Competitive reactivities of vinylthiyl radicals thermally generated from haloethylenes and hydrogen sulfide

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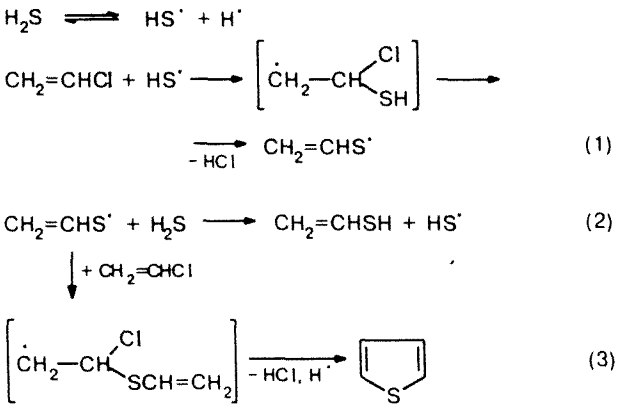
Acetylene and its derivatives have been used for the first time as "traps" for vinylthiyl radicals generated *in situ* from hydrogen sulfide and haloethylenes in gas-phase processes. The competitive reactivity of the vinylthiyl radicals has been studied at 500—570 °C in the presence of two chemical "traps." The efficiency of chemical "traps" for the vinylthiyl radicals decreases in the following sequence: $HC{\equiv}CPh > HC{\equiv}CH > MeC{\equiv}CH > CH_2{=}CHCl$. Acetylene is a more efficient "trap" for the vinylthiyl radicals than 1,2-dichloroethylene, from which they have been generated. The β-phenylvinylthiyl radicals generated during cothermolysis of halostyrene—hydrogen sulfide—acetylene component ternary systems undergo first of all intramolecular ring closure to give benzothiophene, which is a thermodynamically favorable system; the reaction of these radicals with acetylene and its derivatives occurs much more slowly than heterocyclization. Phenylacetylene is a more efficient "trap" than acetylene. α-Phenylvinylthiyl radicals mostly react with acetylene to yield 2-phenylthiophene.

Key words: acetylene, phenylacetylene, gas-phase reactions, thiyl radicals, haloethylenes, hydrogen sulfide.

Vinylthiyl radicals are generated during gas-phase thermolysis of various organic compounds of sulfur, especially lower dialkyl sulfides and dialkyl disulfides.[1—2] In the absence of efficient chemical "traps", they undergo intermolecular or intramolecular (butenylthiyl radicals) cyclization to give thiophene. In the presence of such compounds as haloarenes or haloethylenes, vinylthiyl radicals efficiently react with them. In this case, the molecules of thiophene or its derivatives are also formed.[3—6] For example, the thermal reaction of vinyl chloride with hydrogen sulfide at 550—560 °C affords vinylthiol and thiophene, which result from the initial generation of vinylthiyl radicals from vinyl chloride and hydrogen sulfide.[6] Then the vinylthiyl radicals are converted into vinylthiol through the reaction with hydrogen sulfide and give thiophene by the reaction with the starting vinyl chloride (Scheme 1).

Scheme 1



To make the synthesis of thiophene according to Scheme 1 predominating, a 3—5-fold excess of vinyl chloride over hydrogen sulfide is needed. Acetylene compounds have not been used as "traps" for the vinylthiyl radicals, thermally generated from haloethylenes.

In the present work we continued investigation of the competitive reactivity of vinylthiyl radicals in the presence of two chemical "traps" for thiyl radicals.[7] For this purpose, we studied the transformations of the vinyl chloride—hydrogen sulfide—acetylene (or its derivatives) system in the gas phase at 500—570 °C. At these temperatures, hydrogen sulfide does not react with acetylene but is efficiently combined with vinyl chloride according to reaction (1), yielding vinylthiyl radicals. The transformation of the latter in the second step can follow two parallel pathways: 1) reaction (3) with vinyl chloride to give thiophene and 2) reaction (4) with acetylene, which also affords thiophene:

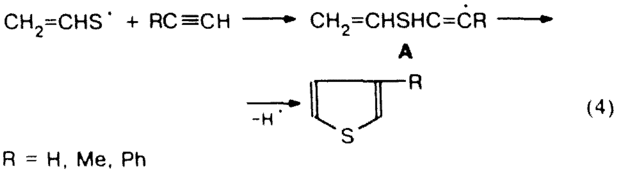


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Table 1. Transformations in the hydrogen sulfide—vinyl chloride (VC)—acetylenic compound (AC) system (acetylene was used in runs 1—7, methylacetylene[a] was used in runs 8—9, and phenylacetylene was used in runs 10—12)

Run	Ratio of reactants XB:H_2S:AC	Reaction temperature/°C	Degree of conversion (%)	Yields of the reaction products (%, based on the reacted VC) Thiophene	R-Substituted thiophene 2-Me-	3-Me-	2-Ph-	3-Ph-
1	1:1.1:1	500	43	73	—	—	—	—
2	1:1.1:1	530	60	78	—	—	—	—
3	1:1.2:0.9	550	78	80	—	—	—	—
4	1:1:1	520	58	76	—	—	—	—
5	1:1.3:1	520	60	68	—	—	—	—
6	1:0.9:1	520	53	58	—	—	—	—
7	1:1.1:0.9	570[b]	87	48	—	—	—	—
8	1:1:1	500	54	16	37	37	—	—
9	1:1.1:1	540	62	13	39	40	—	—
10	1:1:0.9	530	47[c]	Traces	—	4[d]	15	63
11	1:1:0.8	550	83[c]	Traces	—	11[d]	16	50
12	1:1:0.8	570	93[c]	Traces	—	16[d]	12	35

[a] The industrial methylacetylene fraction containing 90 % methylacetylene and 10 % allene was used. [b] At higher temperatures, the selectivity of the reaction decreased. [c] Degree of conversion of phenylacetylene. [d] The yield of benzo[*b*]thiophene is given.

The data of Table 1 indicate that transformation in the vinyl chloride—hydrogen sulfide—acetylene system (gas phase, 500—550 °C) yields thiophene in 73—80 % yield at an equimolar ratio between the reactants or even with a deficiency of vinyl chloride, whose conversion does not exceed 78 %. It is quite obvious that the vinylthiyl radicals generated from vinyl chloride and hydrogen sulfide according to reaction (1) react predominantly thereafter with acetylene according to reaction (4), rather than with vinyl chloride by reaction (3). Thiophene is formed in this ternary system due to the coupling of vinylthiyl radicals with acetylene, which is a more efficient "trap" for them than vinyl chloride. The highest yield of thiophene is observed at 550 °C and at 1:1.2:0.9 ratio between the reactants. At lover temperatures, the degree of conversion of vinyl chloride decreases, and at higher temperatures, the side processes yielding hydrocarbons and thienothiophene are accelerated[8] (Table 1).

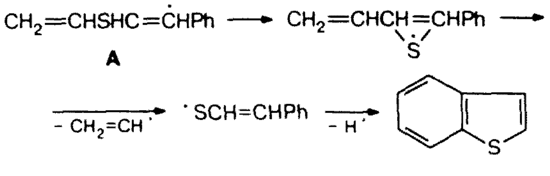
The reaction in the vinyl chloride—hydrogen sulfide—methylacetylene system gives 2-methylthiophene and 3-methylthiophene (in an overall yield of about 80 %) and thiophene (13—16 %) as major products (Table 1). Methylacetylene, like acetylene, is a more efficient "trap" for vinylthiyl radicals than vinyl chloride, the α- or β-carbon atom of the triple bond being attacked by the radicals according to reaction (4) with equal probabilities (the yields of 2- and 3-methylthiophene are identical). However, methylacetylene binds the vinylthiyl radicals less efficiently than acetylene. The radicals partially react with vinyl chloride according to reaction (3), which is indicated by the formation of thiophene (13—16 %). It has been shown previously that the propenylthiyl radicals do not react efficiently with acetylene.[9] Thus, the formation of the radical adducts from such pairs as methylacetylene—vinylthiyl radical (**B**) or acetylene-propenylthiyl radical (**C**) is hampered; this may be caused by the effect of the methyl group, which probably prevents delocalization of the unpaired electron by the π-conjugation mechanism:

$CH_2{=}CHSHC{=}\dot{C}Me$ **B**

$MeC{=}CHSC{=}\dot{C}H_2$ **C**

This does not occur in the reaction of vinyl chloride with the hydrogen sulfide—phenylacetylene system, which yields 3-phenylthiophene as the major product (in a yield of up to 63 %). 2-Phenylthiophene (12—16 %) and benzothiophene (4—16 %) are also formed (Table 1). The absence of thiophene indicates that phenylacetylene wins in the competition with vinyl chloride for trapping the vinylthiyl radicals. The vinylthiyl radicals attack predominantly the β-carbon atom of the triple bond according to reaction (4) (3-phenylthiophene is the major reaction product).

The formation of benzothiophene may be due to the parallel transformations of radical adduct **A** according to reaction (5):



(5)

The results of the study of the competitive reactivity of the vinylthiyl radicals generated *in situ* in the gas-phase transformations of the vinyl chloride—hydrogen sulfide—acetylenic component systems indicate that the efficiency of the chemical "traps" for the vinylthiyl radicals decreases in the following sequence:

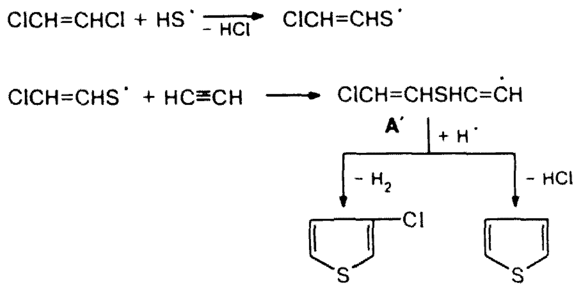
$CH_2=CHCl < MeC{\equiv}CH < HC{\equiv}CH < HC{\equiv}CPh$.

The lower reactivity of vinyl chloride compared to that of acetylene compounds is apparently due to the lower electron density of the sp^2-hybridized carbon atom, which is attacked by electrophilic thiyl radicals. The low reactivity of methylacetylene as an acetylenic "trap" in the reaction with vinylthiyl radicals is determined by the lesser possibility of stabilization of radical adduct **A**.

In the presence of acetylene, along with vinylthiyl radicals, their β-substituted derivatives were generated *in situ*. The behavior of the 1,2-dichloroethylene—hydrogen sulfide—acetylene system at 1:1:1 ratio between the components was studied at 500—600 °C. Cothermolysis of these compounds gave thiophene (in a yield of up to 40 %), a mixture of 2- and 3-chlorothiophene (10—15 %), thienothiophenes (2—5 %), and benzo[*b*]thiophene (~3 %). The isomeric composition of chlorothiophenes varied with an increase in the temperature in the following way: at 500—530 °C 2-chlorothiophene predominated in the mixture, at 560 °C the ratio between the isomers was close to 1:1, and at 600 °C 3-chlorothiophene was formed predominantly. Simultaneously, the overall yield of chlorothiophenes decreased from 15 to 10 %.

The formation of thiophene and chlorothiophenes can be represented by Scheme 2 involving the generation of β-chlorovinylthiyl radicals:

Scheme 2

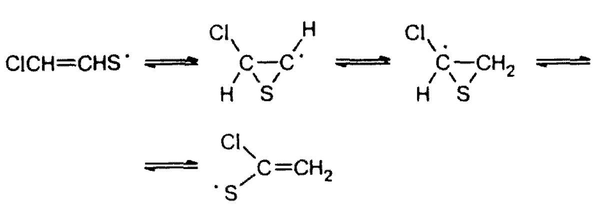


The stabilization of transition state **A**′ with the formation of thiophene as shown in Scheme 2 is thermodynamically more favorable, since it involves elimination of hydrogen chloride, which is thermally more stable than hydrogen, and yields thiophene, which exceeds chlorothiophenes in aromaticity.

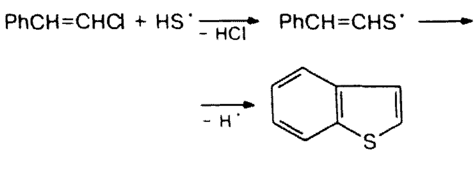
β-Chlorovinylthiyl radicals virtually do not react with the starting dichloroethylene, since the condensates do not contain the products of this reaction, *viz*., bis(chlorovinyl) sulfides (which are formed in the gas-phase reaction of 1,2-dichloroethylene with hydrogen sulfide[10]). Therefore, one may believe that acetylene is a rather efficient "trap" for β-chlorovinylthiyl radicals and that the chlorine atom participates in the stabilization of transition state **A**′.

The formation of 2-chlorothiophene, along with 3-chlorothiophene, according to Scheme 2 results apparently from the thermal isomerization of β-chlorovinylthiyl radical to the α-isomer (Scheme 3). The reaction of the latter with acetylene according to Scheme 2 affords 2-chlorothiophene. Scheme 3 is supported by the previously observed[10] formation of mixed α,β-bis(chlorovinyl) sulfide in the reaction of 1,2-dichloroethylene with hydrogen sulfide. As the temperature increases, isomerization according to Scheme 3 decelerates, which is most likely due to the rapid coupling of the β-isomer with acetylene according to Scheme 2.

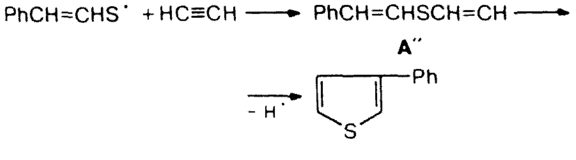
Scheme 3



It has been shown previously that the gas-phase reaction of β-chlorostyrene with hydrogen sulfide at 600—620 °C affords mostly benzo[*b*]thiophene, whose yield reaches 90 %.[11] We studied the transformations in the β-chlorostyrene—hydrogen sulfide—acetylene ternary system at 580—650 °C with ratio of reactants 1:1:1 or 1:2:1. The major products of the cothermolysis of these compounds were benzo[*b*]thiophene (yield 17—52 %) and 3-phenylthiophene (yield 3—6 %). In addition, 2-phenylthiophene (1—3 %), benzene (4—10 %), and thiophene (5—30 %) were formed (Table 2). The formation of benzothiophene and 3-phenylthiophene may be described by reactions (6) and (7), according to which the β-phenylvinylthiyl radicals, generated from β-chlorostyrene and hydrogen sulfide, as has been shown previously,[11] mostly undergo intramolecular heterocyclization and react with acetylene much more slowly.



(6)



(7)

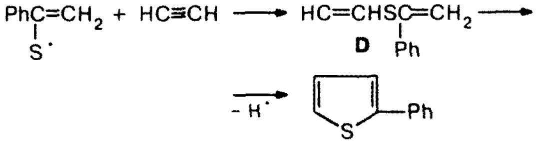
Table 2. Reaction of hydrogen sulfide with the β-chlorostyrene (CS) — acetylenic compound (AC) system (acetylene was used in runs 1—4, phenylacetylene was used in run 5)

Run	Ratio of reactants XC:H_2S:AC	Reaction temperature/°C	Degree of conversion (%)	Yields of the reaction products (%, based on the reacted CS)			
				Benzothiophene	2-Phenylthiophene	3-Phenylthiophene	Thiophene[a]
1	1:1:1	580	64	17.2	1.5	3.2	5.1
2	1:1:1	620	92	52.5	2.4	4.1	16.0
3	1:1:1	650	94	42.0	1.4	3.2	18.1
4	1:2:1	650	87	49.0	3.3	6.7	30.6
5	1:1:1	650	96[b]	45.1	2.3	12.1	—

[a] Benzene was also formed in 4, 6, 10, 8, and 30 % yields, respectively.

[b] The degree of conversion of phenylacetylene was 100 %.

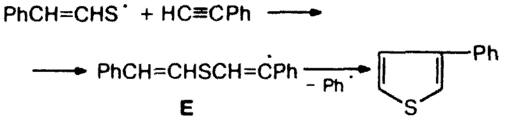
2-Phenylthiophene is apparently formed due to the partial isomerization of β-phenylvinylthiyl radical to the α-isomer, similarly to the reaction shown in Scheme 3. The α-phenylvinylthiyl radical thus generated reacts with acetylene to give radical adduct **D**, heterocyclization of which affords 2-phenylthiophene according to reaction (8):


(8)

The foregoing is supported by the cothermolysis of the α-bromostyrene—hydrogen sulfide—acetylene system at 500 °C and 525 °C, which affords 2-phenylthiophene in 65 % and 73 %, yields, respectively. It is likely that the α-phenylvinylthiyl radicals also isomerize to give the β-isomers, which is indicated by the formation of benzo[*b*]thiophene (3 % and 6 %) and 3-phenylthiophene (8 % and 10 %) in this system.

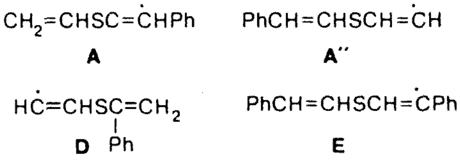
At high temperatures of 620—650 °C, radical adduct **A″** probably partially disproportionates to give thiophene and the phenyl radical, as shown by the high yields of both thiophene and benzene (up to 30 %, Table 2).

The cothermolysis of the β-chlorostyrene—hydrogen sulfide—phenylacetylene system at 650 °C and at a 1:1:1 ratio of reactants is accompanied by the formation of benzothiophene (yield 45 %) and 3-phenylthiophene (yield 12 %, *i.e.*, 3 times higher than that with acetylene) as the major thiylation products. The yield of 2-phenylthiophene is as low as 2%. In addition, a substantial amount of benzene is produced (yield 33 %). This implies that the β-phenylvinylthiyl radicals formed in reaction (8) also undergo, first of all, intramolecular heterocyclization, and that they react in parallel with phenylacetylene according to reaction (9), this reaction occurring more rapidly than the corresponding reaction with acetylene and involving mostly the β-position at the phenyl group:


(9)

After that, radical adduct **E** undergoes intramolecular cyclization to 3-phenylthiophene with the elimination of phenyl radical Ph˙, which reacts with hydrogen sulfide to give benzene. Disproportionation of radical adduct **E** cannot lead to thiophene, which actually was not detected among the products of reaction (9).

Thus, in the cothermolysis of a halostyrene—hydrogen sulfide—acetylenic component ternary system, the β-phenylvinylthiyl radicals generated in the first step according to reaction (6) undergo, first of all, intramolecular cyclization, yielding a thermodynamically favorable structure, *viz.*, benzo[*b*]thiophene. The reaction of these radicals with acetylene or its derivatives is much slower than the heterocyclization, and the interaction with haloethylenes does not occur at all. Phenylacetylene is a more efficient "trap" for these radicals than acetylene. Conversely, the α-phenylvinylthiyl radicals react predominantly with acetylene, yielding 2-phenylthiophene *via* transition state **D**.


$CH_2{=}CHSC{=}\dot{C}HPh$ **A**

$PhCH{=}CHSCH{=}\dot{C}H$ **A″**

$H\dot{C}{=}CHSC(Ph){=}CH_2$ **D**

$PhCH{=}CHSCH{=}\dot{C}Ph$ **E**

A mere comparison of the structural formulas of radical adducts **A**, **A″**, **D**, and **E** indicates that the phenyl groups in radicals **A** and **E** participate to the greatest extent in the delocalization of the unpaired electron. This obviously accounts for the fact that phenylacetylene is the most efficient chemical "trap" for the vinylthiyl radicals. β-Phenyl-substituted vinylthiyl radicals are trapped by acetylenic systems less selectively, because they are able to undergo intramolecular cyclization and because, in this case, a less stabilized radical adduct is formed. α-Phenyl-substituted vinylthiyl radicals react with acetylene virtually in the same manner as the nonsubstituted vinylthiyl radicals. The replacement of the hydrogen atom in the β-position of vinylthiyl radical by a chlorine atom is favorable for the selective trapping of the radical by acetylene.

The regularities established above should be taken into account in the development of target-directed syntheses of thiophene derivatives and fused systems incorporating a thiophene ring.

Experimental

The liquid reaction products were analyzed by GLC on an LKhM-8MD-2 chromatograph, with linear programming of the temperature of the column, using a column with a length of 2 m and a diameter of 3 mm, 5 % of the DS 550 liquid phase on Chromaton N-AW-HMDS, and helium as the carrier gas.

The GC/MS analysis was carried out on an LKB-2091 GC/MS spectrometer (capillary column, SE-30 phase, linear programming of temperature of column from 135 °C to 240 °C at rate of 8 deg min^{-1}). The ionization energy was 70 eV.

The gas-phase thermal reaction of haloarenes with hydrogen sulfide and acetylene was carried out in a quartz hollow tubular reactor placed into an electric furnace with a heating area of 30×650 mm. The starting haloarenes were injected into the reactor using an automatic injecting feeder at a rate of 20 mL h^{-1}. The gaseous reactants (H_2S and C_2H_2) obtained in Kipp's apparatus were supplied to the reactor at rates corresponding to the required ratio between the reactants. The temperature in the reactor was controlled by a thermocouple mounted in the middle of the heating area outside the reactor and connected to an automatic controller. The condensates collected in the traps at the outlet of the reactor were subjected to GLC analysis. The target products were isolated by vacuum distillation.

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