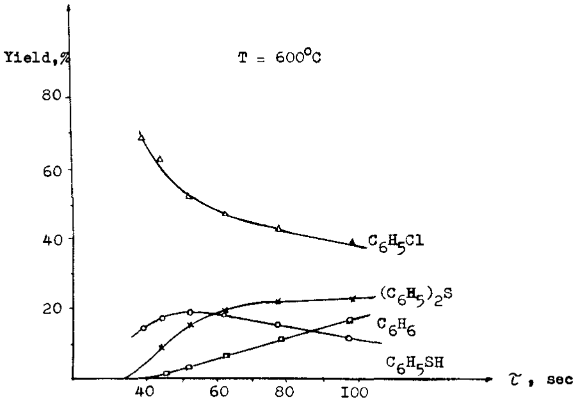


FIGURE 4 Yield/contact time dependence in the H_2S + C_6H_5Cl reaction ($H_2S : RCl = 2$, $T = 600°C$).

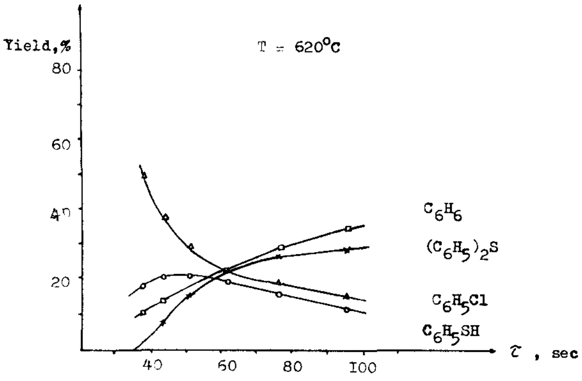


FIGURE 5 Yield/contact time dependence in the H_2S + C_6H_5CL reaction ($H_2S : RCl = 2$, $T = 620°C$).

yield reaches its constant highest value at a contact time of over 70–80 s. This seems to be caused by a higher rate of the competitive parallel reaction (4) to afford benzene from chlorobenzene owing to which the latter is involved to a lesser extent in reaction (2). Chlorobenzene conversion increases with the reaction temperature and the contact time.

The free-radical mechanism of the reaction of hydrogen sulfide with chlorobenzene is confirmed by data on its initiation and inhibition. Phenol and cyclohexene, the inhibitors of the free-radical processes, make the process under consideration markedly slower, reducing chlorobenzene conversion at 600°C by a factor of two (Table II). Under the same conditions a number of compounds capable of generating free radicals (acetone, tetrachloroethylene, etc.), on the contrary, accelerate the above reaction increasing chlorobenzene conversion and selectively affecting individual steps (1), (2) and (4) of the reaction (Table II).

Thermal decomposition of acetone forms hydrocarbon radicals[15] which react with hydrogen sulfide and bind the hydrogen atom thus generating sulfhydryl radicals, for example

$$\cdot CH_3 + H_2S \rightarrow CH_4 + HS\cdot \qquad (13)$$

Tetrachloroethylene dissociating at 550–600°C to give the $Cl_2C{=}CCl\cdot$ radical[16] mainly initiates only the chlorobenzene reduction reaction (the benzene yield increases from 5 to 60–70% at 600°C) with high chlorobenzene conversion (91–95%). This radical can undergo the exchange reaction with chlorobenzene at a very high rate

$$Cl_2C{=}CCl\cdot + C_6H_5Cl \rightarrow Cl_2C{=}CCl_2 + \cdot C_6H_5 \qquad (14)$$

The phenyl radicals formed are reduced by hydrogen sulfide to benzene

$$\cdot C_6H_5 + H_2S \rightarrow C_6H_6 + HS\cdot \qquad (15)$$

All these data confirm the above scheme of a radical-chain mechanism and make it possible to optimize the reaction of hydrogen sulfide with chlorobenzene.[19]

An enlargement of the reaction zone surface, all other conditions being equal (Table III), decreases chlorobenzene conversion without affecting the main

TABLE II

Effect of homogeneous addition of inhibitors and initiators on the high temperature reaction of hydrogen sulfide with chlorobenzene

($T = 600°C$, contact time 65 s, $H_2S : C_6H_5Cl$ molar ratio = 2)

Additive	Amount mol %	Conversion C_6H_5Cl, %	Yield calculated from C_6H_5Cl involved, %		
			C_6H_6	C_6H_5SH	$(C_6H_5)_2S$
—		45.4	4.6	45.0	35.6
Phenol	5	32.6	8.5	45.2	35.3
Cyclohexene	5	21.2	11.5	42.5	26.4
Acetone	10	80.1	8.8	41.9	27.4
Tetrachloroethylene	5	91.2	60.2	7.5	3.8

TABLE III

Effect of the reactor surface/volume relation on the reaction $H_2S + C_6H_5Cl$ ($T = 620°C$, $H_2S:C_6H_5Cl = 2$)

Volume rate of C_6H_5Cl l/l·h	Contact time, s	Conversion of C_6H_5Cl		Yield calculated from C_6H_5Cl involved, %					
				C_6H_5SH		$(C_6H_5)_2S$		C_6H_6	
		I	II	I	II	I	II	I	II
13.4	95.0	82.5	59.0	14.7	19.0	35.0	37.3	42.3	38.4
17.9	68.4	79.5	55.4	22.2	25.4	30.9	34.1	31.6	25.9
22.4	50.6	71.2	52.4	29.0	29.1	22.7	30.3	23.0	18.6
27.9	43.4	62.3	46.0	32.3	37.7	22.4	25.2	20.1	15.9

I—reactor volume = 0.46 l (an empty quartz tube); II—reactor volume = 0.32 l (the same tube filled with quartz crumbs).

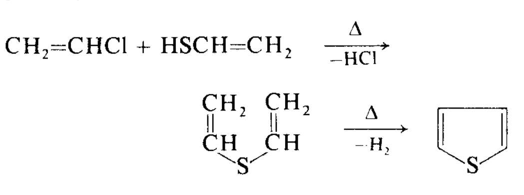
kinetic regularities that determine the product yield. This indicates that the high temperature substitution of halogen in the aromatic ring by thiylic radicals occurs in the gaseous phase. The generation and destruction of thiylic radicals may take place even at the reactor walls, since at temperatures below 730°C, the formation rate under a simple impact of molecules is not high enough to lead to a HS· radical concentration capable of initiating the chain process.[17]

Chloro-substituted ethylenes react with hydrogen sulfide like chloroderivatives of the aromatic series. Thus, the reaction of vinyl chloride with an excess of hydrogen sulfide ($H_2S:CH_2{=}CHCl$ molar ratio $\geqslant 2$) may afford vinylthiol. The reaction is performed in an empty quartz tube in a flow system at 530–550°C

$$CH_2{=}CHCl + H_2S \xrightarrow[-HCl]{\Delta} CH_2{=}CHSH \qquad (16)$$

Vinylthiol proves to be fairly stable at such a high temperature. Its yield exceeds 65%.†

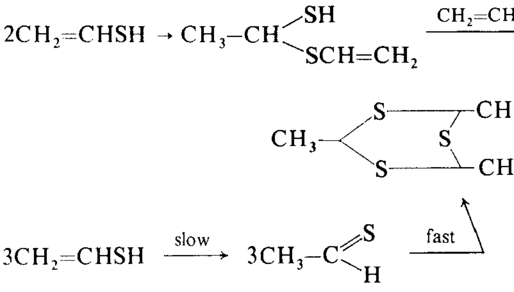
Thiophene is the reaction side product forming in 25% yield according to scheme (17). As the $H_2S:CH_2{=}CHCl$ molar ratio decreases, the thiophene yield rises and may be brought up to 60%.†[18]



(17)

At room temperature vinylthiol converts gradually to a stable *β*-trithioacetaldehyde, 2,4,6-trimethyl-1,3,5-trithiane.

In a ^1H nmr spectrum of condensate kept for several hours at room temperature some signals of protons of a trimer appear (Table IV). Twelve to fifteen hours later this trimer turns out to be the main component of the reaction mixture. No protons of monomeric thioacetaldehyde have been found in the condensate. This indicates that the conversion of vinyl thiol into its trimer may occur in two ways.



(18)

TABLE IV

^1H nmr parameters of products of high temperature reaction of vinyl chloride with hydrogen sulfide

Compound	δ, ppm			^3J, Hz	^2J, Hz
	CH	CH_2	CH_3		
$CH_2{=}CHSH$[a], I	6.10 q	5.25 dd 5.23 dd	— —	6.5 14.1	1.0
$CH_2{=}CHSH$[b], I	6.29 q	5.43 dd 5.47 dd	— —	6.5 14.1	1.0
Thioacetaldehyde, II	9.71 q	—	2.10 d	2.8	
Thiirane, III	—	2.07 s	—	—	
Trithioacetaldehyde, IV	3.98 q	—	1.50 d	7.0	

[a] Undiluted condensate obtained from reaction (16). Spectral parameters coincide with those published before.

[b] In mixture with compounds (II) and (III).

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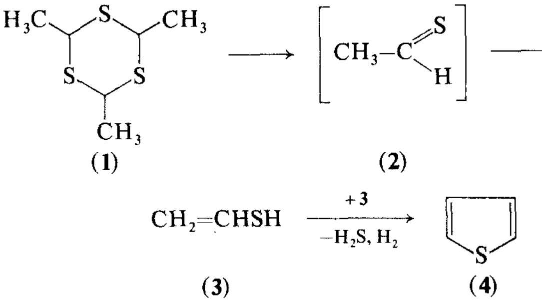
† Calculated from the amount of vinyl chloride involved in the reaction.

Further kinetic studies are necessary for the reaction mechanism to be proved.

At 450–650°C in an atmosphere of nitrogen, trithioacetaldehyde converts into vinylthiol and thiophene in 1 : 1 ratio (the contact time is 100–170 s).



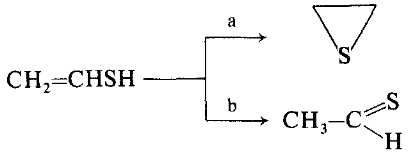
(19)

Under the conditions studied the primary product of trithiane decomposition, monomeric thioacetaldehyde, isomerizes into thermally stable vinylthiol. The inverse reaction, conversion of thiol into trithiane, proceeds readily at low temperatures (approximately 20°C). The formation of thiophene from vinylthiol occurs according to the known scheme.[18]

Thus, thione-thiolic vinylthiol-thioacetaldehyde equilibrium depends sufficiently upon temperature and is totally shifted to the thiolic form in the gaseous phase at 450–600°C. The thiolic form is stable even at very low temperatures (below −60°C).

After neutralization of the HCl formed in reaction (16) by aqueous alkali, an immediate formation of trithioacetaldehyde precipitating as a crystallizable oil is observed. Condensation of reaction (16) products in a 1 : 1 mixture of 10% aqueous alkali and dimethylsulfoxide (DMSO) followed by distillation affords isolation of a low-boiling fraction (26–40°C) which is a 1 : 1 : 4 mixture of vinylthiol, thioacetaldehyde and thiirane, according to ^1H nmr data. The total yield of these three isomeric products of the same C_2H_4S composition is not high (10–12% calculated from vinyl chloride involved in the reaction) owing to the formation of sufficient amounts of trithioacetaldehyde during distillation.

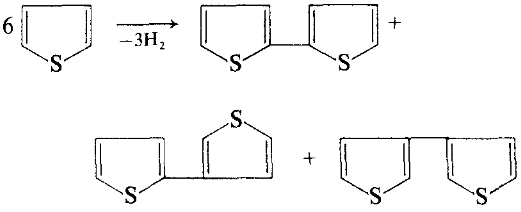
The mixture used (KOH–DMSO solution) seems to induce isomerization of vinylthiol into thiirane and monomeric thioacetaldehydė with stabilization of the latter



(20)

We have also established that hydrogen sulfide dissociating into free radicals at temperatures above 400°C may initiate many high-temperature organic reactions that hardly occur in its absence or lead to only a negligible yield of the desirable product.

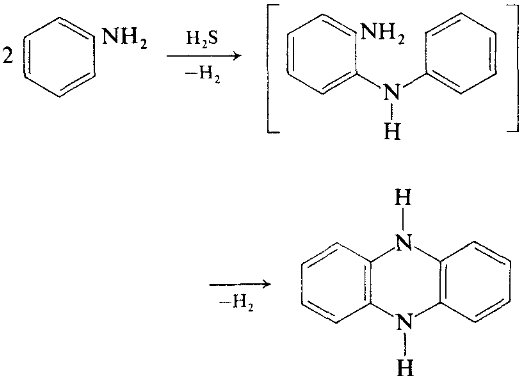
Thus, for example, at 750–800°C in an atmosphere of hydrogen sulfide, thiophene converts into a mixture of isomeric dithienyls in a general yield of 90% according to the following scheme:



(21)

The 2,2′-, 2,3′- and 3,3′-dithienyl ratio is 1 : 6 : 3, respectively.

At 720–750°C in an atmosphere of hydrogen sulfide, aniline undergoes pyrolytic dehydrodimerization converting into 5,10-dihydrophenazine in 50% yield.



(22)

Benzaldehyde converts into *trans*—stilbene in 60% yield at 500°C in an atmosphere of hydrogen sulfide. Benzene, toluene, water and elemental sulfur are by-products of this reaction

$$2C_6H_5CHO + 2H_2S \rightarrow C_6H_5CH{=}CHC_6H_5 + H_2O + 2S \qquad (23)$$

$$C_6H_5CHO + 2H_2S \rightarrow C_6H_5CH_3 + H_2O \qquad (24)$$

$$C_6H_5CHO \rightarrow C_6H_6 + CO \qquad (25)$$

In the absence of hydrogen sulfide in an atmosphere of nitrogen benzaldehyde pyrolysis only proceeds at temperature above 650°C to give benzene, diphenyl and terphenyl.

Toluene is a possible intermediate of reaction (23), converting into stilbene in the reaction with sulfur according to the following scheme:

$$2C_6H_5CH_3 + 2S \rightarrow C_6H_5CH{=}CHC_6H_5 + H_2S \qquad (26)$$

Thus, initiation of high temperature organic reactions by thiylic radicals is rather promising in organic synthesis.

EXPERIMENTAL

The reactions of hydrogen sulfide and thiophenols with halogen derivatives of the unsaturated, aromatic and thiophenic series, as well as pyrolytic processes were carried out in an atmosphere of nitrogen in an empty quartz tube (650 mm × 30 mm) placed in an electric furnace. The reactions started after equalization of the temperatures within the whole reaction zone. The halogen derivative was introduced automatically into the reaction zone in a hydrogen sulfide flow. Mixtures of thiophenol and halogen derivative were analogously introduced in a dry nitrogen flow. The reaction products were condensed in traps, cooled to −75°C, and analyzed by glc. All synthesized compounds were isolated in pure form by distillation or recrystallization. Their structures were identified by ir- and ^{1}H nmr-spectroscopy, mass-spectroscopy and glc. Physicochemical constants of known compounds were consistent with the literature data. The data of elemental analysis were in agreement with the calculated composition.

The data on the reactions performed as well as the yields and physical constants of the sulfur compounds obtained are given in reactions (4)–(14).

Kinetics of the reaction of hydrogen sulfide with chlorobenzene was studied under similar conditions.[19] The contact time was calculated by the following expression:

$$t\ (\mathrm{s}) = \frac{3600 \cdot v}{k(n \times 22.4 + V)}$$

where v is the reactor volume (l), k is the temperature scaling coefficient, n is the number of chlorobenzene moles per h, V is the hydrogen sulfide rate (l/h).

Equations of the second order regression describing concentration variations of chlorobenzene and the products of its reaction with hydrogen sulfide (mol.) are as follows:

(*i*) *Chlorobenzene*

$$\begin{aligned} \mathrm{Y}_A = {} & 121.245 + 0.538T - 0.443V_1 - 1.246V_2 \\ & + 0.004TV_2 - 0.034V_1V_2 + 0.018V_1^2 - 0.006V_2^2 \end{aligned}$$

(*ii*) *Thiophenol*

$$\begin{aligned} \mathrm{Y}_B = {} & 88.614 + 0.303T - 0.244V_1 - 0.803V_2 \\ & + 0.001TV_1 + 0.007V_1V_2 - 0.011V_1^2 + 0.039V_2^2 \end{aligned}$$

(*iii*) *Diphenyl Sulfide*

$$\begin{aligned} \mathrm{Y}_C = {} & -43.087 + 0.119T + 0.069V_1 + 1.8301V_2 \\ & - 0.004TV_2 + 0.005V_1V_2 - 0.005V_1^2 + 0.008V_2^2 \end{aligned}$$

(*iv*) *Benzene*

$$\begin{aligned} \mathrm{Y}_D = {} & 254.713 - 0.934T + 0.57V_1 + 1.865V_2 \\ & + 0.001TV_1 - 0.004TV_2 + 0.006V_1V_2 \\ & + 0.001T^2 + 0.003V_1^2 + 0.001V_2^2 \end{aligned}$$

where V_1 is the volume rate of chlorobenzene, l/(1 · h)
V_2 is the flow rate of hydrogen sulfide, l/h
T is the temperature, K.

Reaction of Vinyl Chloride with Hydrogen Sulfide

Hydrogen sulfide ($V = 6$ l/h) and vinyl chloride ($V = 2$ l/h) were simultaneously introduced into an empty quartz tube (650 mm × 30 mm) heated to 530°C. $H_2S{:}CH_2{=}CHCl = 3$. The contact time is 50 s, the reaction time 4 h. The reaction products were condensed in a receiver cooled to −80°. Unreacted vinyl chloride was condensed in graduated traps cooled to −40°; at this temperature its specific gravity is 1. Conversion is 50%. Obtained: 10.0 g of condensate frozen at −80°, containing vinylthiol (80%) and thiophene (20%) according to ^{1}H nmr and GLC data:†

The yield of vinyl thiol and thiophene is 67.0% and 24.0%, respectively, as calculated from vinyl chloride involved in reactions (16) and (17). When the condensate is kept in the air for 15–20°C, trimer crystals precipitate, mp 125°C.

The reaction of vinyl chloride with hydrogen sulfide was carried out analogously. The condensate was collected into a mixture of 10% KOH (50 ml) with DMSO (50 ml). Rectification of the resultant solution of the reaction products gave a light fraction, bp 25–46°C (2.0 g), representing a 1 : 1 : 4 mixture of vinylthiol, thioacetaldehyde and thiirane, according to ^{1}H nmr data. The total yield is 17%. The second fraction, bp 37–56°C (3.0 g) is mainly thiirane, according to ^{1}H nmr and glc data. The total yield of thiirane is 30%.

Synthesis of Stilbene

The pyrolysis of benzaldehyde in a hydrogen sulfide medium was performed in a recycling system in a quartz tube (520 mm × 30 mm), $\tau = 3$–5 s. Of 28 g of benzaldehyde, 16.6 g of stilbene was obtained for 6 h (60% as calculated from the benzaldehyde involved). *trans*-Stilbene was isolated by distillation under vacuum and purified by recrystallization from ethanol, mp 123°.

Synthesis of 5,10-Dihydrophenazine

The pyrolysis of aniline in hydrogen sulfide was carried out in a recycling system in an empty quartz tube (520 mm × 30 mm), $\tau = 5$ s. Of 70 g of aniline, 27.5 g of dihydrophenazine (50% as calculated from the aniline involved in the reaction) was obtained during 7.5 h. In a flow system (660 mm × 30 mm quartz tube), $\tau = 40$–50 s, aniline conversion into 5,10-dihydrophenazine is 33% per run.

Dihydrophenazine was isolated by distillation under vacuum (bp 200–220°C/1 mm) and purified by recrystallization from toluene, mp 238°C (according to the literature, mp 255, 315–316°C[20]). Found: C, 79.19; H, 5.23; N, 15.03%. Calc. for $C_{12}H_{10}N_2$: C, 79.11; H, 5.52; N, 15.38%. Soluble in DMSO, hot

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† The GLC analysis is carried out on a column (3m × 3 mm I.D.) with 15% PPhE on Chromatone. Operating conditions: column temperature, 100°C; carrier gas nitrogen at 2 l/h; τ of vinylthiol, 40 sec; τ of thiophene, 3 min.

benzene and toluene. The ir spectrum of the compound shows all wave numbers completely identical with those in the ir spectrum for 5,10-dihydrophenazine[21] where, contrary to the phenazine ir spectrum, the N–H bond stretching vibrations have been found at 3410 cm^{-1}. The ^{1}H nmr (DMSO) spectrum contains proton signals of the NH group in low-field (singlet, 10.7 ppm) and of the aromatic system (multiplet, 7.3 ppm). The mass spectrum confirms the structure of the compound, *m/e* (%): 182 (100), 181 (84), 168 (30.7), 167 (56), 166 (56), 166 (40), 155 (22.7), 154 (46.6), 153 (20).

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