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Thermal reactions of thiyl radicals

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ABSTRACT. The review presents data on the methods of generation and properties of thiyl radicals. The results of studies on the reactivities of thiyl radicals in thermal processes, permitting the synthesis of a wide variety of organic sulphur compounds and compounds of other types, are surveyed.

The bibliography includes 167 references.

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I. Introduction

Thiyl (sulphur-centred) free radicals are short-lived reactive sulphur-containing intermediates RS$^{\cdot}$ (R = H or an organic group) whose sulphur atom has an unpaired electron. They participate in many chemical reactions, including various industrial and natural processes and are therefore of practical and theoretical interest.

The stability of free radicals is determined by the degree of delocalisation of the unpaired electron.[1] This can be estimated quantitatively from electronic, spectroscopic, and EPR data. According to Walter's classification, free radicals can be divided into two groups:[2]

1. The radical centre possesses an unshared electron pair together with the unpaired electron. The delocalisation of the electron is promoted by electron-donating substituents at the radical centre.

2. The paramagnetic centre has only the unpaired electron whose delocalisation is promoted by both electron-donating and electron-accepting substituents.

The energy characteristics of the level occupied by the unpaired electron have also been used recently for the classification of free radicals. According to this classification, the radicals can be divided into three groups:[3]

1. Electrophilic radicals containing the unpaired electron in the highest bonding orbital. Such radicals tend to be converted into the energetically more favourable ionic state by capturing an electron.

2. Nucleophilic radicals containing the unpaired electron in the lowest antibonding orbital and exhibiting a tendency to give it up.

3. Amphoteric radicals containing the unpaired electron in a non-bonding orbital.

Thiyl radicals having an unshared electron pair at the radical centre are electrophiles judging from their reactivity. The energies of the highest molecular orbitals occupied by one electron may serve as a characteristic of the relative stability of thiyl radicals.[3]

This review deals for the first time with thermal methods for the generation of thiyl radicals from very simple sources such as hydrogen sulphide and its organic derivatives† as well as the methods for high-temperature organic synthesis using thiyl radicals. The description of these data (mainly obtained by the present authors) is preceded by an account of the general information about the method of generation and detection and the properties of thiyl radicals secured earlier in the study of the photochemical and other types of reactions and frequently quoted in certain reviews and monographs.

II. Generation, detection, structure, and properties of thiyl radicals

1. Generation

Thiyl radicals usually arise in the photolysis, radiolysis, and thermolysis of hydrogen sulphide and its organic derivatives (thiols, sulphides, thionitrites, etc.). They can also be generated on treatment of the above compounds by initiators such as peroxides, diazo-compounds, etc.[6,7] Overall, the dissociation energies of the S–H, S–C, and S–S bonds are fairly high (87, 69, and 63 kcal mol^{-1} respectively) compared with the dissociation energies of other bonds (N–N, O–O, Si–Si, Ge–Ge, Sn–Sn, As–H, Sn–H, Sn–C, etc.) (Table 1).

The strength of the E–H, and E–C bonds involving elements of a given Group of the Periodic System decreases with increase in the atomic number of the element E (Table 1). Accordingly the S–H, and S–C bonds are weaker than the O–H and O–C bonds but are more stable than the Se–H and Se–C bonds respectively. The S–H bonds in alkanethiols are stronger than the CH_2–H bonds in propylene and toluene but weaker than the O–H bond in alkanols.[8]

The strength of the bonds between two identical non-metal atoms or two atoms of an amphoteric non-transition metal (E–E) in Group IV decreases with increase in the atomic number of the element E. On the other hand, the energy of the E–E bonds

† As regards the role of thiyl radicals in reactions of organic compounds with participation of elemental sulphur, see Voronkov, et al.[4,5]

involving Group V–VII elements in the Third Period (P–P, S–S, and Cl–Cl) proves to be a maximum in the given Group, which can apparently be accounted for by the $p-\pi$, $d-\pi$ interaction, as a result of which the effect of the repulsion of the unshared electron pairs loses its importance. By virtue of this, the S–S bond in organic disulphides is much stronger than the O–O, Se–Se, and Te–Te bonds in the isostructural peroxides, diselenides, and ditellurides (Table 1).

Table 1. The average enthalpies of the E–H, E–C, and E–E bonds involving non-metallic elements.

Element E	ΔH°_{298}, kcal mol^{-1}*		
	E–H	E–C	E–E
C	99	83 (76)	83 (76)
Si	76	76	46 (42)
Ge	69	57	38
Sn	60	46	39
N	89 (93)	73	21 (27)
P	77 (63)	63	51
As	47	55	43
O	105 (110)	80 (85)	45
S	87	69	63
Se	75	60	48
Te	63	48	36
F	134	116	38
Cl	102	76	58
Br	86	63	46
I	71	43	36

Note. The data were taken from handbooks: V I Vedeneev, L V Gurvich, V N Kondriat'ev, et al. *Energii Razryva Khimicheskikh Svoiazei* (Chemical Bond Dissociation Energies), Izd. Akad. Nauk SSSR, Moscow, 1962, 215 pp; A J Gordon, R A Ford *A Chemist's Companion* (Translated into Russian), Izd. Mir, Moscow, 1976, p. 134

*The values determined by other methods are given in brackets.

The structure of the alkyl groups linked to the sulphur atom in alkanethiols, alkyl sulphides, and alkyl disulphides has little influence on the strength of the S–H, S–C, and S–S bonds. On the other hand, the presence of a π-electron system at the sulphur atom reduces the strength of these bonds[9,10] (Table 2).

The difference between the dissociation energies of the C=S and C–S bonds (45 kcal mol^{-1}) is much smaller than the difference between the dissociation energies of the C=O and C–O bonds (73 kcal mol^{-1}). The conversion of thiyl radicals into thiocarbonyl compounds is usually not observed, while the analogous reactions involving oxyl radicals, readily affording carbonyl compounds, do take place.

The steric hindrance in the reactions involving thiyl radicals is less significant than in the reactions involving oxyl radicals, since the C–S bond length (1.81 Å) is greater by almost 30% than the C–O interatomic distance (1.42 Å).[1]

The electron affinity of thiyl radicals is greater than that of oxyl radicals, which is apparently due to the presence of unoccupied *d* orbitals in the sulphur atom. The stabilisation of thiyl radicals at low temperatures is difficult, since, in contrast to oxyl radicals, they readily recombine (cf. the S–S and O–O bond energies listed in Table 1).

Table 2. The dissociation energies (E_D) of the S–H, C–S, and S–S bonds in certain organic sulphur compounds.[9,10,11]

Compound	E_D(S–H) kcal mol^{-1}	Compound	E_D(S–C), kcal mol^{-1}	Compound	E_D(S–S), kcal mol^{-1}
HS–H	92.0±1.0	HS–Me	75.0±1.5	HS–SH	66.0±2.0
MeS–H	92.0±1.5	HS–Et	72.0±1.5	MeS–SMe	74.0±2.0
EtS–H	92.0±2.0	HS–Pr	72.0±1.0	AlkS–SAlk	74.0±2.0
AlkS–H	92.0±2.0	HS–Pr-iso	71.0±1.5	FS–SF	61.0±4.0
PhS–H	82.0±1.5	HS–Bu-t	69.0±1.5	PhS–SH	61.0±1.5
CH_2=CHS–H	84.0±2.0	HS–CH_2CH=CH_2	54.3±1.0	PhS–SMe	65.0±1.5
HS_2–H	70.0±1.5	HS–CH=CH_2	83.0±3.0	PhS–SPh	55.0±1.5
$AlkS_2$–H	70.0±1.5	HS–Ph	86.0±2.0	HS_2–SH	50.0±2.0
HS_3–H	70.0±1.5	HS–CHO	74.0±2.0	HS_2–SMe	54.0±2.0
HS_{3+n}–H	70.0±1.5	HS–COMe	73.0±2.0	HS_2–SAlk	54.0±2.0
$AlkS_{3+n}$–H	70.0±1.5	MeS–Me	77.0±1.5	HS_2–SPh	44.0±2.0
		MeS–Et	74.0±1.5		
		AlkS–Me	77.0±1.5		
		MeS–CH_2Ph	59.4±2.0		
		PhS–Me	67.4±1.5		
		AlkS–Bu-n	71.0±1.5		
		MeS–Ph	89.2±2.0		
		MeS–CN	97.0±1.5		

The enthalpy of formation of the sulphydryl radical HS$^{\cdot}$ varies in the range 31.9–35.0 kcal mol^{-1} according to different data.[9,12–14] The dipole moments, obtained by the EPR method, are contradictory (0.62 D [15] or 1.47 D [16]). The ν(SH) and ν(SD) frequencies in the IR spectra of HS$^{\cdot}$ and DS$^{\cdot}$ radicals matrix-isolated in argon are respectively 2450.8 and 1847.8 cm^{-1}.[12] The ionisation potential of HS$^{\cdot}$ is 10.5 eV [12] and its electron affinity varies in the range from 53.1 kcal mol^{-1} at −273 °C to 58.8 kcal mol^{-1} at 1527 °C.[17]

The enthalpy of formation of alkanethiyl radicals decreases with increasing length and degree of branching of the alkane chain from 31 for $CH_3S^{\cdot}$ to 15 for n-$C_4H_9S^{\cdot}$ and 11 kcal mol^{-1} for t-$C_4H_9S^{\cdot}$.[4] The entropy and heat generating capacity increase in the same sequence.[18]

The simplest arenethiyl radical $C_6H_5S^{\cdot}$ is distinguished by a high enthalpy of formation (ΔH°_{298} = 56.8 ± 2.0 kcal mol^{-1}).[14] Its stabilisation energy (9.6 kcal mol^{-1}) is close to the stabilisation energy of the benzyl radical (13.5 kcal mol^{-1}), but is appreciably lower than that of the phenoxyl radical (17.5 kcal mol^{-1}).[14]

The molecular and electronic structures of the $CH_3S^{\cdot}$ and $C_2H_5S^{\cdot}$ radicals, which have the C_s symmetry, were calculated by the MNDO method. The molecular orbital is localised predominantly on the sulphur atom, is located at right angles to the C–S bond, and has the A' symmetry.[19] This agrees with experimental data characterising the Mo of thiyl radicals as π orbitals. The heats of the rearrangement reaction involving the migration of a hydrogen

atom in the $CH_3S^{\cdot}$ and $C_2H_5S^{\cdot}$ radicals have been calculated:

$$CH_3S^{\cdot} \rightarrow \dot{C}H_2SH \ (0.6 \text{ kJ mol}^{-1}),$$

$$CH_3CH_2S^{\cdot} \rightarrow CH_3\dot{C}HSH \ (26.4 \text{ kJ mol}^{-1}).$$

The values obtained indicate the exothermic character of these reactions.

The rearranged radicals $\dot{C}H_2SH$ and $CH_3\dot{C}HSH$ have the C_s symmetry, while the molecular orbital is located at right angles to the CSH plane and has the A'' symmetry.

2. Detection

In contrast to the alkoxyl radicals $RO^{\cdot}$, the alkanethiyl radicals $RS^{\cdot}$ cannot be detected in the liquid phase by the EPR method since their $p-\pi$ orbitals are degenerate and the spin–orbital interaction constants for the sulphur atom are large.[20,21] The EPR spectra of alkanethiyl radicals in the solid state have a fairly anisotropic g-tensor,[22–24] whose components can differ appreciably depending on the structure of the radical.[25] In the thiyl radicals where the sulphur atom is linked to a π-electron system ($CH_2=CH$, C_6H_5, etc.), the degeneracy of the π levels is removed as a result of the delocalisation of the unpaired electron over the multiple bond. Their EPR spectra can be recorded in certain cases even in liquid media. The photochemically generated 2,4,6-tri-(t-butyl)benzenethiyl radical gives in its EPR spectrum a singlet ($\Delta\beta$ = 2.89) with g = 2.0103 and an unresolved hyperfine structure due to the hydrogen atoms.[26] This radical is in equilibrium with the dimer below 313 K (ΔH = –23.3 kcal mol^{-1}). After prolonged photolysis of thiophenols, a very complex effect of the chemically induced dynamic electronic polarisation (CIDEP), which promotes a marked decrease of the signal, was observed. In many cases, after the removal of the source of irradiation, the height of the lines in the EPR spectra of thiyl radicals increases suddenly and then slowly diminishes.[27]

A strong signal with a typically anisotropic g-factor was detected in the EPR spectrum of diphenyl disulphide irradiated with UV light at –200 °C.[28] The g-tensor is almost axially symmetrical and has the extremum values g = 2.006 and 2.012. The marked anisotropy of the g-factor is caused by the localisation of the unpaired electron on the sulphur atom of the $C_6H_5S^{\cdot}$ radical.[28,29] The absorption spectrum of $C_6H_5S^{\cdot}$ contains bands of 355 and 380 nm, while the luminescence spectrum has bands at 374 and 240 nm.[30] The colour of the 4-dimethylaminobenzenethiyl and 4-diphenylaminobenzenethiyl radicals is appreciable even at –73 °C.[29]

Thiyl radicals have also been identified by EPR spectroscopy in the form of their spin-adducts with different trapping agents. The spin-adducts of thiyl radicals with nitroso-compounds are unstable and are therefore detected only when they are generated directly in the resonator of the spectrometer.[31,32]

Thiyl radicals have been detected as spin-adducts with 2-nitrosopropane, 2-methyl-2-nitrosopropane, nitrosobenzene, pentamethylnitrosobenzene, nitrosodurene, 2, 4, 6-tri-(t-butyl)nitrosobenzene, and 5,5-dimethyl-Δ^1-pyrroline N-oxide.[33–37]

Thiyl radicals react at a high rate with stable radicals. The rate constants for the reactions between *para*-substituted benzenethiyl radicals and free radicals such as di(t-butyl)nitroxyl (DBNO$^{\cdot}$) and galvinoxyl (Q$^{\cdot}$) have been determined.[37] In the case of Q$^{\cdot}$ (ρ^+ = +0.25), the reaction is controlled solely by the stability of the thiyl radical, while for DBNO$^{\cdot}$ the polarity of the transition state (ρ^+ = +0.75) is also important.

The radical $C_6H_5S^{\cdot}$ reacts at a higher rate with pentamethylnitrosobenzene than with 2-methyl-2-nitrosopropane or nitrosodurene.[38]

The EPR spectra of the spin-adducts of the thiyl radicals with 2-methyl-2-nitrosopropane consist of a triplet with similar values of the g-factor and a_N constants in the range 16.5–18.5 G, whose values are characteristic solely of thiyl radicals.[20,21,39–42]

A specific feature of these spin-adducts is the rapid disappearance of the signal when irradiation ceases.[43] The g-factor of thiylalkyl(thiylaryl)nitroxyls is greater than the g-factor for the free electron.[40] The temperature and the solvent do not affect the parameters of the EPR spectra of thiylnitroxyls.

3. Chemical properties

The characteristic reactions of thiyl radicals involve addition to multiple bonds and the abstraction of a hydrogen atom from organic molecules. The rates of these processes depend on polar effects as a consequence of the high electron affinity of thiyl radicals and the strength of the S–H bond arising when they are generated. In reactions involving the abstraction of a hydrogen atom from hydrocarbons, thiyl radicals are more selective than the bromine atom or the trichloromethyl radical.[44]

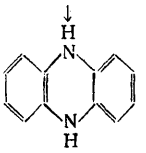
Thiyl radicals function as agents transferring hydrogen atoms from molecules to radicals.:[45]

$$RS^{\cdot} + HR' \rightleftarrows RSH + {}^{\cdot}R'. \quad (1)$$

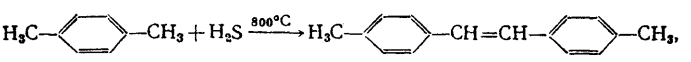
Reaction (1) is sensitive to steric hindrance in molecules and radicals. As a result of the transfer of a hydrogen atom, thiyl radicals accelerate the pyrolysis of hydrocarbons or even alter its direction[8,46–52] and they catalyse the decarbonylation of aldehydes[53] and the conversion of a series of alcohols into ketones.[54] At temperatures above 450 °C in hydrogen sulphide, the thermal conversions of aniline into 5,10-dihydrophenazine,[55] of benzaldehyde into stilbene,[56] of p-xylene into 4,4'-dimethylstilbene,[57] and of hexachlorocyclopentadiene into hexachlorobenzene[58] are initiated.

Hydrogen sulphide accelerates with thermal dehydrodimerisation of thiophen into isomeric bithienyls[59] [reaction (6)]:

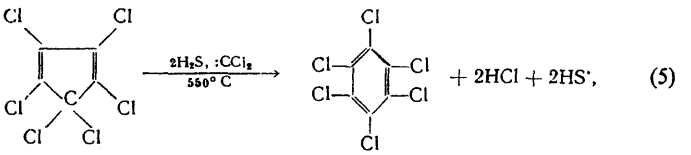
$$C_6H_5NH_2 + HS^{\cdot} \xrightarrow{750^\circ C} C_6H_5\dot{N}H + H_2S, \quad (2)$$



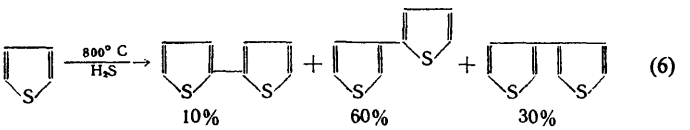
$$2C_6H_5CHO + 2H_2S \xrightarrow{500^\circ C} C_6H_5CH{=}CHC_6H_5 + 2H_2O + 2S, \quad (3)$$



(4)



(5)



(6)

In a hydrogen sulphide atmosphere, ethyl vinyl ether is transformed, with a high degree of conversion, preferentially into s-butyl vinyl ether. The interaction with hydrogen sulphide over iron sulphide leads to the almost complete conversion of ethyl vinyl ether into acetaldehyde diethylacetal:[60]

$$CH_2{=}CHOCH_2CH_3 \xrightarrow{Z} \underset{(A)}{CH_3CH(OC_2H_5)_2} + \underset{(B)}{CH_2{=}CHOCH(CH_3)C_2H_5}.$$

Reagent Z	N_2	H_2S	H_2S over FeS
Yield of (A), %	8.5	7.0	90
Yield of (B), %	8.5	64.0	—

In the hydrogen sulphide–iodine system, the decomposition of alkyl vinyl ethers at 250 °C leads to trithioacetaldehyde and ethanol.[61] The catalytic effect of iodine apparently consists in the initiation of the formation of thiyl radicals[62] [reaction (7)] which subsequently substitute the RO group in the ether via reaction (8):

$$I_2 \rightleftarrows 2I^{\cdot}; \quad I^{\cdot} + H_2S \rightleftarrows HI + HS^{\cdot}, \tag{7}$$

$$CH_2{=}CHOR + HS^{\cdot} \rightarrow CH_2{=}CHSH + {}^{\cdot}OR,$$

$$CH_2{=}CHSH \rightarrow CH_3CHS \rightarrow {}^1/_3(CH_3CHS)_3,$$

$$RO^{\cdot} + H_2S \rightarrow ROH + HS^{\cdot},$$

$$R = C_2H_5, \quad n\text{-}C_4H_9. \tag{8}$$

The chemical properties of thiyl radicals are reflected most clearly by their reactions with unsaturated compounds. The free-radical addition of hydrogen sulphide and thiols to multiple bonds (the thiylation reaction) is usually initiated by peroxides, azo-compounds, and also by radiation and UV irradiation.[7, 63–78] These reactions confirm the electrophilic nature of thiyl radicals, since they attack the reaction centre with the highest electron density. The mechanism of the thiylation reaction is described by the following general scheme:

$$RSH \rightarrow RS^{\cdot} + H^{\cdot}, \tag{9}$$

$$RS^{\cdot} + \rangle C{=}C\langle \rightleftarrows RS{-}\overset{|}{C}{-}\overset{|}{\underset{\cdot}{C}}\langle, \tag{10}$$

$$RS{-}\overset{|}{C}{-}\overset{|}{\underset{\cdot}{C}}\langle + HSR \rightleftarrows RS{-}\overset{|}{C}{-}\overset{|}{C}{-}H + RS^{\cdot}. \tag{11}$$

Reactions (9)–(11) cannot be achieved with thermal initiation apparently because of the low thermal stability of the sulphides formed, which promotes the reversibility of the process.[79] Reactions (10) and (11) are appreciably exothermic, which leads to rapid chain propagation.

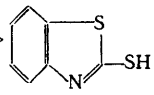
The stability of the radicals RS$^{\cdot}$ exerts the greatest influence on the rate of homolytic thiylation. The radicals are stabilised by electron-donating substituents and are destabilised by electron-accepting ones.[80] The rate of abstraction of the hydrogen atom from the HS group in alkanethiols diminishes approximately by a factor of 20 in the following sequence based on different alkyl groups:[45,81–83]

$$C_5H_{11} > C_4H_9 > (CH_3)_2CHCH_2 > (CH_3)_3C.$$

The sulphydryl hydrogen atom is abstracted from thiophenol several hundred times more readily than from butanethiol.[84]

The ability of thiols to generate thiyl radicals has been estimated quantitatively from the rate of their oxidation, which decreases in the following sequence:[85,86]

$$ArSH > C_6H_5CH_2SH > HOCOCH_2SH > RCH_2SH >$$

$$> RR'CHSH > RR'R''CSH > \text{}$$

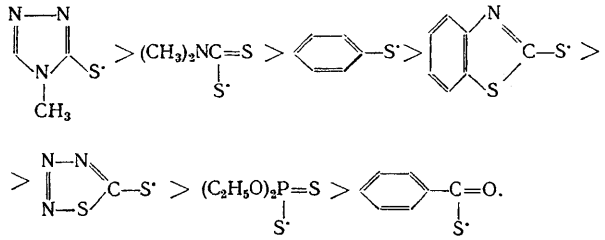
In reactions involving addition to a double bond, the reactivity of the radicals RS$^{\cdot}$ diminishes in the following sequence of substituents R:[84]

$$Cl_3CCO > Cl_2CHCO > ClCH_2CO > CH_3CO > C_6H_5 > HCOCH_2.$$

The rate of addition of arenethiyl radicals 4-$XC_6H_5S^{\cdot}$ to vinyl monomers is inversely proportional to the electron-donating properties of the *para*-substituents X.[87,88] The latter stabilise benzenethiyl radicals in the following sequence:[88]

$$Cl < H < CH_3 < CH_3O.$$

The stability series of thiyl radicals has also been established by their combined elimination in reactions of ketodithials with tributylstannane:[89]



Thiyl radicals substitute fairly readily different groups linked to polyvalent heteroatoms in organoelement compounds.[90]

III. High-temperature reactions of thiyl radicals

During the last one and a half decades, extensive studies have been carried out on the high-temperature reactions of thiyl radicals with organic compounds.[91–94] They have shown, in particular, that hydrogen sulphide is the most readily available and promising source of thiyl radicals, which subsequently initiate a wide variety of thermal and organic reactions.

1. Thermolysis of hydrogen sulphide

As early as 1852, Cluzel[95] established that hydrogen sulphide decomposes on heating into its constituent elements—hydrogen and sulphur. This process begins at 350–400 °C [96] and becomes appreciable at 1300–1600 °C.[97] The degree of decomposition of hydrogen sulphide is 0.003% at 700 °C,[98] 15–20% at 930 °C,[99] and 83% at 1700 °C.[98] Equilibrium is established after 10 s at 430 °C and after 0.4 s at 930 °C.[99] The thermolysis of hydrogen sulphide is characterised by a small exothermic effect:[100]

$$H_2S \rightarrow H_2 + 0.25S_4, \quad \Delta H^0_{298} = 13 \text{ kcal mol}^{-1}.$$

The energy of the dissociation of hydrogen sulphide into atoms is 173 kcal mol^{-1}.[101] The study of the thermal degradation of hydrogen sulphide in shock waves when it is present at low concentrations in argon revealed the most energy consuming stage:

the dissociation into free radicals with participation of argon molecules:[102,103]

$$H_2S + Ar \xrightarrow{2400-3500\,^{\circ}C} HS^{\cdot} + H^{\cdot} + Ar. \quad (12)$$

The activation energy for reaction (12) is 92 kcal mol^{-1} according to Nagashima[98] or 74 kcal mol^{-1} according to Bowman and Dodge[103] and is close to the dissociation energy of the S–H bond in the hydrogen sulphide molecule: 98.3,[104] 95.0,[105] 81.2,[106] and 92.0 kcal mol^{-1}.[9] The inhibition of the thermolysis of hydrogen sulphide by nitrogen oxide[102] and the initiation of this process by atomic hydrogen[102–107] indicate its radical mechanism. The exothermic reaction of hydrogen sulphide with atomic hydrogen, occurring at a high rate, plays a significant role in the homolytic decomposition of hydrogen sulphide. It also initiates the decomposition of hydrogen sulphide into the elements via the stage involving the generation of sulphydryl radicals:[107]

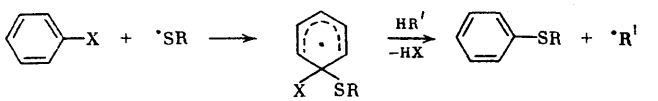
$$H_2S + H^{\cdot} \rightarrow HS^{\cdot} + H_2;$$

$$2HS^{\cdot} \rightarrow H_2S + S; \quad HS^{\cdot} + S \rightarrow H^{\cdot} + S_2. \quad (13)$$

Reaction (13) ensures a low activation energy (37 kcal mol^{-1}) for the thermolysis of undiluted hydrogen sulphide[108] at 400–1000 °C. Under these conditions, hydrogen sulphide does not decompose into the elements via a molecular mechanism in view of the reversibility of the synthesis of H_2S from sulphur and hydrogen.[109]

2. Gas-phase reactions of hydrogen sulphide with aromatic halogeno-compounds and hetero-compounds

The thermal reactions of hydrogen sulphide with aromatic and unsaturated chloro- and bromo-substituted hydrocarbons and their derivatives have been studied in greatest detail. These readily available organic compounds have a high thermal stability[110] and a low reactivity in nucleophilic thiylation.[111] On the other hand, the thermal reactions involving the *ipso*-substitution of a halogen atom in the aromatic ring by sulphydryl and arene- or ethylene-thiyl radicals are promoted by the electrophilic nature of thiyl radicals, the enhanced electron density in the C_{sp^2}–X (X = Cl, Br) bond, the possibility of the formation of an intermediate radical-adduct stabilised with participation of the π-system of the aromatic ring, and also the removal of the halogen atom in the form of a thermally stable hydrogen halide.[112]



X = Cl, Br; R = H, CH_2=CH, Ar

Such reactions were carried out in standard flow systems (empty quartz tube), which model, in terms of their size, the conditions in an ideal displacement reactor.

The gas-phase reaction of hydrogen sulphide with chlorobenzene begins at 550 °C, takes place effectively at 600–700 °C (the degree of conversion of chlorobenzene is 40–90%) with formation of thiophenol, diphenyl sulphide, and benzene. Their ratios are to a large extent determined by the reaction temperature. The yield of thiophenol and diphenyl sulphide reaches a maximum in the narrow temperature range 600–620 °C, above which the formation of benzene increases significantly. In the same temperature range, diphenyl sulphide cyclises partially to dibenzothiophen.[113,114] The excess hydrogen sulphide promotes an increase in the yields of thiophenol, while the excess chlorobenzene increases the yield of diphenyl sulphide.[115–117] The kinetic curves characterise the reaction of chlorobenzene with hydrogen sulphide as a complex process consisting of consecutive-parallel irreversible reactions. Chlorobenzene is converted in succession, via the intermediate formation of thiophenol, into diphenyl sulphide and is at the same time reduced to benzene:[116]

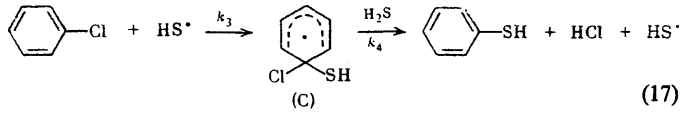
$$C_6H_5Cl + H_2S \xrightarrow{k_1} C_6H_5SH + HCl, \quad (14)$$

$$C_6H_5Cl + C_6H_5SH \xrightarrow{k_2} C_6H_5SC_6H_5 + HCl, \quad (15)$$

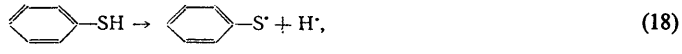
$$C_6H_5Cl + H_2S \rightarrow C_6H_6 + HCl + S. \quad (16)$$

The reaction conditions leading to the maximum yield of thiophenol have been optimised by mathematical experimental design.[115] The yield of C_6H_5SH reaches 30% relative to the initial chlorobenzene and 90% relative to the reacted chlorobenzene at 600–620 °C for the molar ratio H_2S:C_6H_5Cl = 3:1 and a contact time of 38–48 s.

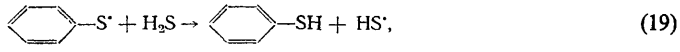
Since the thermolysis of chlorobenzene with dissociation of the C–Cl bond does not yet begin at 600 °C while the dissociation of hydrogen sulphide with formation of thiyl radicals does already occur, on the basis of the kinetic data the mechanism of the formation of thiophenol and diphenyl sulphide can be represented by the following scheme:[118]



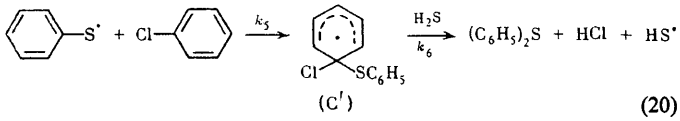
(C) (17)



(18)



(19)



(C′) (20)

According to this scheme, the *ipso*-substitution of the chlorine atom in the aromatic ring by thiyl radicals takes place via a bimolecular chain mechanism. Thiyl radicals are generated preferentially in the chain transfer stages. Radical-adduct formation stages (17) and (20) are slowest. Stage (20) is evidently rate-limiting, since the concentration of benzenethiyl radicals is always lower than that of sulphydryl radicals. This scheme is confirmed by the fact that alkyl chlorides are not thiylated by hydrogen sulphide in the gas phase and are merely reduced. Benzene also does not react with hydrogen sulphide under the conditions investigated.

The Arrhenius expressions for the rate constants for the formation of thiophenol (k_1) and diphenyl sulphide (k_2) via reactions (14) and (15) and as a result of the direct reaction of thiophenol with chlorobenzene (k_2') assume the following form:[118]

$$k_1 = 10^{5.15\pm0.9}\exp[(-27.7\pm0.37)/RT],\ s^{-1},$$

$$k_2 = 10^{8.30\pm0.14}\exp[(-29.0\pm0.6)/RT),\ \text{litre mol}^{-1}\ s^{-1},$$

$$k_2' = 10^{10.17\pm0.63}\exp[(-33.6\pm3.0)/RT],\ \text{litre mol}^{-1}\ s^{-1}.$$

The activation energies for reactions (14) and (15) are similar, which shows that the change in the hybridisation of the carbon atom of the C–Cl bond in chlorobenzene on formation by the latter of the

activated complex (C) or (C′) with a thiyl radical makes the decisive contribution to the activation energy in all cases. The low entropies of activation indicate bimolecular mechanisms of the formation of thiophenol and diphenyl sulphide. The rate constant for the formation of diphenyl sulphide in the chlorobenzene–thiophenol system (k_2') is approximately five times greater than the analogous constant obtained in the chlorobenzene–hydrogen sulphide system.

Eqn. (21) for the constant k_2, obtained by comparing the functional identities of the differential equations describing the real chlorobenzene thiylation process [reactions (14) and (15)] and its mechanism [reactions (17)–(20)], shows that this constant includes also the rate constant for the rate-limiting stage [the formation of the activated complex (C′)] and depends on the ratio of the concentrations of the benzenethiyl radical and thiophenol:

$$k_2 = k_5[C_6H_5S^{\cdot}]/[C_6H_5SH]. \quad (21)$$

The constant k_2 increases on direct interaction of chlorobenzene with thiophenol in the absence of hydrogen sulphide. The excess of the latter promotes the occurrence of reaction (19), as a result of which there is an increase in the concentration of thiophenol [the denominator in Eqn. (21)] and the rate constant for the formation of diphenyl sulphide (k_2) diminishes. This entails an increase in the selectivity of the synthesis of thiophenol by reaction (14).

The initiators and inhibitors of free-radical reactions respectively influence the rate and direction of the reaction of hydrogen sulphide with chlorobenzene. Phenol and cyclohexene retard this reaction, lowering the degree of conversion of chlorobenzene by a factor of 2.[116] Chloromethanes, generating on thermolysis free radicals and carbenes,[119] accelerate the thiophenol formation stage apparently as a result of the additional initiation of the chain decomposition of hydrogen sulphide.[120] An increase in the surface area of the reaction zone lowers the degree of conversion of chlorobenzene without altering the kinetics of its reaction with hydrogen sulphide, which shows that the latter occurs in the bulk phase.

The walls of the reactor promote the generation and destruction of thiyl radicals[116] and the material of the reactor therefore influences significantly the rates of reactions (14) and (15). For the same contact time, the degree of conversion of chlorobenzene in a steel reactor is approximately 30% greater than in a quartz reactor. In this case, the ratio of the reaction products changes in favour of thiophenol and benzene.[121] Evidently the walls of the steel reactor participate in the formation of the radicals $HS^{\cdot}$ and $C_6H_5^{\cdot}$ as a result of the catalysis of the thermolysis of hydrogen sulphide and chlorobenzene by nickel and chromium sulphides and polysulphides,[122] formed on passivation of the reaction surface by hydrogen sulphide. In a copper reactor, hydrogen sulphide does not react with chlorobenzene. The *para*-substituted derivatives of chlorobenzene 4-XC_6H_4Cl react with hydrogen sulphide in the gas phase similarly to chlorobenzene itself. The formation under these conditions of the corresponding thiol 4-XC_6H_4SH and the sulphide $(4\text{-}XC_6H_4)_2S$ indicates the *ipso*-substitution of the chlorine atom by thiyl radicals and confirms the mechanism described by reactions (17)–(20).[123] The following reactions then take place:

$$4\text{-}XC_6H_4Cl + H_2S \rightarrow 4\text{-}XC_6H_4SH + HCl, \quad (22)$$

$$4\text{-}XC_6H_4Cl + 4\text{-}XC_6H_4SH \rightarrow (4\text{-}XC_6H_4)_2S + HCl, \quad (23)$$

$$4\text{-}XC_6H_4Cl + H_2S \rightarrow 4\text{-}XC_6H_5 + HCl + S,$$

$$X = H,\ Cl,\ OH,\ CH_3,\ CF_3. \quad (24)$$

Chloropentafluorobenzene reacts similarly with hydrogen sulphide, affording C_6F_5SH and $(C_6F_5)_2S$. The optimum temperature for the formation of the thiol and the sulphide is determined by the nature of the substituent X (in the case of chlorobenzene) and also by the nature of the benzene ring (in the case of C_6F_5Cl). It decreases with increase in the capacity of the C–Cl bond for homolytic dissociation.

The sequence in which the degree of conversion of the chloro-derivatives increases is identical with the sequence based on the increase in electron density at the chlorine atom. Accordingly, the degree of conversion of 4-XC_6H_4Cl in the reaction with H_2S and also the physicochemical parameters of the C–Cl bond vary in the following sequence of substituents X:

	OH	< Cl	< CF_3	< H	< CH_3
Charge Q (Cl), eV	−0.16	—	0.15	−0.17	−0.17
$\nu(^{35}Cl$ NQR), cm^{-1}	34.9	34.8	34.7	34.65	34.5
$\delta[^{13}C(C^1)]$ relative to X = H, p.p.m.	−8.74	−1.71	3.88	0.00	−3.21
Charge on C^1 (π) atom, eV	−0.04	—	3.03	0.00	−0.02

The ratio of the thiylation products (thiol/sulphide) depends significantly on the reactivity of the intermediate thiol. It is correlated with parameters of the electronic structure of the compounds 4-XC_6H_4SH and their reactivity, increasing in the following sequence of substituents X:

$$Cl < CH_3 < H < CF_3 < OH.$$

$C_5F_5Cl[\nu(^{35}Cl$ NQR) = 39.4 $cm^{-1}]$ reacts most slowly with hydrogen sulphide among all the *para*-substituted chlorobenzenes. The thiol/sulphide ratio in the thiylation products is highest in this instance.

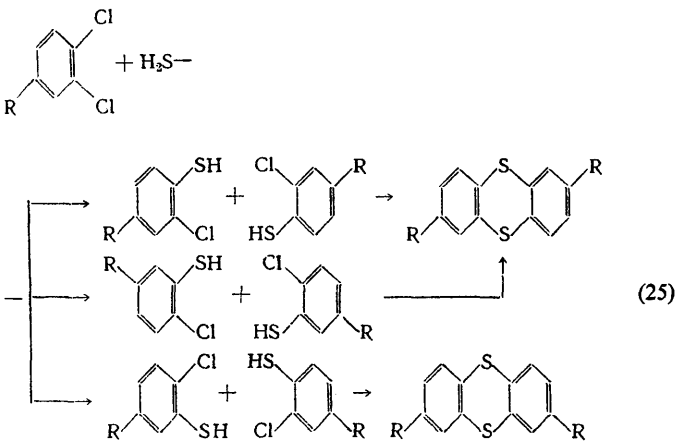
The reactivity of these thiols is largely determined by the degree of localisation of the HOMO on the sulphur atom, since the other parameters of the electronic structure (the ionisation potential and the charge on the sulphur atom) depend little on the nature of the substituent X or the benzene ring.

The degree of localisation of the HOMO on the sulphur atom is correlated only with the resonance component of the substituent X, increasing with decrease in its electron-donating capacity. The thiol/sulphide ratio is correlated directly with the degree of localisation of the HOMO on the sulphur atom of the thiol, diminishing with enhancement of the π-electron-donating properties of the substituent X. Thus the π-electron-accepting substituents X in the thiol 4-XC_6H_4SH decrease the reactivity of the thiol in its interaction with the initial chloro-derivative [scheme (23)], while π-electron-donating substituents increase it. From the standpoint of the free-radical mechanism of reactions (22) and (23), the formation of the arenethiyl radical, which then participates in the second stage of scheme (20) under the conditions of the competing interaction with H_2S [see scheme (19)], determines the capacity of this radical for stabilisation.

It has been suggested that the distribution of the unpaired electron in 4-$XC_6H_4S^{\cdot}$ is analogous to the distribution of the HOMO in 4-XC_6H_4SH, so that π-electron-donating substituents X stabilise the arenethiyl radicals, whilst π-electron-accepting substituents destabilise them, as a result of which in the latter case the radicals are formed at a lower rate and subsequently react preferentially with hydrogen sulphide in accordance with scheme (19) and not with the initial chloro-derivatives in accordance with scheme (20). 4-Hydroxythiophenol is an exception, which is evidently associated with the autoinhibition of the free-radical process in this case. By increasing the dehydrating activity of the 4-$XC_6H_4S^{\cdot}$

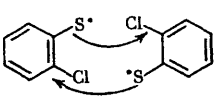
radical, π-electron-accepting substituents X promote the formation of the thiol 4-XC_6H_4SH via scheme (22) with a high selectivity (for a low degree of conversion of the initial chloride). C_6F_5SH is formed with the highest selectivity. *ortho*-Substituted chlorobenzenes react with hydrogen sulphide in the gas phase via pathways different from those for the *para*-substituted derivatives. The main product of the thiylation of 2-chlorotoluene or chloromesitylene is the corresponding thiol [scheme (14)], since the steric effect of the *ortho*-ethyl group hinders the interaction of the 2-methylbenzenethiyl or mesitylenethiyl radical in the sulphide formation stage via scheme (20).[124]

The interaction of 1,2-dichloro- or 1,2,4-trichloro-benzenes with hydrogen sulphide results in the formation of a thianthrene or dichlorothianthrenes respectively according to scheme (25):[125]



(25)

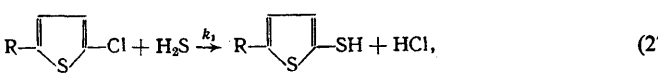
Their formation is apparently determined by the intermolecular cyclisation of *ortho*-chloro-substituted benzenethiyl radicals proceeding via scheme (26) at a high rate:



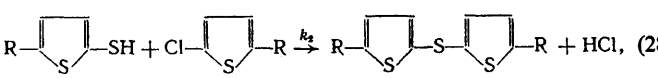
(26)

In contrast to *p*-chlorophenol, *o*-chlorophenol reacts with hydrogen sulphide more effectively and with a more selective formation of 2-hydroxythiophenol in accordance with scheme (22).[126]

The reaction of hydrogen sulphide with 2-chlorothiophen, leading to thiophen-2-thiol and di(2-thienyl)sulphide takes place at lower temperatures (500–540 °C) than in the case of chlorobenzene:[127]



(27)



(28)

R=H, Cl, C_2H_5.

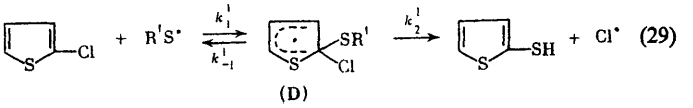
Reaction (28), leading to the sulphides, then proceeds at a higher rate than in the case of chlorobenzene [scheme (14)].

Arrhenius expressions have been obtained for the rate constants k_1 and k_2 for the formation of thiophen-2-thiol and di(2-thienyl)-sulphide [schemes (27)–(28)]:

$$k_1 = 10^{14.2\pm0.4}\exp[(-52.0\pm3.4)\times10^3/RT],\ s^{-1},$$

$$k_2 = 10^{13.8\pm0.2}\exp[(-55.7\pm2.9)\times10^3/RT],\ mol^{-1}\ s^{-1}.$$

The high activation energies for both reaction stages and the high pre-exponential factors indicate a unimolecular mechanism of the reaction. This can be due to the faster attack by the thiyl radicals HS˙ and RS˙ on the polarised double bonds of the thiophen ring and the greater stability of the activated complex (D), which decomposes slowly in the rate-limiting stage in accordance with scheme (29):[128]



(29)

(D)

R^1 = H, R.

5-Ethylthiophen-2-thiol is formed from 2-chloro-5-ethylthiophen via schemes (27) and (28) in a higher yield and 5-chlorothiophen-2-thiol is formed from 2,5-dichlorothiophen in a lower yield than that of thiophen-2-thiol formed from 2-chlorothiophen. In the absence of hydrogen sulphide, 2,5-dichlorothiophen dehydrodimerises at 560–570 °C to tetrachloro-3,3′-bithienyl.[129]

The reaction of hydrogen sulphide with bromobenzene begins at 500 °C, i.e. at a temperature lower by 50 K than the reaction of H_2S with chlorobenzene. At all the temperatures investigated, the degree of conversion of bromobenzene is higher than that of chlorobenzene, while the products of the reaction with hydrogen sulphide are similar. However, their ratios and yields differ.[130] The reactions of hydrogen sulphide with bromobenzene and its substituted derivatives lead mainly to the corresponding sulphides [via schemes analogous to schemes (22) and (23)].

The bromo-derivatives of condensed aromatic hydrocarbons (naphthalene, anthracene, phenanthrene) react with hydrogen sulphide even in the liquid phase at 150–250 °C,[131] forming only the corresponding sulphides.

Iodobenzene reacts with hydrogen sulphide already at 480 to 500 °C, being converted preferentially into diphenyl sulphide and benzene. Thiophenol and diphenyl disulphide are formed in small amounts in addition to the above compounds. In the interaction of halogenobenzenes with hydrogen sulphide, the optimum temperature for the formation of thiophenol and diphenyl sulphide decreases with increase in the atomic number of the halogen:

Cl (600—620° C) > Br (550—580° C) > I (480—500° C).

The degree of conversion of the halogeno-derivative increases and the thiol/sulphide ratio decreases in the same sequence. The sequence in the variation of the mobility of the halogen corresponds to the variation of the C–X bond strength in halogenobenzenes (Table 1) and is characteristic of radical reactions.[132] Fluorobenzene does not react with hydrogen sulphide even at 700 °C. Above this temperature, it is partly converted into a mixture of isomeric mono- and di-fluorobiphenyls.

3. Gas-phase reactions of thiophenol with aromatic and heteroaromatic halogeno compounds

Thiophenol interacts with aromatic halogeno-derivatives at 400–600 °C primarily with formation of asymmetric aromatic sulphides in accordance with the general mechanism[133]

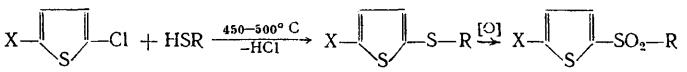
$$C_6H_5SH + RX \rightarrow C_6H_5SR + HX, \quad (30)$$

R = aryl, thienyl, naphthyl; X = Cl, Br.

Reaction (30) is favoured by an excess of the halogeno-derivatives and the lowest possible temperature. With increase in temperature and in the concentration of thiophenol, processes involving the reduction of the halogeno-derivative, exchange reactions, and

cyclisation reactions of diaryl sulphides and thiyl radicals are accelerated. The reactions of thiophenol with *ortho*-substituted halogenobenzenes are accompanied by the formation of sulphur-containing heterocyclic compounds: thus the interaction of thiophenol with 2-chlorotoluene led to the isolation of thioxanthrene,[134] the interaction with *o*-dihalogenobenzene afforded thianthrene,[125] and the interaction with *o*-chlorobenzene gave rise to 4-hydroxydibenzothiophen.[135]

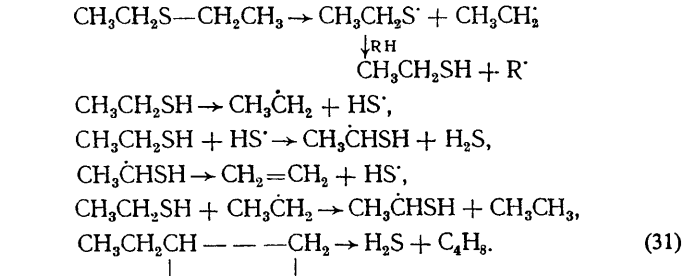
Many asymmetric aryl thienyl sulphides were obtained for the first time by the reaction of aromatic thiols with 2-chlorothiophen and its 5-substituted derivatives[136] (yield 44–76%):



$X = H,\ C_2H_5,\ Cl;$
$R = C_6H_5,\ 4\text{-}H_3CC_6H_4,\ 1\text{-}C_{10}H_7.$

4. Gas-phase reactions of alkanethiols, dialkyl sulphides, and dialkyl polysulphides with aromatic halogeno-compounds

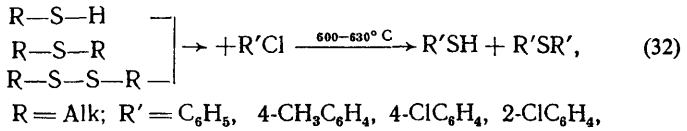
The readily available alkanethiols, dialkyl sulphides and polysulphides, or their mixtures can be used as sources of thiyl radicals for the interaction of the latter with aromatic halogeno-compounds. The thiols and sulphides decompose in the gas phase with formation of hydrogen sulphide and alkenes via a free-radical mechanism with the immediate generation of thiyl radicals,[137] for example:



(31)

$D_{C_2H_5SH}(C-S) = 63.5$ kcal mol^{-1};
$D_{H_2S}(S-H) = \sim 90$ kcal mol^{-1}.

The high-temperature reactions of alkanethiols, dialkyl sulphides, and dialkyl disulphides with chloro-derivatives of benzene, thiophen, and naphthalene lead to the same thiylation products as in the case where hydrogen sulphide is used.[138–140] This indicates a unique mechanism of reactions involving the participation of thiyl radicals according to schemes (17)–(20):



(32)

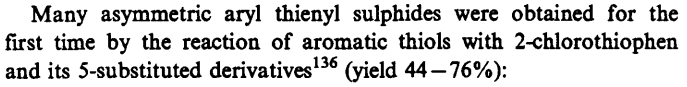
$R = Alk;\ R' = C_6H_5,\ 4\text{-}CH_3C_6H_4,\ 4\text{-}ClC_6H_4,\ 2\text{-}ClC_6H_4,$
$4\text{-}CF_3C_6H_4,\ C_6F_5,\ 3,4\text{-}Cl_2C_6H_3,\ C_{10}H_7,\ C_4H_3S.$

The reactions of alkanethiols with aryl halides differ by the increased selectivity in the formation of the thiol R'SH [scheme (32)]. The alkenes formed via scheme (31) probably inhibit the rate-limiting stage in the formation of the sulphide R'SR'.

IV. Liquid-phase thermal reactions of thiyl radicals

Thiyl radicals can be generated in the liquid phase from diaryl disulphides, arenethiols, and the sulphur–hydrogen sulphide system even at moderately high temperatures (100–250 °C).

Heating of diphenyl disulphide with bromoarenes at 125–230 °C in hydrogen sulphide at atmospheric pressure leads to the corresponding aryl phenyl sulphides:[141]



$Ar = C_6H_5,\ 2\text{-}HOC_6H_4,\ 4\text{-}HOC_6H_4,\ 4\text{-}C_2H_5OC_6H_4,$
$C_{10}H_7,\ 2\text{-}HOC_{10}H_6.$

Aromatic chloro-compounds and 2-chlorothiophen hardly enter into reaction (33), which is apparently due to the high strength of the C–Cl bond, the boiling points of the initial reactants being inadequate for the homolysis of the latter. The temperature of the thiylation of bromoarenes in accordance with scheme (33) diminishes after the introduction of a π-electron-donating substituent into the benzene ring. Above this temperature, the reactions leading to the reduction of the halogeno-derivative to the corresponding aromatic hydrocarbon are accelerated. Thiophenol and diphenyl sulphides are formed simultaneously in a low yield from diphenyl disulphide as a result of thermolysis and hydrothiolysis.

Reaction (33) is initiated by the free radicals formed in the thermolysis of the initial compounds:

Reactions (34)–(36) of free radicals with H_2S lead to the formation of thiophenol and the products of the reduction of Br$^\cdot$ and Ar$^\cdot$. In the reactions of the latter with thiophenol, which is a stronger H-donor than hydrogen sulphide, benzenethiyl radicals are generated. They are responsible for the chain thiylation of ArBr via scheme (20).

The radicals $C_6H_5S^\cdot$ play the role of agents transferring hydrogen atoms from hydrogen sulphide to the radicals Br$^\cdot$ and Ar$^\cdot$ in reaction (33).

When thiophenol is heated with aryl bromides, the corresponding aryl phenol sulphides are also formed [see schemes (37), (38), and (20)].[142] However, a more limited amount of bromide enters into the reaction with thiophenol, which is due to the inadequately high boiling point of the reaction mixture (the boiling point of thiophenol is 180 °C).

Fairly simple methods of synthesis of aryl phenyl sulphides have been developed on the basis of the reactions of Ph_2S (in H_2S or thiophenol) and ArBr.

Thiophen-2-thiol and 1-thionaphthol do not react with aryl bromides in the liquid phase to form the corresponding sulphides. The initial bromides are merely reduced to the corresponding aromatic hydrocarbons, while the thiols are then converted into symmetrical sulphides. This shows that the thiophen-2-thiyl and naphthalene-1-thiyl radicals are weaker hydrogen atom transferring agents than the benzenethiyl radical. Overall, this disturbs the process and leads to the termination of the chain transfer stage.

The sulphydryl radicals HS$^{\cdot}$ can be generated on interaction of elemental sulphur with hydrogen sulphide even at 110–230 °C. Thus 1-chloronaphthalene, 1-bromo-4-chlorobenzene, and 4-bromotoluene react in accordance with scheme (39) with the sulphur–hydrogen sulphide system at 180–230 °C, forming the corresponding diaryl sulphide in 8–88% yield:[43]

$$ArX \xrightarrow[180-230^{\circ}C]{H_2S+S} Ar_2S + HX. \quad (39)$$

The reaction of 4-bromophenol with the S + H_2S system takes place already at 110–125 °C, being completed after 2 h by the formation of di(hydroxyphenyl) sulphides and phenol.

At 200 °C, 4-chlorophenol reacts with hydrogen sulphide and sulphur via the same pathway, but the reaction is completed after 45 h. 2-Bromophenol reacts with the S + H_2S system more slowly than does 4-bromophenol and at a higher temperature (200 °C):[144]

$$H_2S + S \rightleftarrows 2HS^{\cdot},$$

$$4\text{-}BrC_6H_4OH + HS^{\cdot} \xrightarrow[110-125^{\circ}C]{H_2S} 4\text{-}HOC_6H_4SH + HBr + HS^{\cdot}, \quad (40)$$

$$4\text{-}BrC_6H_4OH + 4\text{-}HOC_6H_4SH \rightarrow (4\text{-}HOC_6H_4)_2S + HBr + HS^{\cdot},$$

$$4\text{-}HOC_6H_4Br \rightarrow 4\text{-}HOC_6H_4^{\cdot} + Br^{\cdot},$$

$$4\text{-}HOC_6H_4^{\cdot} + H_2S \rightarrow C_6H_5OH + HS^{\cdot}. \quad (41)$$

The nature of the halogen atom in the molecules of aryl halide influences the rate and direction of the liquid-phase reaction of aryl halides with the S–H_2S system in the same way as it affects the rate of their reaction with gaseous hydrogen sulphide. This confirms that HS$^{\cdot}$ radicals are generated from hydrogen sulphide in the presence of sulphur and react with halogenoarenes via schemes (40) and (41) under mild conditions.

V. Reactions of hydrogen sulphide, thiols, and dialkyl sulphides and polysulphides with halogenoalkenes

At 400–550 °C, hydrogen sulphide condenses with halogenoalkenes. The simplest of these (vinyl chloride) reacts with hydrogen sulphide at 530–560 °C to form ethylenethiol and thiophen. In the presence of an excess of hydrogen sulphide ethylenethiol is the main reaction product (yield 60%), while in the presence of an excess of vinyl chloride mainly thiophen is formed (yield 60–80%):[145]

$$CH_2{=}CHCl + H_2S \rightarrow CH_2{=}CHSH + HCl, \quad (42)$$

$$CH_2{=}CHCl + HSCH{=}CH_2 \xrightarrow{-HCl} \xrightarrow{-H_2} . \quad (43)$$

At the outlet for the gas phase, ethylenethiol is stabilised by being cooled to −70 °C after which it is warmed rapidly and analysed.[146] It trimerises rapidly at room temperature.

Reactions (42) and (43) proceed with participation of thiyl radicals which add to the carbon atom of the double bond of the halogenoalkene linked to the halogen atom. This leads to the *ipso*-substitution of the latter via the following scheme:

$$CH_2{=}CHCl + HS^{\cdot} \rightarrow {}^{\cdot}CH_2{-}CH(Cl)(SH) \xrightarrow{H_2S} CH_2{=}CHSH + HCl + HS^{\cdot}$$

$$\xrightarrow[-HCl]{} CH_2{=}CHS^{\cdot} \xrightarrow{CH_2=CHCl} \rightarrow \left[\text{Cl-thiophenyl}\right] \xrightarrow[-HCl,\ -H^{\cdot}]{H_2S} \text{thiophen} \quad (44)$$

(A)

$$(A) \xrightarrow[-HCl,\ -HS^{\cdot}]{H_2S} \text{thiophen} \xrightarrow{-H_2}$$

The ethylenethiyl radical is generated thermally from the primary product of reaction (44)—ethylenethiol. The radical then initiates the chain thiylation of vinyl chloride. Thiophen can be the product of the cyclisation of the radical-adduct (A) or of divinyl sulphide. Scheme (44) is confirmed by the fact that neither ethylene nor acetylene react with hydrogen sulphide under analogous conditions. This is also confirmed by the pathway followed in the reactions of dichloroethylenes with hydrogen sulphide and its organic derivatives (see below).

In contrast to vinyl chloride, vinyl bromide reacts with hydrogen sulphide at 450–500 °C to form only ethylenethiol (regardless of the reaction conditions[147]) in accordance with scheme (42). This may be due to the inhibiting effect of the hydrogen bromide evolved during the reaction. Being a stronger hydrogen donor than hydrogen sulphide, it reacts rapidly with the ethylenethiyl radical, as a result of which the latter does not participate in the stages of reaction (44) leading to thiophen.

The reactions of dichloroethylene with hydrogen sulphide take place mainly in accordance with schemes (42)–(44). However, under these conditions a mixture of organosulphur compounds is formed, which is due to the secondary reactions of labile intermediates. The interaction of 1,2-dichloroethylene with hydrogen sulphide is illustrated by scheme (45), which explains the formation of all the reaction products detected:[148]

$$ClCH{=}CHCl + H_2S \rightarrow ClCH{=}CHSH + HCl,$$

$$ClCH{=}CHSH + ClCH{=}CHCl \rightarrow ClCH{=}CHSCH{=}CHCl + HCl,$$

$$2ClCH{=}CHSCH{=}CHCl \rightarrow \text{Cl-thiophenyl} + \text{Cl-thiophenyl} + 2HCl,$$

$$\text{Cl-thiophenyl} + H_2S \longrightarrow \text{SH-thiophenyl} + HCl,$$

$$\text{SH-thiophenyl} + ClCH{=}CHCl \longrightarrow \text{SCH=CHCl-thiophenyl} \xrightarrow{-HCl}$$

$$\longrightarrow \text{thiophen} + \text{thiophen} \quad (45)$$

An excess of 1,2-dichloroethylene promotes the preferential formation of 2- and 3-chlorothiophens, whose yield reaches 30–35%.

A mixture of 2- and 3-chlorothiophens, thiophen, thiophen-2-thiol, thiophen-3-thiol, thienothiophens, and vinyl sulphides is formed from 1,1-dichloroethylene and hydrogen sulphide at 470–550 °C via schemes analogous to scheme (45).[149] However, the sulphides obtained under these conditions contain a chlorine atom not in the β-position but in the α-position relative to the sulphur atom. This shows that the primary product of the reaction of 1,1-dichloroethylene with hydrogen sulphide is α-chloroethylenethiol, from which the α-chloroethylenethiyl radical, responsible for the formation of all the subsequent reaction products, is generated:

$$CH_2{=}CCl_2 + HS^{\cdot} \rightarrow {}^{\cdot}CH_2CCl(SH)_2 \xrightarrow[-HCl,\ -[HS^{\cdot}]]{H_2S}$$

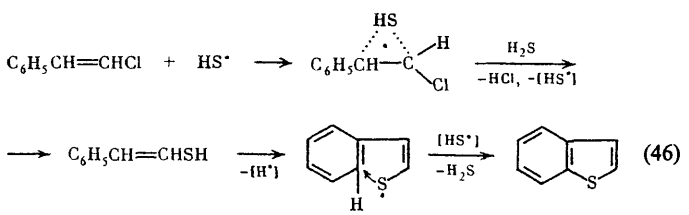
$$\downarrow -HCl$$

$$\rightarrow CH_2{=}CClSH \rightarrow CH_2{=}CClS^{\cdot}$$

The regiospecificity of the thermal addition of thiyl radicals to halogenoalkenes, namely to the carbon atom linked to the halogen atom, is unambiguously demonstrated in this case.

The reaction of trichloroethylene with hydrogen sulphide in the gas phase does not lead to sulphur-containing compounds.[150] The reaction of tetrachloroethylene with hydrogen sulphide at 450 °C leads to tetrachlorothiophen (yield 75%) but it is slower than in the case of other chloroalkenes having polarised double bonds.[151]

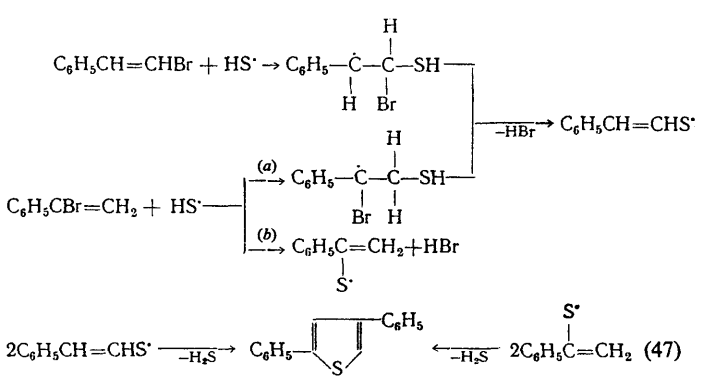
Virtually the only product of the reaction of β-chlorostyrene with hydrogen sulphide at 600 °C is benzo[*b*]thiophen (yield 85%). The 2-phenylethylenethiol formed initially readily generates the 2-phenylethylenethiyl radical (stabilised as a result of the π,π-conjugation of the ring and the double bond), which undergoes intramolecular condensation to benzothiophen at a high rate:[152,153]



(46)

Instead of β-chlorostyrene, its gas-phase precursor (αβ-dichloroethylbenzene) can be introduced into reaction (46), and instead of hydrogen sulphide lower alkanethiols can be introduced.

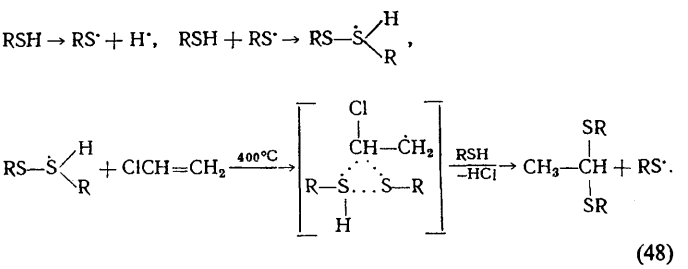
In the liquid phase, boiling β-chlorostyrene does not react with hydrogen sulphide, whereas α- and β-bromostyrenes interact with hydrogen sulphide in the liquid phase even at 150–170 °C, affording mainly 2,4-diphenylthiophen (yield 37%). Apparently in the liquid phase phenylethylenethiyl radicals undergo merely intermolecular condensation, leading to the same product of reaction (47)—2,4-diphenylthiophen[154] (the cage effect and the fairly high concentration of radicals at the instant of formation exert an influence):



(47)

Benzothiophen is formed in the gas phase in 76% yield from β-bromostyrene and hydrogen sulphide and in 9% yield from α-bromostyrene and hydrogen sulphide. In the latter case, the β-phenylethylenethiyl radicals are formed to some extent, but this direction of attack by the thiyl radical HS˙ on the halogenoalkene molecule takes place to an insignificant degree [scheme (47), pathway (*b*) is preferred to pathway (*a*)] even when a radical-adduct of the benzyl type is formed.

Organic derivatives of hydrogen sulphide (thiols, dialkyl sulphides, and dialkyl disulphides) react with halogenoalkenes both in the gas phase and in the liquid phase. The products of their reactions with vinyl chloride at 400 °C are 1,1-di(alkylthio)ethanes (yield 10–33%), formed as a result of the preliminary thermal condensation of alkanethiyl radicals with the initial sulphide reagent via scheme (48):[155]



(48)

Alkyl vinyl sulphides are not intermediates in the formation of dithioacetals under these conditions, since the thermal addition of alkanethiols to them under analogous conditions leads to the usual anti-Markovnikov adducts. On the other hand, the conversion of 1,2-di(alkylthio)ethanes to the isomeric dithioacetals is also not observed under these conditions:

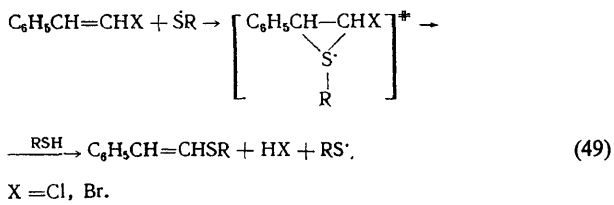
$$RSH + CH_2{=}CHSR \rightarrow RSCH_2{-}CH_2SR.$$

The gas-phase reactions of vinyl chloride with aromatic thiols and thiophen-2-thiol lead to the corresponding aryl vinyl sulphides or 2-thienyl vinyl sulphide respectively. The selective occurrence of this reaction is promoted by a large excess of the chloro-derivative:[156]

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

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

Aromatic thiols and thiophen-2-thiol react with β-chloro- and β-bromostyrenes in the liquid phase even at 80–160 °C with formation of 1-phenyl-2-arylthio- or 1-phenyl-2-thienylthio-ethylenes respectively (yield 70–95%):[157]

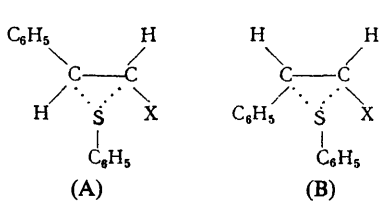


(49)

X = Cl, Br.

Reaction (49) begins already at 80 °C and proceeds efficiently at 140–160 °C.

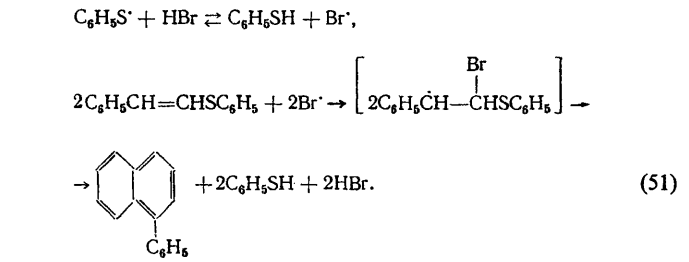
At 80–100°, only the *trans*-isomer of the β-halogenostyrene enters into reaction (49), whilst at 140–160 °C both isomers react. The process takes place rigorously stereospecifically, which is apparently due to the stabilisation of the radical-adduct with participation of the β-phenylthio-group. The transition state (A), which is sterically less strained than the state (B), is then formed from the *trans*-isomer of the β-halogenostyrene:



(50)

Thiophenthiol reacts with β-bromostyrene more slowly than with β-chlorostyrene owing to the inhibiting effect of hydrogen bromide, which functions as a trapping agent for thiyl radicals and initiates

the decomposition via scheme (51) of the sulphide formed:



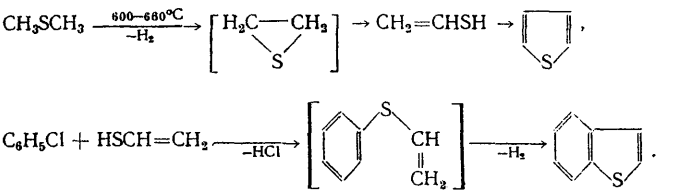
(51)

In particular, 1-phenyl-2-naphthylthioethylene and 1-phenyl-2-thienylthioethylene have been obtained via scheme (51).

VI. Thermal synthesis of thiophen and its derivatives and analogues

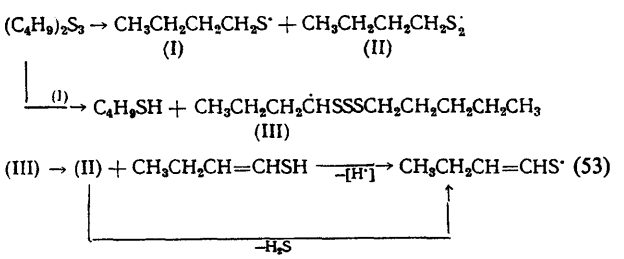
The study of the thermal reactions of thiyl radicals generated from different types of organic sulphur compounds has made it possible to develop a wide variety of methods of synthesis of thiophen, benzothiophen, dibenzothiophen, thianthrene, thioxanthene, and other sulphur-containing heterocycles. They are all based on thermal cyclisations and condensations of different types of αβ-unsaturated thiyl radicals.[158] Some of these methods have already been mentioned (see Section III above).

Thiophens are the products of the thermolysis of dialkyl sulphides, which decompose in accordance with a unique mechanism which includes a stage involving the generation of ethylenethiol. The ethylenethiyl radical formed from the latter undergoes intermolecular condensation to a thiophen, for example, in accordance with the following scheme:[159,160]



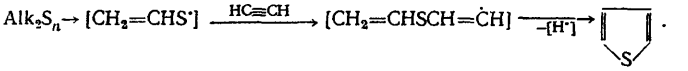
(52)

Thiophen is also formed in the pyrolysis of vinyl sulphides and dialkyl polysulphides.[161,162] The dibutyl polysulphides $(C_5H_9)_2S_n$ are thermolysed to thiophen most selectively under these conditions:[162]

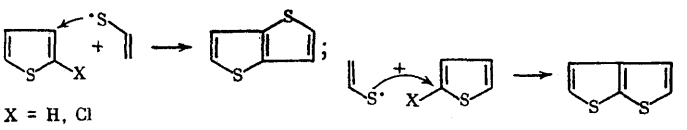


For n = 3, the maximum yield of thiophen reaches 43% at 500–520 °C. According to scheme (53), the trisulphide molecule is in fact the richest source of butenethiyl radicals, which subsequently cyclise to thiophen.[161]

Acetylene is an effective trapping agent for ethylenethiyl radicals. Its cothermolysis with low-molecular-weight dialkyl polysulphides at 470–520 °C leads to thiophen (yield up to 62%):[169]



Two isomeric thienothiophens are then formed together with thiophen, apparently as a result of the interaction of the ethylenethiyl radical with the thiophen ring (in proportions of 1 : 1):

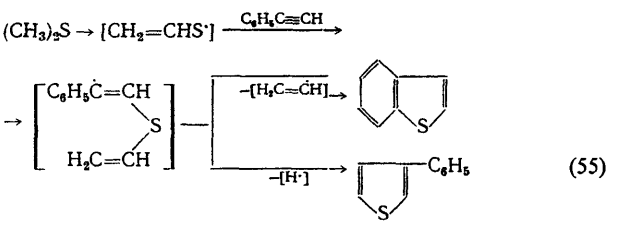


X = H, Cl

(54)

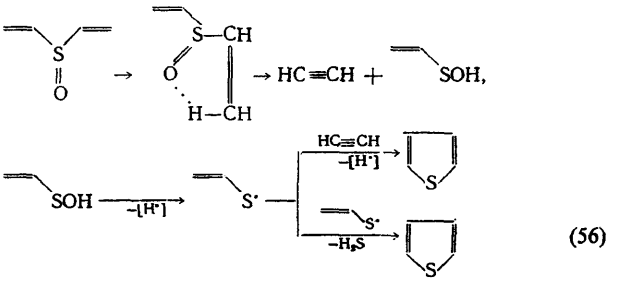
The cothermolysis of 2-chlorothiophen with a mixture of diethyl polysulphides also results in the formation, in accordance with scheme (54), of isomeric thienothiophens, but the [2,3-*b*]-isomer predominates in it.[164] This confirms the preferential attack by the thiyl radical on the sp^2-hybridised carbon atom linked to the halogen atom.

The cothermolysis of phenylacetylene with dimethyl sulphide at 450–500 °C leads to 3-phenylthiophen and benzo[*b*]thiophen in accordance with the following scheme:[165]



(55)

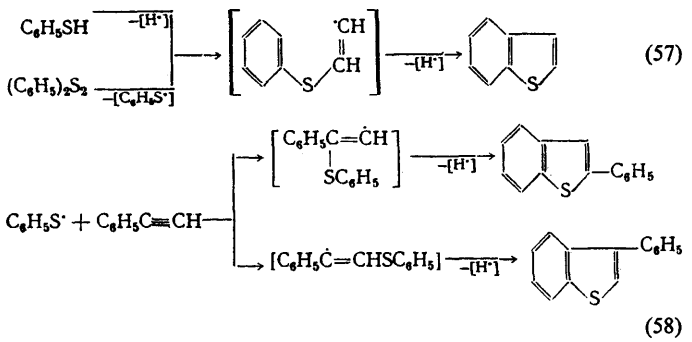
The main product of the gas-phase thermolysis of divinyl sulphoxide is thiophen, whose maximum yield (60%) is attained at 400 °C.[166] The mechanism of reaction (56) includes a stage in which ethylenethiyl radicals are generated:



(56)

Thiophenol reacts with acetylene at 550–590 °C, while diphenyl disulphide reacts at 500 °C with selective formation of benzo[*b*]thiophen. The products of the reaction of phenylacetylene with diphenyl disulphide are 2- and 3-phenylbenzo[*b*]thiophen (in proportions of 1 : 1.5). The mechanisms of reactions (57) and (58) include stages in which benzenethiyl radicals are generated and

add to multiple bonds:[167]



(57)

(58)

VII. Conclusion

The study of the thermal generation and reactivity of thiyl radicals established the following features:

1. The radicals $HS^{\cdot}$, $CH_2{=}CHS^{\cdot}$, and $ArS^{\cdot}$, generated from hydrogen sulphide and its organic derivatives, readily enter into reactions involving the *ipso*-substitution of the halogen atom linked to the sp^2-hybridised carbon atom.

2. Alkanethiyl radicals are incapable of such reactions. However, they undergo thermal condensation with alkanethiols, dialkyl sulphides, and dialkyl disulphides with formation of the corresponding sulphuranyl radicals $R\dot{S}_nR_2$. The latter are trapped in the gas phase by halogenoalkanes with formation dithioacetals.

3. Ethylenethiyl radicals undergo intramolecular or intermolecular cyclisation in the gas phase to heterocyclic compounds of the thiophen and benzothiophen series.

4. Acetylene and phenylacetylene are effective trapping agents for thiyl radicals. The sulphydryl radicals $HS^{\cdot}$ do not react with alkynes, alkenes, and arenes in the gas phase, but readily add to the multiple bonds of halogenoalkenes and halogenoarenes.

The observed features of the thermal reactions of thiyl radicals with organic compounds are important for the elucidation of the mechanism of the formation of sulphur-containing components of petroleums, coal, shale, and natural gas and also the products of their heat treatment.

Numerous methods for the synthesis of a wide variety of organic sulphur compounds have been developed on the basis of the reactions of thiyl radicals investigated. Many of them can be achieved on an industrial scale using readily available intermediates and sulphur-containing waste of the petrochemical, coal-chemical, chemical gas, and cellulose-paper industries.

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