Aqueous high-temperature chemistry of carbo- and heterocycles. 14. Mercaptans and sulfonic acids

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Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 14.[1] Mercaptans and Sulfonic Acids

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Phenylmethanethiol and phenylethanethiol are highly reactive under both thermolytic and aquathermolysis conditions. 3-Phenylpropanethiol shows some conversion, but 75% or more remains after 5 days at 250 °C. Initial coupling reactions of such mercaptans to form disulfides which then lose H_2S provide facile pathways for the formation of H_2S during the steam stimulation process used to recover heavy bitumens. 2-(2-Pyridyl)- and 2-(4-pyridyl)ethanesulfonic acids give a wide variety of derivatives under both thermal and aqueous conditions, with 2- and 4-methylpyridines as major products. By contrast 2-phenylethanesulfonic acid is unreactive, and its sodium salt gives only traces of styrene under aquathermolysis conditions.

Introduction

Heavy oil bitumens contain significant quantities of organic sulfur (2–6%),[2] and steam stimulation of a reservoir containing these oils is known to cause chemical breakdown of some of the organosulfur compounds, resulting in the formation of H_2S and other compounds.[3] The extreme conditions used in steam stimulation (200–300 °C for up to 50 days) are partially responsible for these reactions, but the influence of aqueous vs thermal chemistry is not well understood. A considerable influence of aqueous metal species generated by the action of steam on the reservoir minerals has been noted.[4-6] Soluble metal species, particularly aluminum, vanadium, and nickel, promote the desulfurization of simple organosulfur compounds.[7] The reductive cleavage of the carbon–sulfur bond is important in organic synthesis as well as in desulfurization processes of fossil fuels.[8]

The previous paper in this series was concerned with thermolysis and aquathermolysis of sulfides and disulfides. We now report on the behavior of thiols and sulfonic acids. As in earlier parts of the series, the GC behavior of all the compounds included in the present paper (starting materials and products) is collected in Table I. Table II records the source and mass spectral fragmentation patterns of the authentic compounds used, either as starting materials or for the identification of products. Tables III and IV record the mass spectral fragmentation patterns of products for which authentic samples were not available and which were identified by comparison with a published MS (Table III) or by deduction of their structure from the MS fragmentation pattern (Table IV). All the results obtained are collected in Tables V and VI, and the transformations are summarized in Schemes II–V. Tables II and III have been deposited as supplementary material

Scheme I

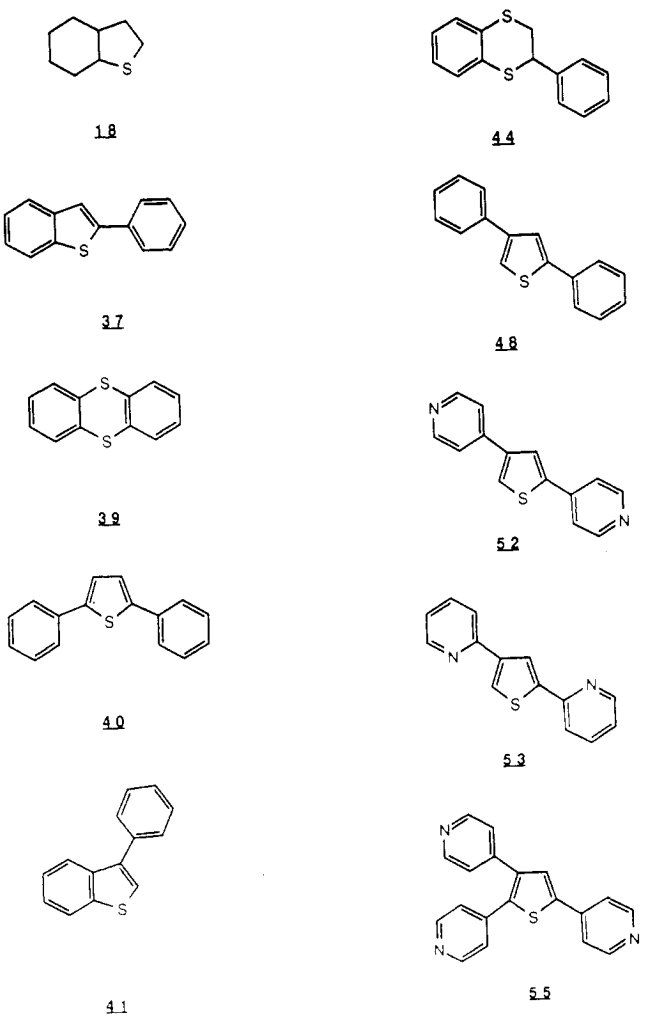

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Table I. Structure and Identification of Starting Materials and Products

no.	t_R, min	structure	mol wt	equiv wt	identification basis	response factor
1	0.50	PyH	79	79	Table II	0.80
2	0.70	$PhCH_3$	92	92	Table II	1.12
3	0.80	$2PyCH_3$	93	93	Table II	0.86
4	1.00	$4PyCH_3$	93	93	Table II	0.82
5	1.03	$PhCH_2CH_3$	106	106	Table II	0.96
6	1.15	$PhCH{=}CH_2$	104	104	Table II	0.96
7	1.20	$2PyCH_2CH_3$	107	107	Table II	0.91
8	1.45	$C_6H_{11}SH$	116	116	Table III	0.72
9	1.57	$PhCH_2CH_2CH_3$	120	120	Table II	0.95
10	1.58	$4PyCH_2CH_3$	107	107	Table II	0.83
11	1.60	PhSH	110	110	Table II	0.72
12	1.84	PhOH	94	94	Table II	0.76
13	2.18	$PhCH{=}CHCH_3$	118	118	Table III	0.95
14	2.44	$PhCOCH_3$	120	120	Table II	0.75
15	2.80	$PhCH_2SH$	124	124	Table II	0.72
16	3.95	$PhCH_2CH_2SH$	138	138	Table II	0.71
17	4.43	$Ph(CH_2)_3OH$	136	136	Table II	0.77
18	4.87	perhydrobenzo[*b*]-thiophene	142	142	Table III	0.70
19	5.30	$PhCH_2CH_2CH_2SH$	152	152	Table II	0.71
20	5.75	$PhCO_2H$	122	122	Table II	0.51
21	6.90	$PhCH_2Ph$	168	84	Table II	0.85
22	8.00	$PhCH_2CH_2Ph$	182	91	Table II	0.87
23	8.54	$2PySC_6H_{11}$	193	193	Table IV	0.55
24	8.70	PhSPh	186	93	Table II	0.68
25	8.71	$4PySC_6H_{11}$	193	193	Table IV	0.55
26	8.75	$PhSC_6H_{11}$	192	192	Table IV	0.68
27	8.84	$2PyCH_2CH_2SO_2H$	171	171	Table IV	0.06
28	9.00	$2PyCH_2CH_2Py2$	184	92	Table II	0.74
29	9.10	$4PyCH_2CH_2SO_2H$	171	171	Table IV	0.06
30	10.14	$PhCH{=}CHPh$	180	90	Table II	0.83
31	10.24	$PhCOCH_2Ph$	196	98	Table II	0.75
32	10.50	$4PyCH_2CH_2Py4$	184	92	Table II	0.71
33	10.70	$Ph(CH_2)_4Ph$	210	105	Table II	0.92
34	11.20	$PhCH_2SCH_2Ph$	214	107	Table II	0.66
35	11.30	PhSSPh	218	109	Table II	0.42
36	11.42	$PhSSC_6H_{11}$	224	224	Table IV	0.42
37	12.05	2-phenylbenzo[*b*]-thiophene	210	105	Table III	0.67
38	12.50	$PhCH_2CH_2SCH_2CH_2Ph$	242	121	Table IV	0.66
39	12.70	thianthrene	216	108	Table II	0.42
40	12.88	2,5-diphenylthiophene	236	118	Table III	0.66
41	12.90	3-phenylbenzo[*b*]-thiophene	210	105	Table III	0.67
42	13.65	$PhCH_2SSCH_2Ph$	246	123	Table II	0.41
43	13.70	$C_6H_{11}SSSC_6H_{11}$	262	87.3	Table IV	0.24
44	14.02	2,3-dihydro-2-phenylbenzo-1,4-dithiin	244	122	Table IV	0.41
45	14.20	$Ph(CH_2)_3SC_6H_4(CH_2)_2CH_3$	270	135	Table IV	0.65
46	14.65	$PhCH_2CH_2C_6H_4CH_2Ph$	272	90.7	Table IV	0.89
47	14.78	$Ph(CH_2)_3C_6H_4(CH_2)_2CH_2SH$	270	135	Table IV	0.66
48	15.05	2,4-diphenylthiophene	236	118	Table III	0.66
49	15.70	$Ph(CH_2)_3S(CH_2)_3Ph$	270	135	Table IV	0.65
50	15.90	$PhCH_2SSSCH_2Ph$	278	139	Table IV	0.22
51	15.94	$PhCH_2CH_2SSCH_2CH_2Ph$	274	137	Table IV	0.39
52	16.29	2,4-di-4-pyridyl-thiophene	238	119	Table IV	0.40
53	16.47	2,4-di-2-pyridyl-thiophene	238	119	Table IV	0.40
54	17.70	$Ph(CH_2)_3SS(CH_2)_3Ph$	302	151	Table IV	0.39
55	21.82	2,3,5-tri-4-pyridyl-thiophene	315	105	Table IV	0.25
56	*a*	$PhCH_2CH_2SO_3H$	186	186	Table II	
57	*a*	$2PyCH_2CH_2SO_3H$	187	187	Table II	
58	*a*	$4PyCH_2CH_2SO_3H$	187	187	Table II	

[a] Not volatile enough to pass through GC column.

(see paragraph at end of paper regarding supplementary material).

Mass Spectral Assignments

The structures of products **23**, **25–27**, **29**, **36**, **38**, **43–47**, **49**, and **51–55** were deduced from their starting materials and their fragmentation patterns (Table IV).

Products **23**, **25**, **26**, and **36** are all obtained in small quantities from runs carried out in cyclohexane. In agreement with the assigned structures[1] ($ArSC_6H_{11}$ and $ArSSC_6H_{11}$), they display strong molecular ions. The main fragmentations occur by the loss of cyclohexyl moieties to give peaks characteristic for ArS^+. In the case of disulfide **36**, homolysis of the S–S bond gives the base peak at m/z 109 for PhS.

Products **27** and **29** both possess pyridylethanesulfinic acid structures and show molecular ions at m/z 171 together with strong M – H fragment ions at m/z 170. Fragmentation occurs by the loss of the fragments O, SO, and SO_2, to give peaks in the mass spectrum at m/z 155, m/z 123, and m/z 106, respectively.

Bis(2-phenylethyl) sulfide (**38**) and bis(2-phenylethyl) disulfide (**51**) show their molecular ions at m/z 242 [35% relative intensity (r.i.)] and at m/z 274 (35% r.i.), respectively. Scission of the central carbon–sulfur bond and loss of sulfur leads to a fragment ion at m/z 105 ($PhCH_2CH_2^+$), which in both cases is the base peak.

Dicyclohexyl trisulfide (**43**) obtained in small amounts (0.2%) displays a molecular ion at m/z 262 (50% r.i.) and loses C_6H_{11} and $C_6H_{11}S$ radicals as well as sulfur, leading to fragment ions at m/z 179, m/z 147, and m/z 115, respectively. The base peak at m/z 83 is characteristic of the cyclohexyl radical.

2,3-dihydro-2-phenylbenzo-1,4-dithiin (**44**) shows a molecular ion at m/z 244 (50% r.i.). Structure **44** is supported by the expected loss of methyl and of phenyl radicals, as well as of sulfur. In this way fragment ions at m/z 229 (100% r.i.), m/z 167 (35% r.i.), and m/z 103 (20% r.i.) are formed.

Compound **46** is a benzyl-substituted bibenzyl ($PhCH_2CH_2C_6H_4CH_2Ph$) that displays a molecular ion at m/z 272 (30% r.i.) and easily loses a benzyl radical to give a fragment at m/z 181 (85% r.i.). Subsequent steps in the fragmentation patterns are identical with those for bibenzyl itself (Table II).

Products **45**, **47**, and **49**, obtained from 3-phenylpropanethiol, display low-intensity molecular ions at m/z 270 but differ in fragmentation patterns. Compound **45** loses ethyl and phenylpropyl radicals to give ions at m/z 241 (5% r.i.) and m/z 151 (5% r.i.), respectively. The base peak at m/z 91 is for $PhCH_3^+$. In the case of product **47**, loss of a benzyl radical followed by loss of a H_2S molecule leads to ions at m/z 179 (45% r.i.) and m/z 145 (10% r.i.). The base peak appears at m/z 75 ($CH_3CH_2CH{=}SH^+$). Bis(3-phenylpropyl) sulfide (**49**) displays the expected major fragments at m/z 118 (100% r.i.) for $PhCH_2CH{=}CH_2^+$ and at m/z 91 (50% r.i.) for $PhCH_2$.

Bis(3-phenylpropyl) disulfide (**54**) displays a molecular ion at m/z 302, which is also the base peak. Fragmentation occurs by the loss of sulfur followed by a phenyl radical to give a fragment ion at m/z 193 (50% r.i.). The next steps in the fragmentation path are losses of ethylene and propylene leading to ions at m/z 165 (90% r.i., $PhCH_2CH_2CH_2SCH_2^+$) and m/z 152 (45% r.i., $PhCH_2CH_2CH_2SH^+$), respectively.

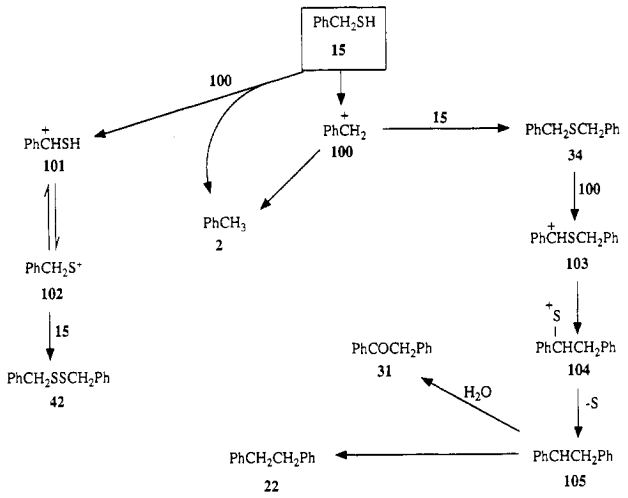
Products **52** and **55** obtained from β-4-pyridylethanesulfonic acid are di- and tri-4-pyridylthiophenes. They display strong molecular ions at m/z 238 (80% r.i.) and m/z 315 (100% r.i.), respectively, as well as intense M – H fragment ions. Subsequent steps in the fragmentation patterns are the losses of one or two HCN molecules and a pyridyl radical.

2,4-di-2-pyridylthiophene (**53**), obtained as a product from 2-(2-pyridyl)ethanesulfonic acid, displays the mo-

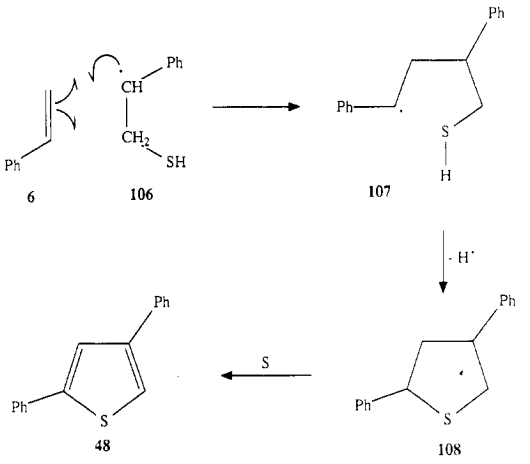
Table IV. Identification of Products from Spectral Fragmentation Patterns

no.	compound	MW	fragmentation pattern, m/z (% relative intensity, structure of fragment ion)
23	$2PySC_6H_{11}$	193	193 (100, M); 160 (45, M - SH); 111 (35, M - C_6H_{10}); 83 (10, C_6H_{11}); 78 (25, C_5H_4N)
25	$4PySC_6H_{11}$	193	193 (25, M); 192 (95, M - H); 111 (20, M - C_6H_{10}); 110 (100, M - C_6H_{11}); 83 (10, C_6H_{10}); 78 (30, C_5H_4N)
26	$PhSC_6H_{11}$	192	192 (100, M); 110 (50, M - C_6H_{10}); 109 (20, M - C_6H_{11}); 83 (5, C_6H_{11}); 77 (10, C_6H_5)
27	$2PyCH_2CH_2SO_2H$	171	171 (70, M); 170 (100, M - H); 155 (35, M - O); 123 (20, M - SO); 106 (170 - SO_2)
29	$4PyCH_2CH_2SO_2H$	171	171 (100, M); 170 (60, M - H); 169 (55, M - H_2); 155 (40, M - O); 123 (15, M - SO); 106 (15, 170 - SO_2); 115 (10, 142 - HCN); 78 (40, C_5H_4N)
36	$PhSSC_6H_{11}$	224	224 (70, M); 191 (20, M - SH); 142 (20, M - C_6H_{10}); 109 (100, PhS)
38	$PhCH_2CH_2SCH_2CH_2Ph$	242	242 (35, M); 151 (25, M - $PhCH_2$); 105 (100, 151 - CH_2S); 91 (95, $PhCH_2$); 77 (85, C_6H_5)
43	$C_6H_{11}SSSC_6H_{11}$	262	262 (50, M); 179 (5, M - C_6H_{11}); 147 (5, M - $C_6H_{11}S$); 115 (35, $C_6H_{11}S$); 83 (100, C_6H_{11})
44	2,3-H_2-2-Ph-benzo-1,4-dithiin	244	244 (50, M); 229 (100, M - CH_3); 167 (35, M - Ph); 152 (10, 229 - Ph); 103 (20, 167 - S_2)
45	$Ph(CH_2)_3SC_6H_4(CH_2)_2CH_3$	270	270 (10, M); 241 (5, M - CH_2CH_3); 151 (5, M - $(CH_2)_3Ph$); 119 (45, $Ph(CH_2)_3$); 91 (100, $PhCH_2$)
46	$PhCH_2CH_2C_6H_4CH_2Ph$	272	272 (30, M); 181 (85, M - $PhCH_2$); 165 (30, 181 - CH_3); 91 (100, $PhCH_2$)
47	$Ph(CH_2)_3C_6H_4(CH_2)_3SH$	270	270 (5, M); 179 (45, M - CH_2Ph); 145 (10, 179 - H_2S); 117 (15, $PhCH_2CH{=}CH$); 91 (60, $PhCH_2$); 75 (100, C_3H_7S)
49	$Ph(CH_2)_3S(CH_2)_3Ph$	270	270 (20, M); 118 (100, $PhCH_2CH{=}CH_2$); 117 (55, $PhCH_2CH{=}CH$); 91 (50, $PhCH_2$)
51	$PhCH_2CH_2SSCH_2CH_2Ph$	274	274 (35, M); 137 (15, M - $PhCH_2CH_2S$); 105 (100, $PhCH_2CH_2$); 91 (50, $PhCH_2$); 77 (35, C_6H_5)
52	2,4-di-4-pyridylthiophene	238	238 (80, M); 237 (100, M - H); 210 (30, 237 - HCN); 184 (15, M - 2HCN); 159 (10, 237 - Py)
53	2,4-di-2-pyridylthiophene	238	238 (100, M); 237 (30, M - H); 206 (10, M - S); 193 (25, M - CHS); 160 (20, M - Py); 78 (80, C_5H_4N)
54	$Ph(CH_2)_3SS(CH_2)_3Ph$	302	302 (100, M); 193 (50, M - S - Ph); 165 (90, 193 - C_2H_4); 152 (45, $PhCH_2CH_2CH_2SH$)
55	2,3,5-tri-4-pyridylthiophene	315	315 (100, M); 314 (85, M - H); 287 (50, 314 - HCN); 260 (65, 287 - HCN); 182 (30, 260 - Py); 150 (30, 182 - S)

Scheme II



Scheme III



lecular ion at m/z 238 as the base peak. It also easily loses a hydrogen atom; the next steps in the fragmentation are dominated by the loss of S and CHS radicals. Contrary to the fragmentation of compounds **52** and **55**, no HCN loss in observed.

Results and Discussion

In Schemes II–V, reaction intermediates postulated but not detected as products by the GC/MS system are given numbers ≥100.

The Phenylalkanethiols: $PhCH_2SH$ (15), $PhCH_2SH$ (16), and $PhCH_2CH_2CH_2SH$ (19) (Table V). Phenylmethanethiol (**15**) is only 13% converted in cyclohexane but is 74% converted in water at 200 °C for 1 day. In water, ionic reactions reasonably account for the formation of toluene (**2**, 12%) and of diphenyl sulfide (**34**, 13%) via the stable benzyl carbocation **100**. The coupling needed to give the dibenzyl disulfide (**42**, 46%) probably involves intermediate **102**. Conversion is complete in both systems during 5 days at 250 °C when the main products are toluene and 1,2-diphenylethane (**22**, 38% in cyclohexane and 22% in water). An ionic sulfur extrusion mechanism via **103**, **104**, and **105** would account for the formation of **22**, but a radical route may also be followed to this product (cf. part 13[1]). Hydration of the intermediate **105** during aquathermolysis and oxidation by sulfur would account for the observed acetophenone (**14**, 5.5%), Scheme II.

2-Phenylethanethiol (**16**) is 9% converted in cyclohexane and 30% in water in 1 day at 200 °C. Its reactions are similar to those of phenylmethanethiol. Complete conversion over 5 days at 250 °C leads to ethylbenzene (**5**, 83% in cyclohexane and 69% in water). Also formed in both systems are thianthrene (**39**) and 2,4-diphenylthiophene (**48**). The high yields of ethylbenzene show that sulfur is readily lost at 250 °C. This provides a very vigorous oxidation system which attacks the side chain to give the observed toluene (0.5% in cyclohexane, 13.1% in water) and probably some benzene (which passes through the GC column close to the solvent front). Thianthrene can be prepared in a number of different ways.[11] An observation relevant to the present work was that benzene heated with sulfur at 350 °C for 24 h gave a mixture of thianthrene, thiophenol, diphenyl sulfide, and diphenyl disulfide.[12]

One initial desulfurization product is phenylethene (**6**, 0.7% detected after 1 day at 200 °C). This is probably the intermediate in the formation of 2,4-diphenylthiophene

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Table V. Products of Aquathermolysis of Phenylmethanethiol (15), Phenylethanethiol (16), and Phenylpropanethiol (19)

	compound	$PhCH_2SH$				$PhCH_2CH_2SH$				$PhCH_2CH_2CH_2SH$	
	solvent	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O
	temp, °C	200	200	250	250	200	200	250	250	250	250
	time, days	1	1	5	5	1	1	5	5	5	5
no.	structure										
2	$PhCH_3$	1.3	12.2	50.3	66.6			0.5	13.1		
5	$PhCH_2CH_3$					1.0	1.8	82.8	68.8	0.1	0.8
6	$PhCH{=}CH_2$					0.7					
8	$C_6H_{11}SH$			1.3				1.0			
9	$PhCH_2CH_2CH_3$									1.0	1.4
11	PhSH			4.3				5.5			
13	$PhCH{=}CHCH_3$									0.6	0.1
14	$PhCOCH_3$								5.5		
15	$PhCH_2SH$	87.5	26.2	0.2	0.3						
16	$PhCH_2CH_2SH$					90.6	69.6	0.3			
17	$PhCH_2CH_2CH_2OH$										1.8
18	per-H-benzo[*b*]thiophene							0.3			
19	$PhCH_2CH_2CH_2SH$									74.4	79.2
20	$PhCO_2H$				3.5						
21	$PhCH_2Ph$			0.3							
22	$PhCH_2CH_2Ph$			37.7	22.1						
24	PhSPh							0.8	0.9		
26	$PhSC_6H_{11}$			0.2							
30	$PhCH{=}CHPh$			1.5	1.3						
31	$PhCOCH_2Ph$				2.5						
33	$PhCH_2CH_2CH_2CH_2Ph$							0.2			
34	$PhCH_2SCH_2Ph$	0.9	13.3								
35	PhSSPh			0.4				0.6			
36	$PhSSC_6H_{11}$			0.4							
37	2-Ph-benzo[*b*]thiophene							0.4			
38	$PhCH_2CH_2SCH_2CH_2Ph$					1.1	21.3	0.7			
39	thianthrene			0.4				1.5	4.0		
40	2,5-$(Ph)_2$-thiophene							0.3			
41	3-Ph-benzo[*b*]thiophene				0.9						
42	$PhCH_2SSCH_2Ph$	9.2	45.7								
43	$C_6H_{11}SSSC_6H_{11}$			0.9							
44	2-Ph-benzo-1,4-dithiane							0.6			
45	$Ph(CH_2)_3SC_6H_4(CH_2)_2CH_3$									0.3	0.7
46	$PhCH_2CH_2C_6H_4CH_2Ph$			2.1	2.8						
47	$Ph(CH_2)_3C_6H_4(CH_2)_3SH$									1.6	2.8
48	2,4-$(Ph)_2$-thiophene							4.5	7.7		
49	$Ph(CH_2)_3S(CH_2)_3Ph$									4.0	3.2
50	$PhCH_2SSSCH_2Ph$	1.4	2.3								
51	$PhCH_2CH_2SSCH_2CH_2Ph$					6.6	7.3				
54	$Ph(CH_2)_3SS(CH_2)_3Ph$									17.9	10.0

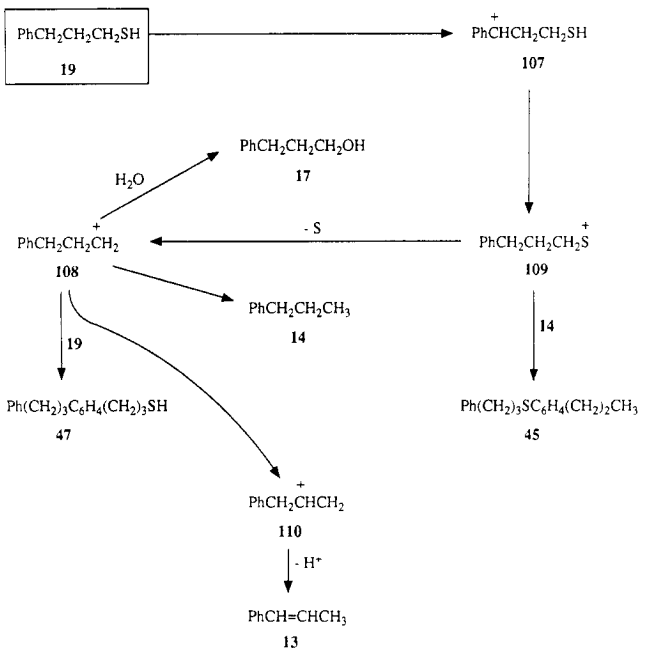
Table VI. Products of Aquathermolysis of 2-Pyridinesulfonic acid (57) and 4-Pyridinesulfonic acid (58)

	compound	$2PyCH_2CH_2SO_3H$			$4PyCH_2CH_2SO_3H$		
	solvent	C_6H_{12}	*n*-C_6H_{14}	H_2O	C_6H_{12}	*n*-C_6H_{14}	H_2O
no.	structure						
1	PyH	12.2	11.0	17.4	0.5	0.4	11.1
3	$2PyCH_3$	52.6	65.6	74.9			
4	$4PyCH_3$				39.6	70.8	64.9
7	$2PyCH_2CH_3$	12.2	11.6	3.2			
8	$C_6H_{11}SH$	1.8			1.5		
10	$4PyCH_2CH_3$				21.3	5.3	0.2
11	PhSH	6.2					
12	PhOH	1.3			0.9		
18	per-H-benzo[*b*]thiophene				0.3		
23	$2PySC_6H_{11}$	3.9					
24	PhSPh						
25	$4PySC_6H_{11}$				0.5		
27	$2PyCH_2CH_2SO_2H$		2.9	3.6			
28	$2PyCH_2CH_2Py2$	2.0					
29	$4PyCH_2CH_2SO_2H$					5.3	3.2
32	$4PyCH_2CH_2Py4$				10.2	3.0	0.2
35	PhSSPh				2.4		
39	thianthrene				1.5		
52	2,4-di-4-pyridylthiophene				7.6	2.4	17.4
53	2,4-di-2-pyridylthiophene	7.8	8.9	0.9			
55	2,3,5-tri-4-pyridylthiophene				13.8	12.8	2.9

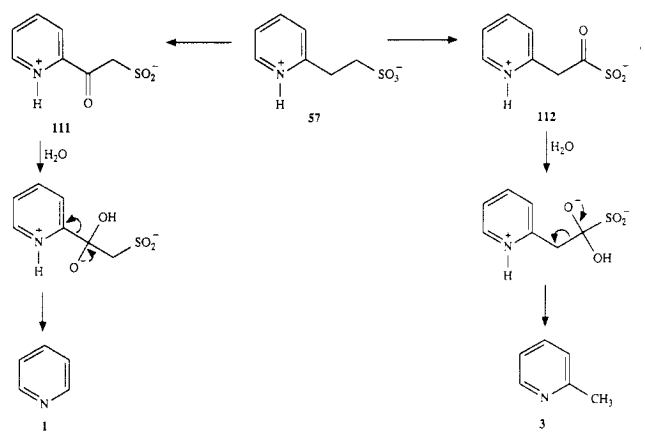
(48), where the crucial mechanism would be as shown in Scheme III.

3-Phenylpropanethiol (**19**) is much less reactive. It is only 26% and 21% converted in 5 days at 250 °C in cyclohexane and water, respectively. A radical coupling gives its main product, bis(3-phenylpropyl) disulfide (**54**, 18% and 10%, respectively). There are also significant amounts of bis(3-phenylpropyl) sulfide (**49**) and compound **47**. Ionic

Scheme IV



Scheme V



pathways to most of the observed products are suggested in Scheme IV, but most can probably also be formed by radical mechanisms since rather more conversion occurs in the nonpolar solvent in this case.

Sulfonic Acids. 2-Phenylethanesulfonic acid, $PhCH_2CH_2SO_3H$ (**56**), is unchanged under both aquathermolysis and thermolysis conditions (250 °C). Its sodium salt gives only traces of styrene (**6**, 0.6%) under aquathermolysis conditions.

2-(2-Pyridyl)ethanesulfonic Acid (57), (Table VI). All reactions were run for 5 days at 250 °C. The main products in cyclohexane are 2-methylpyridine (**3**, 53%), pyridine (**1**, 12%), and 2-ethylpyridine (**7**, 12%). In water, the first two heterocycles are seen in increased amounts at the expense of 2-ethylpyridine, which is only a minor product. The production of pyridine and 2-methylpyridine would be accounted for by the reactions of Scheme V. The sulfonic acid group is an oxidizing agent, and at 250 °C over 5 days it is reasonable that oxidations to give ketones **113** and **114** and sulfinic acid **27** would occur. Both side-chain positions are activated, one by the pyridine ring and the other by the sulfonic acid group. Attack by water would then break the side chain to give pyridine (**1**) from **113** and 2-methylpyridine (**3**) from **114**. In cyclohexane or hexane, similar intermediates formed by radical processes would give these products and a radical-induced loss of sulfur trioxide would give 2-ethylpyridine (**7**).

Among the minor products, cyclohexanethiol (**8**, 1.8%) was accompanied by thiophenol (**11**, 6.2%), but neither product is found when the reaction is conducted in hexane. It is known that six-membered alicyclic rings can be aromatized[13] in a number of ways, e.g., by elemental sulfur[14] which combines with the hydrogen evolved to give H_2S. The mechanism of dehydrogenation of hydroaromatic or alicyclic compounds by sulfur is not completely understood, but the evidence is consistent with a radical mechanism involving abstraction of a hydrogen atom followed by combination with a sulfur radical and subsequent loss of H_2S or dimerization to form disulfides.[15] In our case, significant amounts of elemental sulfur as well as H_2S were observed during the workup procedure. Thus, the thiophenol may come from aromatization of cyclohexanethiol or from aromatization of cyclohexane followed by radical substitution of the benzene so obtained. The cyclohexane reaction also gave significant yields of 2,4-di-2-pyridylthiophene (**53**, 8%) and 1,2-di-2-pyridylethane (**28**, 2%). The former reaction would follow a radical mechanism similar to that shown in Scheme III, and the latter would be formed by a radical-induced dimerization of 2-methylpyridine (**3**).

2-(4-Pyridyl)ethanesulfonic acid (**57**) gives a very similar pattern of reactivity as can be seen in Table VI. The mechanisms follow from those discussed above for 2-(2-pyridyl)ethanesulfonic acid. Benzene or thiphenol, produced from the cyclohexane as described above, must combine with sulfur to give the small yield of thianthrene (**39**, 1.5%); cf. discussion under phenylethanethiol (**16**).

Conclusions

In this paper the reactivity of a series of organic thiols and sulfonic acids under aqueous and thermal conditions are discussed.

Phenylalkyl mercaptans [$Ph(CH_2)_{1-3}SH$] generally react more rapidly under aqueous than thermal conditions. This is in marked contrast with the reaction of the dialkyl sulfides discussed in the previous part of this series. There the reactions went faster under thermal conditions. It is very likely that ionic and free-radical reactions run side by side for both groups of compounds, but it was appropriate to discuss mainly radical reactions in part 13 and mainly ionic reactions for the products reported in the present paper. Large amounts of disulfides form under mild conditions but under more severe reaction conditions either do not form or react further. These reactions are accompanied by complete desulfurization to give toluene, ethylbenzene, and propylbenzene as major products plus some diphenylalkane coupling products—1,2-diphenylethane and 1,4-diphenylbutane. The reactivity of the mercaptans decreases as the number of methylene groups between the phenyl ring and the mercaptan group increases. Mechanistically, this mercaptan chemistry provides the most facile pathway for the formation of hydrogen sulfide during the steam stimulation used to recover heavy bitumens. A minor amount of radical cyclization to form benzothiophenes and dithianes also occurs.

2-Phenylethanesulfonic acid is unreactive under aquathermolysis conditions, but the corresponding 2-(2-pyridyl)- and 2-(4-pyridyl)ethanesulfonic acids are quite reactive, yielding pyridine and 2- and 4-picoline as major products. Thermally 2- and 4-ethylpyridine are formed. In cyclohexane, thiophenol and diphenyl sulfide are also

(13) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.
(14) House, W. T.; Orchin, M. *J. Am. Chem. Soc.* **1960**, *82*, 639.
(15) Silverwood, H. A.; Orchin, M. *J. Org. Chem.* **1962**, *27*, 3401.

produced by reaction of elemental sulfur formed in these systems with the cyclohexane solvent. Additionally, on aquathermolysis of the pyridylethanesulfonic acids, high molecular weight products, e.g., di- and tripyridylthiophenes, are found.

Registry No. 1, 110-86-1; 2, 108-88-3; 3, 109-06-8; 4, 108-89-4; 5, 100-41-4; 6, 100-42-5; 7, 100-71-0; 8, 1569-69-3; 9, 103-65-1; 10, 536-75-4; 11, 108-98-5; 12, 108-95-2; 13, 637-50-3; 14, 98-86-2; 15, 100-53-8; 16, 4410-99-5; 17, 122-97-4; 18, 5745-52-8; 19, 24734-68-7; 20, 65-85-0; 21, 101-81-5; 22, 103-29-7; 23, 119520-56-8; 24, 139-66-2; 25, 78526-47-3; 26, 7570-92-5; 27, 128925-86-0; 28, 4916-40-9; 29, 128925-87-1; 30, 588-59-0; 31, 451-40-1; 32, 4916-57-8; 33, 1083-56-3; 34, 538-74-9; 35, 882-33-7; 36, 29627-27-8; 37, 1207-95-0; 38, 27846-24-8; 39, 92-85-3; 40, 1445-78-9; 41, 14315-12-9; 42, 150-60-7; 43, 15619-03-1; 44, 128925-88-2; 45, 128925-92-8; 46, 30176-46-6; 47, 128925-93-9; 48, 3328-86-7; 49, 76216-52-9; 50, 6493-73-8; 51, 27846-22-6; 52, 128925-89-3; 53, 128925-90-6; 54, 89987-96-2; 55, 128925-91-7; 56, 34292-93-8; 57, 68922-18-9; 58, 53054-76-5; C_6H_{12}, 110-82-7; $H(CH_2)_6H$, 110-54-3; H_2O, 7732-18-5.

Supplementary Material Available: Table II listing properties and mass spectral data of starting materials and Table III comparing experimental and literature mass spectral fragmentation data of products (3 pages). Ordering information is given on any current masthead page.