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Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 21.¹ Reactions of Sulfur-Containing Compounds in Supercritical Water at 460 °C

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Ten sulfur-containing compounds were selected to serve as models for the sulfur-containing impurities in heavy oils. They were subjected to aquathermolysis in water, 15% aqueous formic acid, and 15% aqueous sodium formate solution for 7 min at 460 °C. Refractory materials were rerun over 1 h at the same temperature. In each instance the sulfur compound was exposed to the same time/temperature regime in cyclohexane in order to compare any thermal decomposition with the aqueous results. Thiophene (5) was completely unchanged, and benzo[b]thiophene (33) showed little (<4%) or no change in any medium over 1 h. Diphenyl sulfide (44) was rapidly reduced to benzene (2) in formic acid over 1 h but showed little change in other media. Likewise, thiophenol (22) was rapidly converted to benzene (2) over 1 h in aqueous formic acid and more slowly in aqueous sodium formate, where diphenyl sulfide was the major product. In water it gave mainly diphenyl sulfide (44). However, even in cyclohexane considerable quantities of benzene (2) and diphenyl sulfide (44) were produced over 1 h. 1-Naphthalenethiol (43) paralleled the reactions of thiophenol (22). Cyclohexyl phenyl sulfide (45) showed high conversions in all four media over 7 min to give mixed product slates. Again, acid-catalyzed reduction to benzene (2) and 1-methylcyclopentene (1) was dominant in the aqueous formic acid. 1-Naphthyl phenyl sulfide (52) could be completely desulfurized in formic acid, giving benzene (2) and naphthalene (32) in 1 h along with minor amounts of secondary products. In water an equilibrium developed between the starting material (52), 1,1'-dinaphthyl sulfide (55) and diphenyl sulfide (44). Cyclohexane gave a comparatively low conversion and aqueous sodium formate a high conversion, but in both cases a long product slate was seen. 1-Phenylthiotetralin (51) was highly reactive in all four media. Desulfurization was complete within 7 min in formic acid to give benzene (2), naphthalene (32), and tetralin (30). Significant extrusion of sulfur was also seen in the runs in water and sodium formate, although thiophenol (22) was still a major product in each case. Dioctyl sulfide (50) showed almost complete conversion after 7 min to give mainly the hydrocarbons 1-heptene (8) and 1-octene (12). Tetrahydrothiophene (10) was found to be reactive in all four solvents after 1 h, yet the products were presumably volatile hydrocarbons and were not identified.

Introduction

The existence of sulfur compounds, such as aromatic mercaptans, sulfides, and disulfides, in coals and heavy oils is well-known.²⁻⁵ Their removal from fuels derived from the above precursors is essential in order to avoid pollution. The removal of sulfur from these compounds is presently achieved by catalytic hydrodesulfurization. However, this process is relatively expensive, and alternative approaches have been considered. One such approach is the thermal transformation of such organic

compounds in aqueous environments.⁶⁻¹⁶ A study of the aquathermolyses of model compounds should illuminate

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the feasibility of this approach and also enhance our understanding of the formation and modification of the world's fossil fuel resources.

The initial subcritical aquathermolysis investigation of organosulfur compounds was carried out by Clark *et al.* on thiophene (5), tetrahydrothiophene (10), and benzo-[b]thiophene (33).^{6,7} They found that thiophene (5) and tetrahydrothiophene (10) hydrolyzed very slowly in water⁶ but more rapidly in acidic media at 350 °C,⁷ producing small quantities of hydrogen sulfide and low molecular weight hydrocarbons, along with a complex array of liquid products. Tetrahydrothiophene (10) was more susceptible to hydrolysis than thiophene (5) and showed some reactivity at high pH. Clark also demonstrated that aqueous cationic species (e.g., Sc^{3+} , Cr^{3+} , Ni^{2+} , Cu^{2+} , and Al^{3+}) strongly interact with thiophene (5) and tetrahydrothiophene at 240 °C for 28 days resulting in some desulfurization, to give mainly complex mixtures of organic products.⁸

Substantial work has been done in our laboratories on the reactivity of various organosulfur compounds in aqueous systems,⁹⁻¹⁴ and all these previous aquathermolysis results are briefly mentioned in the Results and Discussion section of this report under the relevant model compounds. To our knowledge, only two sulfur-containing organic compounds have thus far been reacted in supercritical water. Klein demonstrated that benzyl phenyl sulfide underwent cleavage (at 386 °C, for up to 2 h) to give toluene, thiophenol, and benzaldehyde,¹⁵ yet dibenzothiophene was virtually unreacted at 550 °C, even after 4 h.¹⁶

We now report the reactions of a number of sulfides, thiols, and sulfur heterocycles at 460 °C in water, 15% aqueous formic acid, and 15% aqueous sodium formate for 7 min. If little or no change was detected, the reactions were repeated for 1 h. In every case, a fourth solution in cyclohexane was subjected to the same conditions in order to compare the thermal breakdown with the aquathermolysis breakdown. Certain model compounds were also subjected to 15% aqueous sodium carbonate and 15% aqueous phosphoric acid at 460 °C for the above-mentioned reaction times.

Experimental Section

Thiophenol (22), diphenyl sulfide (44), benzo[b]thiophene (33), thiophene (5), tetrahydrothiophene (10), and dioctyl sulfide (50) were obtained from Aldrich. 1-Naphthalenethiol (43) was obtained from Kodak. 1-Naphthyl phenyl sulfide (52), mp 38–40 °C (lit.¹⁷ 40–41 °C), and cyclohexyl phenyl sulfide (45), bp 115 °C/1.0 mm (lit.¹⁸ 108 °C/0.8 mm), were prepared according to the literature procedures.

1-Phenylthiotetralin (51). $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1 mL) was added to a mixture of 1,2-dihydronaphthalene (1.00 g, 7.69 mmol) and thiophenol (0.85 g, 7.69 mmol) in anhydrous benzene (20 mL) at 0 °C and left overnight. The organic layer was washed with NaOH (2 × 30 mL, 15% w/w), water (2 × 30 mL), and brine (1 × 20 mL) and was dried (MgSO_4). Evaporation of the solvent followed by column chromatography (Al_2O_3 :hexane–diethyl ether, 95:5 as eluant) yielded the pure product (51) as a colorless oil (1.75 g, 93% yield): bp 160 °C/1 mm. HRMS: calcd. 240.0973, found 240.0973. MS: m/z = 240 (m^+ , 5%), 131 (100), 109 (10), 91 (17). ^1H NMR (CDCl_3/TMS): δ = 1.75 (m, 1H), 2.00 (m, 2H), 2.33 (m, 1H), 2.81 (m, 2H), 4.47 (t, 1H, J = 4.1 Hz), 7.08–7.50 (m, 9H). ^{13}C NMR (CDCl_3): δ = 18.59, 28.50, 29.09, 47.61, 125.69,

126.94, 127.04, 128.30, 128.91 (2C), 129.22, 130.48, 131.85 (2C), 135.46, 137.58. ν_{max} (film): 3017, 2933, 2862, 1582, 1478, 1438, 1270, 1024, 722, 735, 691.

The purity of all starting materials was checked by GC prior to use, and materials were purified, where necessary, to at least 98% purity. Water, 15% aqueous formic acid, 15% aqueous sodium formate, and cyclohexane were deoxygenated with argon for 1 h just before use. All the GC analyses were carried out on a Hewlett Packard 5890 instrument (flame ionization detector, FID) with a 15-m capillary column (SPB-1), and a temperature program of 10 °C/min from 50 to 250 °C was used.

General Procedure. The procedure for the aquathermal reactions is the same as that in the previous paper¹ and has been described in detail in part 1 of this series.¹⁹

The GC behavior of all the compounds included in the present paper (starting materials and products) is collated in Table 1. Table 2 records the source and mass spectral fragmentation pattern of the authentic compounds used, either as starting materials or for the identification of products. Tables 3 and 4 record the mass spectral fragmentation patterns of products for which authentic samples were not available and which were identified by comparison with published MS data (Table 3) or by deduction of their structure from the MS fragmentation pattern (Table 4). Tables 2, 3 and 4 along with the details of the mass spectral analyses have been deposited as supplementary material (see paragraph at the end of this paper).

Results and Discussion

All the results and the product yields (molar percent), which have been corrected with regard to their response factor,²² are collected in Tables 5–12 (described in detail in part 1¹⁹). The suggested reaction pathways are illustrated in the schemes, where necessary. Compounds with numbers ≥ 100 are postulated as intermediates in the reactions and were not detected by the GC/MS instrument.

Diphenyl Sulfide (44) (Table 5, Scheme 1). Previous work carried out in our group has shown that diphenyl sulfide (44) undergoes very little reaction in water (1.4% conversion) and cyclohexane (1.7% conversion) over 5 days at 250 °C to give minor amounts of biphenyl (39), thiophenol (22), and dibenzothiophene (41).¹⁰ Diphenyl sulfide (44) was also found to be unreactive in an aqueous sodium bisulfite/sodium sulfite (1 mol equiv) mixture after 22 h at 250 °C.¹²

We have now found that at 460 °C for 7 min no reaction occurred in cyclohexane, water, or 15% phosphoric acid, but a 12.7% conversion was seen in aqueous formic acid, with the generation of benzene (2).^{10b} In aqueous sodium formate, a 5.2% conversion into benzene (2) was observed. Aqueous sodium carbonate (15%) generated only a trace of benzene (2, 0.7%). Extending the reaction time to 1 h afforded a 76.4% conversion in aqueous formic acid, essentially completely to benzene (2, 74.3%). Aqueous sodium formate gave a 13.3% conversion into benzene (2, 8.9%) and thiophenol (22, 4.4%). There was no reaction in water. In aqueous sodium carbonate a 9.0% conversion was seen to yield benzene (2, 2.7%), thiophenol (22, 1.4%), dibenzothiophene (41, 1.1%), and some phenol (23, 1.8%); the latter product suggests a slow base-catalyzed hydrolysis *via* 104, which then eliminates thiophenoxide to give

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Table 1. Structure and Identification of Starting Materials and Products

no.	t_R , min	structure	mol wt	equiv wt	identificn basis ^a	response factor ²²
1	0.35	1-methylcyclopentene	82	82	Table 3	1.00
2	0.36	benzene	78	78	Table 3	0.97
3	0.37	cyclohexane	84	84	Table 3	0.97
4	0.38	cyclohexene	82	82	Table 3	0.97
5	0.38	thiophene	84	84	Table 2	0.72
6	0.49	heptane	100	100	Table 3	0.96
7	0.54	toluene	92	92	Table 3	0.96
8	0.67	1-heptene	98	98	Table 3	0.96
9	0.68	octane	114	114	Table 3	0.96
10	0.69	tetrahydrothiophene (thiolane)	88	88	Table 2	0.72
11	0.70	4-octene	112	112	Table 3	0.96
12	0.75	1-octene	112	112	Table 3	0.96
13	0.76	3-octene	112	112	Table 3	0.96
14	0.77	ethylcyclohexane	112	112	Table 3	0.96
15	0.80	2-octene	112	112	Table 3	0.96
16	0.86	ethylbenzene	106	106	Table 3	0.96
17	0.95	cyclohexanol	100	100	Table 3	0.79
18	0.98	cyclohexanone	98	98	Table 3	0.79
19	1.24	cyclohexanethiol	116	116	Table 3	0.72
20	1.27	propylcyclohexane	126	126	Table 3	0.95
21	1.34	propylbenzene	120	120	Table 3	0.95
22	1.38	thiophenol	110	110	Table 2	0.72
23	1.74	phenol	94	94	Table 3	0.79
24	2.56	1-methylindane	132	132	Table 3	0.95
25	2.66	1-octanol	130	130	Table 3	0.78
26	2.77	2-methyl-5-propyltetrahydrothiophene	144	144	Table 4	0.70
27	3.24	(2-methyl)-1-octanethiol	160	160	Table 4	0.73
28	3.27	2-octanethiol	146	146	Table 3	0.71
29	3.29	1-octanethiol	146	146	Table 3	0.71
30	3.33	tetralin	132	132	Table 3	0.95
31	3.53	2-(1-butyl)tetrahydrothiophene	144	144	Table 3	0.70
32	3.63	naphthalene	128	128	Table 3	0.95
33	3.69	benzo[b]thiophene	134	134	Table 2	0.70
34	4.35	2,3-dihydrobenzothiothiophene	136	136	Table 3	0.70
35	5.18	bicyclohexyl	166	84	Table 3	0.94
36	5.19	1-methylnaphthalene	142	142	Table 3	0.94
37	5.35	cyclohexylbenzene	160	160	Table 3	0.94
38	5.45	1-cyclohexenylbenzene	158	158	Table 3	0.93
39	5.98	biphenyl	154	77	Table 3	0.94
40	6.20	1-phenyl-2-methylcyclopentene	158	158	Table 4	0.94
41	6.76	dibenzothiophene	184	184, 92 ^b	Table 3	0.68
42	7.94	1-naphthol	146	146	Table 3	0.94
43	8.06	1-naphthalenethiol	160	160	Table 2	0.70
44	8.40	diphenyl sulfide	186	186, 93 ^c	Table 2	0.68
45	8.50	cyclohexyl phenyl sulfide	192	192	Table 2	0.70
46	8.81	2-cyclohexylthiophenol	192	192	Table 3	0.70
47	10.95	diphenyl disulfide	218	109	Table 3	0.42
48	11.31	1-phenylnaphthalene	204	204	Table 3	0.92
49	11.65	1-cyclohexylnaphthalene	210	105	Table 3	0.92
50	12.49	dioctyl sulfide	258	258	Table 2	0.66
51	13.64	1-phenylthiotetralin	240	240	Table 2	0.66
52	13.96	1-naphthyl phenyl sulfide	236	236	Table 2	0.66
53	14.42	2-naphthyl phenyl sulfide	236	236	Table 3	0.66
54	14.92	cyclohexyl 1-octyl sulfide	228	114	Table 3	0.67
55	18.81	1,1'-dinaphthyl sulfide	286	143	Table 3	0.64
56	18.94	1,2'-dinaphthyl sulfide	286	143	Table 3	0.64
57	20.28	1,1'-dinaphthyl disulfide	318	159	Table 3	0.39

^a Tables 2, 3, and 4 are supplementary material and are listed as an identification basis. ^b Obtained from thiophenol (22) and diphenyl sulfide (44). ^c Obtained from thiophenol (22), 1-naphthyl phenyl sulfide (52), and 1-phenylthiotetralin (51).

phenol (23). In aqueous phosphoric acid (15%), even after 1 h, only a 4.5% conversion was seen, and benzene (2, 2.6%) and thiophenol (22, 1.9%) were the products.

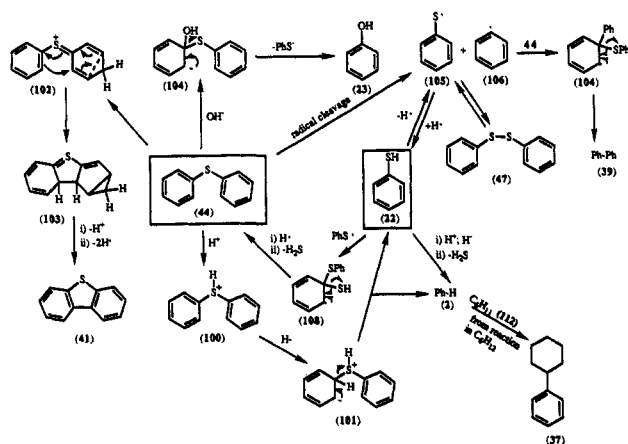
These results suggest that the cleavage of diphenyl sulfide (44) is greatly enhanced by reducing media (formic acid) and that this cleavage is acid-catalyzed. Evidently, radical cleavage (thermal) is not important in this reaction, indicated by the lack of significant conversion in cyclohexane. Also, it seems clear that sulfur extrusion as hydrogen sulfide (the distinctive odor suggests this) is enhanced in formic acid. Presumably, protonation of the sulfur initially gives 100 with subsequent cleavage of the sulfide link, induced by hydride transfer from formate to

give 101, which in turn yields benzene (2) and thiophenol (22). Thiophenol (22) itself then undergoes hydrogen sulfide elimination in a similar manner to yield more benzene (2). The intramolecular cyclization of diphenyl sulfide (44) to dibenzothiophene (41) in the aqueous media probably results *via* an initial protonation of the *para*-position of the benzene ring of diphenyl sulfide (44) to give 102 with subsequent rearrangement and re-aromatization *via* 103. In cyclohexane, only a 4.3% conversion occurred with biphenyl (39) as the only product, demonstrating that radical cleavage is less important. Possibly, diphenyl sulfide (44) undergoes a radical cleavage to give a thiophenol radical (105) and a phenyl radical (106). The

Table 5. Products Obtained from Diphenyl Sulfide (44) Reactions at 460 °C

no.	solvent structure/time (min)	cyclohexane		H ₂ O		HCO ₂ H (15%)		HCO ₂ Na (15%)		Na ₂ CO ₃ (15%)		H ₃ PO ₄ (15%)	
		7	60	7	60	7	60	7	60	7	60	7	60
2	benzene			—	—	12.7	74.3	5.2	8.9	0.7	2.7	—	2.6
22	thiophenol			—	—	—	—	—	4.4	—	1.4	—	1.9
23	phenol			—	—	—	—	—	—	—	1.8	—	—
39	biphenyl		4.3	—	—	—	1.0	—	—	—	—	—	—
41	dibenzothiophene			—	—	—	0.2	—	—	—	1.1	—	—
44	diphenyl sulfide	100	95.7	100	100	87.3	23.6	94.8	86.7	99.3	91.0	100	95.5
47	diphenyl disulfide			—	—	—	0.9	—	—	—	2.0	—	—

Scheme 1



reactive phenyl radical (106) could then react with diphenyl sulfide (44) to give (107), which readily eliminates thiophenol to give biphenyl (39).

Thiophenol (22) (Table 6, Scheme 1). Thiophenol (22) was previously heated in cyclohexane at 250 °C for 84 h and with water at 250 °C for 70 h to afford moderate conversions (17.7% and 14.7%, respectively) to diphenyl sulfide (44), thianthrene, and diphenyl disulfide (47).¹² However, a high conversion (83.2%) was seen after treating thiophenol (22) with a saturated solution of sodium bisulfite/sodium sulfite for 70 h at 250 °C to give as major products diphenyl sulfide (44), thianthrene, and diphenyl trisulfide.

Thiophenol (22) now showed a 94.5% conversion in aqueous formic acid after only 7 min at 460 °C, to benzene (2) (88.0%) and some diphenyl sulfide (44, 6.5%). After 1 h, a complete conversion (100%) to benzene (2) was observed. This further demonstrates the ease with which sulfur can be extruded from sulfides in this medium. In water after 7 min, there was a 77.6% conversion to diphenyl sulfide (44, 74.4%), benzene (2, 0.4%), and dibenzothiophene (41, 2.8%). After 1 h the product slate was very similar; diphenyl sulfide (44, 76.3%) and benzene (2, 2.1%). This may indicate that an equilibrium between thiophenol (22) and diphenyl sulfide (44) is rapidly obtained under these conditions. In aqueous sodium formate at 460 °C for 7 min an 18.4% conversion was seen with the generation of benzene (2, 7.5%) and diphenyl sulfide (44, 9.7%). Extending the reaction time to 1 h gave a 78.6% conversion with increased amounts of both benzene (2, 26.5%) and diphenyl sulfide (44, 52.1%). In aqueous sodium carbonate a somewhat similar product slate is seen after 7 min as seen for the water run. After 1 h a slow reduction gave more benzene (2, 22.0%) with a decrease in the yield of diphenyl sulfide (44). The generation of dibenzothiophene (41) here probably arises *via* diphenyl sulfide (44) with subsequent intramolecular cyclization.

In aqueous phosphoric acid after 7 min at 460 °C, benzene (2, 3.2%) and diphenyl sulfide (44, 29.0%) were generated. After 1 h, conversion was complete and benzene (2) was the only product. However, the involvement of the metal surface in this reaction is possibly a factor because of the highly corrosive nature of the aqueous phosphoric acid on the reaction vessel under these conditions. It is noteworthy that this product slate is similar to that for the run in aqueous formic acid, except the rate of reaction is much faster in formic acid as demonstrated by a 88.0% conversion to benzene after only 7 min.

In cyclohexane at 460 °C for 7 min there was a 27.4% conversion with benzene (2, 0.9%) and diphenyl sulfide (44, 26.5%) as products. Extending the reaction time to 1 h yields increased quantities of benzene (2, 18.0%) and diphenyl sulfide (44, 58.0%). The generation of diphenyl sulfide in cyclohexane is a likely indication of the generation of phenyl sulfide radicals (105). These reactive species would attack at the *ipso* portion of thiophenol to give 108, presumably with the subsequent elimination of hydrogen sulfide.

Cyclohexyl Phenyl Sulfide (45) (Table 7, Scheme 2). Our previous studies at 250 °C showed that after 5.5 days cyclohexyl phenyl sulfide (45) formed 1-methylcyclopentene (1, 5.9% and 22.4%, respectively) and thiophenol (22, 8.3% and 17.8%, respectively) as major products under both thermolysis (in nonane, 20.1% conversion) and aquathermolysis (48.0% conversion).⁹ It was also reported that both reactions were very much accelerated in the presence of an acidic clay (calcium montmorillonite) but that in the presence of a weak base (calcium carbonate) the reactivity was considerably reduced. It was clear that at 250 °C this sulfide underwent cleavage faster under aqueous conditions (ionic pathway) than under thermal conditions (radical pathway). Also, Klein has shown that (as an example of a similar system) benzyl phenyl sulfide cleaves under aquathermolysis conditions (386 °C, for up to 2 h) to give benzaldehyde (*via* benzyl alcohol) as the major product, along with toluene (7) and thiophenol (22).¹⁵

We now report that at 460 °C cyclohexyl phenyl sulfide (45) showed extensive reaction after only 7 min: in cyclohexane an 89.2% conversion was seen and in the aqueous systems 90.9–92.1% conversions occurred. The product slates vary, but in the aqueous systems the major products include 1-methylcyclopentene (1), thiophenol (22), cyclohexylbenzene (37), and biphenyl (39). Only in aqueous formic acid was a substantial amount of benzene (2, 22.9%) observed. As already found with other sulfide and thiol derivatives in this medium, desulfurization occurs readily, presumably *via* acid-catalyzed reduction.

The reactivity pattern for this sulfide is somewhat complex due to the tendency of sulfur compounds to undergo both oxidation and reduction and also because sulfur shows a variety of valence states as compared with,

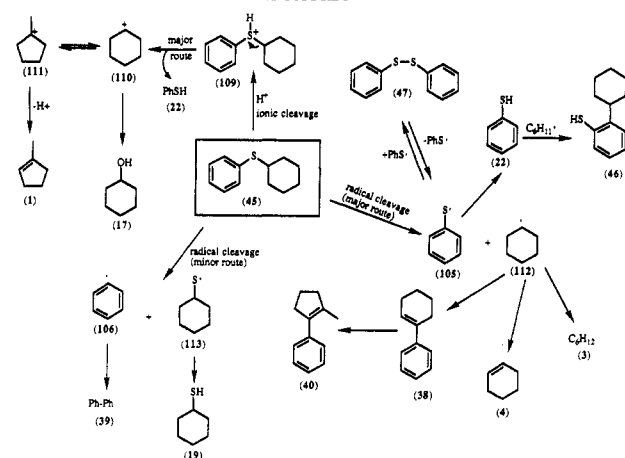
Table 6. Products Obtained from Thiophenol (22) Reactions at 460 °C

no.	solvent structure/time (min)	cyclohexane		H ₂ O		HCO ₂ H (15%)		HCO ₂ Na (15%)		Na ₂ CO ₃ (15%)		H ₃ PO ₄ (15%)	
		7	60	7	60	7	60	7	60	7	60	7	60
2	benzene	0.9	18.0	0.4	2.1	88.0	100	7.5	26.5	4.0	22.0	3.2	100
22	thiophenol	72.6	22.4	22.4	21.6	5.5	—	81.6	21.4	21.7	18.0	67.8	—
37	cyclohexylbenzene	—	0.4	—	—	—	—	—	—	—	—	—	—
39	biphenyl	—	1.2	—	—	—	—	—	—	—	—	—	—
41	dibenzothiophene	—	—	2.8	—	—	—	1.2	—	4.3	—	—	—
44	diphenyl sulfide	26.5	58.0	74.4	76.3	6.5	—	9.7	52.1	70.0	60.0	29.0	—

Table 7. Products Obtained from Cyclohexyl Phenyl Sulfide (45) Reactions at 460 °C

no.	solvent structure/time (min)	cyclohexane		H ₂ O		HCO ₂ H (15%)		HCO ₂ Na (15%)	
		7	7	7	7	7	7	7	7
1	1-methylcyclopentene	—	33.4	26.6	30.2	—	—	—	—
2	benzene	2.4	—	22.9	—	—	—	—	—
3	cyclohexane	—	—	—	5.4	—	—	—	—
4	cyclohexene	26.0	—	—	—	—	—	—	—
7	toluene	0.4	0.2	0.2	—	—	—	—	—
17	cyclohexanol	—	1.6	1.0	1.1	—	—	—	—
19	cyclohexanethiol	1.2	0.3	0.3	0.5	—	—	—	—
22	thiophenol	21.1	30.8	11.4	19.2	—	—	—	—
37	cyclohexylbenzene	17.3	5.6	12.3	11.2	—	—	—	—
38	1-cyclohexenylbenzene	—	0.7	0.8	0.9	—	—	—	—
39	biphenyl	15.0	15.9	12.0	9.6	—	—	—	—
40	1-phenyl-2-methylcyclopentene	0.6	0.8	3.4	5.4	—	—	—	—
45	cyclohexyl phenyl sulfide	10.8	8.2	9.1	7.9	—	—	—	—
46	2-cyclohexylthiophenol	—	0.4	—	1.0	—	—	—	—
47	diphenyl disulfide	5.2	2.1	—	7.6	—	—	—	—

Scheme 2

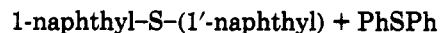


for example, oxygen and nitrogen. The similarity of the product slates between the nonaqueous and aqueous reactions and the number and variety of minor products suggest that radical reactions can occur in all four cases. We speculate that in the aqueous systems the initial cleavage of cyclohexyl phenyl sulfide (45) is acid-catalyzed. Thus, protonation of 45 gives 109 which eliminates thiophenol (22) to give the cyclohexyl cation (110) which rearranges to the more stable tertiary cation (111) which yields 1-methylcyclopentene (1).⁹ However, we believe that radical cleavage competes with the acid-catalyzed cleavage in the aqueous systems. In cyclohexane, we would expect the major homolytic pathway to give phenylthio radicals (105) and cyclohexyl radicals (112) which lead to thiophenol (22) and cyclohexene (4), respectively. The minor radical homolytic pathway would give cyclohexanethiol radicals (113) and phenyl radicals (106), which would give rise to cyclohexanethiol (19) and to benzene (2) and biphenyl (39), respectively.

The mass spectral fragmentation pattern for cyclohexene (4) and that for 1-methylcyclopentene (1) are very similar, but we managed to assign each structure using characteristic patterns in the fragmentations reported.²⁰ Both cyclohexene and 1-methylcyclopentene showed molecular ions at m/z 82, although this was more intense for cyclohexene (4) than for 1-methylcyclopentene (1). Both compounds showed their base peaks at m/z 69 (loss of methyl). However, cyclohexene showed an intense peak at m/z 54 (90%) (loss of ethyl). This was not observed with 1-methylcyclopentene (1). Also, the retention time for 1-methylcyclopentene ($t_R = 0.35$) is slightly lower than that for cyclohexene ($t_R = 0.38$). This could be expected as the boiling point for 1-methylcyclopentene (bp = 75.5 °C) is less than that for cyclohexene (bp = 83 °C).²¹

In the aqueous systems, cyclohexanol (17) is also obtained. Significantly, the least amount of sulfur containing products result from the reaction in aqueous formic acid, indicating that sulfur is extruded readily, probably as hydrogen sulfide or even elemental sulfur (or both). Cyclohexylbenzene (37), cyclohexanethiol (19), biphenyl (39), and 1-phenyl-2-methylcyclopentene (40) were also seen as typical products. Thiophenol (22), as expected from the previous results, was converted on to benzene (2).

1-Naphthyl Phenyl Sulfide (52) (Table 8, Scheme 3). In water at 460 °C, a 28.4% conversion was observed after 7 min to give the exchanged products, diphenyl sulfide (44, 8.3%) and 1,1'-dinaphthyl sulfide (55, 19.1%). After 1 h a 57.6% conversion was seen, and the same two products dominated. It is apparent that in water an equilibrium is reached within 1 h, as follows:



There is also some 1-naphthyl phenyl sulfide (52) to 2-naphthyl phenyl sulfide (53) isomerization and a trace of reduction to naphthalene (32).

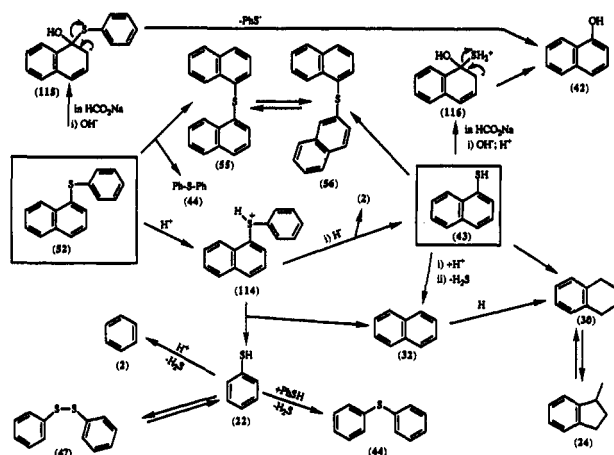
At 460 °C for 7 min, 1-naphthyl phenyl sulfide (52) was more reactive in aqueous formic acid, with a 42.1% conversion than it was in water. In formic acid 52 converts to naphthalene (32, 23.2%) and benzene (2, 10.9%) via an acid catalyzed reduction. Initial protonation of 52 gives 114, which cleaves to thiophenol (22) and naphthalene (32). Thiophenol is then readily reduced to benzene (2). Extending the reaction time to 1 h led to a complete conversion (100%) in aqueous formic acid to yield predominantly benzene (2, 42.6%) and naphthalene (32, 55.7%) as well as a small quantity of tetralin (30, 1.7%) resulting from reduction of the naphthalene substrate. No sulfur-containing products were observed; hydrogen sulfide was released upon opening the reaction vessel. The initial equilibrium clearly gets overtaken within 1 h by reduction in the presence of formic acid.

In aqueous sodium formate after 7 min a 26.0% conversion was seen, and the products generated now

Table 8. Products Obtained from 1-Naphthyl Phenyl Sulfide (52) Reactions at 460 °C

no.	solvent structure/time (min)	cyclohexane		H ₂ O		HCO ₂ H (15%)		HCO ₂ Na (15%)	
		7	60	7	60	7	60	7	60
2	benzene	—	16.7	—	—	10.9	42.6	5.5	12.6
22	thiophenol	—	4.5	—	—	1.2	—	5.5	2.2
24	1-methylindane	—	—	—	—	—	—	—	0.9
30	tetralin	—	—	—	—	—	1.7	—	1.7
32	naphthalene	—	7.9	—	1.0	23.2	55.7	3.4	42.0
36	1-methylnaphthalene	—	1.1	—	—	—	—	—	—
42	1-naphthol	—	—	—	—	—	—	—	1.5
44	diphenyl sulfide	2.1	10.0	8.3	19.4	2.4	—	3.8	16.1
47	diphenyl disulfide	5.7	—	—	—	—	—	—	11.7
48	1-phenylnaphthalene	—	3.5	—	—	—	—	—	1.7
52	1-naphthyl phenyl sulfide	87.4	44.6	71.6	42.4	57.9	—	74.0	8.1
53	2-naphthyl phenyl sulfide	1.6	—	1.0	1.8	0.9	—	1.7	—
55	1,1'-dinaphthyl sulfide	3.2	11.7	19.1	33.7	3.5	—	6.1	1.5
56	1,2'-dinaphthyl sulfide	—	—	—	1.7	—	—	—	—

Scheme 3



included benzene (2, 5.5%), thiophenol (22, 5.5%), naphthalene (32, 3.4%), diphenyl sulfide (44, 3.8%), 2-naphthyl phenyl sulfide (53, 1.7%), and 1,1'-dinaphthyl sulfide (55, 6.1%). After 1 h, a 91.9% conversion to the major products, naphthalene (32, 42.0%), diphenyl sulfide (44, 16.1%) and benzene (2, 12.6%), was obtained. Also, tetralin (30, 1.7%) was generated, a result of the reduction of the naphthalene nucleus. The appearance of a small quantity of 1-naphthol (42, 1.5%) may arise from a base-catalyzed cleavage of 52 via intermediate 115. It is noteworthy that this product is not seen in the other aqueous systems. The presence of 1-phenylnaphthalene (48, 1.7%) (also seen for the reaction in cyclohexane) is indicative of radical reactions also occurring under these conditions. The product slate for the run in aqueous sodium formate is somewhat intermediate between that for water and aqueous formic acid.

In cyclohexane after 7 min at 460 °C only a 12.6% conversion was seen demonstrating that reactions occurring via thermal pathways are less favored than those occurring via aqueous pathways. After 1 h in cyclohexane a 55.4% conversion was seen (again the lowest of four media), and the major products were benzene (2, 16.7%), diphenyl sulfide (44, 10.0%), and 1,1'-dinaphthyl sulfide (55, 11.7%). The presence of 1-methylnaphthalene (36, 1.1%) possibly indicates the involvement of radicals generated from the solvent. It is well-known that aryl sulfides are able to form stable radical as well as stable ionic intermediates,¹³ and this is supported by the varied product slate, which suggests that both ionic and radical pathways participate under aqueous conditions. However, it is clear that the reactions of 1-naphthyl phenyl sulfide

(52) occur much more readily in aqueous formic acid and aqueous sodium formate, especially after 1 h, indicating that ionic reactions are favorable.

1-Naphthalenethiol (43) (Table 9, Scheme 3). Previous investigations into the aquathermolysis of 1-naphthalenethiol (43) at 250 °C for 5 days demonstrated conversions of 74.2% in cyclohexane, 87.5% in water, and 100% both in water containing catalytic amounts of nontronite clay and in aqueous buffer at pH 10.5.¹³ The major product in all runs was 1,1'-dinaphthyl sulfide (55, 67–84%). Aquathermolysis at 300 °C for 3 days gave noticeably different product slates; the conversion was overall slightly lower (85–95%), and high yields of naphthalene (32) were obtained (40–64%). Also, increased amounts of 2,2'-dinaphthyl sulfide with much lower yields of the expected 1,1'- isomer (55) were seen.

We have now found that treatment at 460 °C for 7 min in aqueous formic acid completely converted 1-naphthalenethiol (43) to naphthalene (32, 97.8%) and a small quantity of tetralin (30, 2.2%); this is analogous to the chemistry of thiophenol (22) (see Table 6). Evidently, naphthalene (32) is slowly reduced by hydrogen transfer either from the formate anion or more likely from the generated hydrogen sulfide. It is noteworthy that reaction of naphthalene (32) itself, in a separate reaction in aqueous formic acid for 1 h, only yielded 0.5% of tetralin (30).¹ In aqueous phosphoric acid after 7 min at 460 °C a 91.8% conversion of 43 was seen with naphthalene (32, 43.5%) and 1,1'-dinaphthyl sulfide (55, 43.2%) as major products. This also parallels the reactions seen with thiophenol (22). The quantity of naphthalene (32) generated (43.5%) in this acidic environment is in contrast to the amount (97.8%) generated after the run in aqueous formic acid, demonstrating the influence of the formic acid as a source of hydride on this acid-catalyzed reaction.

At 460 °C for 7 min in cyclohexane, conversion was 86.1%, mainly to 1,1'-dinaphthyl sulfide (55, 82.6%), presumably generated by radical coupling. The intermediacy of radicals is demonstrated by the formation of cyclohexyl radicals to give 1-cyclohexylnaphthalene (49, 1.5%). In water for 7 min, a 78.1% conversion was seen, and 1,1'-dinaphthyl sulfide (55, 48.3%), naphthalene (32, 15.9%), and 1,2'-dinaphthyl sulfide (56, 8.0%) were the products. In aqueous sodium formate after 7 min, conversion was 83.7% to naphthalene (32, 17.1%), 1,1'-dinaphthyl sulfide (55, 55.5%), and 1-naphthol (42, 9.8%). The generation of 1-naphthol (42) probably results from the attack of a hydroxide anion either directly at the *ipso*-position of the thiol functionality to give an intermediate

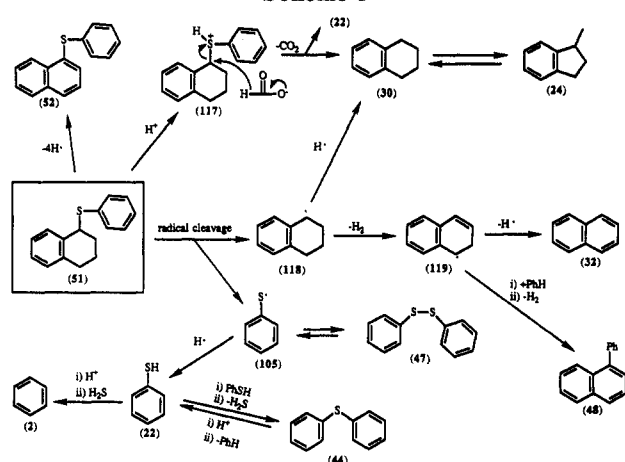
Table 9. Products Obtained from 1-Naphthalenethiol (43) Reactions at 460 °C

no.	solvent structure/time (min)	cyclohexane 7	H ₂ O 7	HCO ₂ H (15%) 7	HCO ₂ Na (15%) 7	Na ₂ CO ₃ (15%) 7	H ₃ PO ₄ (15%) 7
30	tetralin	—	—	2.2	1.3	—	—
32	naphthalene	2.0	15.9	97.8	17.1	11.6	43.5
42	1-naphthol	—	—	—	9.8	14.7	—
43	1-naphthalenethiol	13.9	21.9	—	16.3	12.1	8.2
49	1-cyclohexylnaphthalene	1.5	—	—	—	—	—
55	1,1'-dinaphthyl sulfide	82.6	48.3	—	55.5	12.4	43.2
56	1,2'-dinaphthyl sulfide	—	8.0	—	—	32.2	5.1
57	1,1'-dinaphthyl disulfide	—	5.9	—	—	17.0	—

Table 10. Products Obtained from 1-Phenylthiotetralin (51) Reactions at 460 °C

no.	solvent structure/time (min)	cyclohexane 7	H ₂ O 7	HCO ₂ H (15%) 7	HCO ₂ Na (15%) 7
2	benzene	3.3	1.8	44.5	3.9
22	thiophenol	3.9	41.5	—	22.1
24	1-methylindane	—	0.9	0.9	—
30	tetralin	61.6	19.0	24.1	47.9
32	naphthalene	13.8	33.8	30.5	10.5
44	diphenyl sulfide	—	3.0	—	1.4
47	diphenyl disulfide	3.4	—	—	7.4
48	1-phenylnaphthalene	3.4	—	—	1.7
52	1-naphthyl phenyl sulfide	10.6	—	—	5.1

Scheme 4



like 116 with subsequent elimination of hydrogen sulfide or at the *ipso*-position of the formed dinaphthyl sulfide (55), with elimination of 1-naphthalenethiol. In aqueous sodium carbonate for 7 min, an 87.9% conversion was seen. The product slate included 1-naphthol (42), naphthalene (32), 1,1'-dinaphthyl sulfide (55), 1,2-dinaphthyl sulfide (56), and 1,1'-dinaphthyl disulfide (57). It is noteworthy that the amount of 1-naphthol (42) produced is greater in aqueous sodium carbonate than in aqueous sodium formate (compare 14.7% with 9.8%), which suggests a base-catalyzed hydrolysis. These product slates are similar to those seen in the previous work, in which the mechanism of their formation is discussed.¹³

1-Phenylthiotetralin (51) (Table 10, Scheme 4). This compound (51) underwent 100% conversion in all four media at 460 °C within 7 min. In aqueous formic acid the major products were naphthalene (32, 30.5%), tetralin (30, 24.1%), and benzene (2, 44.5%). A small amount of 1-methylindane (24, 0.9%) was also generated. Again, it is noteworthy that complete desulfurization occurred: sulfur is readily extruded, probably as hydrogen sulfide or elemental sulfur, in this acidic environment. Probably in this medium initial protonation of 51 gives 117 which cleaves *via* hydride attack to give thiophenol (22) and

tetralin (30). Thiophenol (22) is then subsequently reduced to benzene (2). The generation of naphthalene (32) in an essentially reducing environment suggests that sulfur does act as an oxidizing agent during the reaction, with aromatization as the driving force. In aqueous sodium formate the major products were thiophenol (22, 22.1%), tetralin (30, 47.9%), naphthalene (32, 10.5%), and 1-naphthyl phenyl sulfide (52, 5.1%). In this case there is more tetralin (30) than naphthalene (32) present (in contrast to the results in water and aqueous formic acid), suggesting that oxidation reactions occur less readily, possibly due to the generation of less elemental sulfur. Also, initial oxidation of tetralin (30) to 1,2-dihydronaphthalene may be suppressed by the reductive properties of the formate anions. In water, thiophenol (22, 41.5%), tetralin (30, 19.0%), and naphthalene (32, 33.8%) are the major products. Ionic cleavage reactions occur here too, although there is less sulfur extrusion than in formic acid. Not surprisingly, sulfur extrusion is not as facilitated in water as in aqueous formic acid because of the lack of a source of hydride ion. In cyclohexane, the major products were tetralin (30, 61.6%), naphthalene (32, 13.8%), and 1-naphthyl phenyl sulfide (52, 10.6%). Considering the mechanism of cleavage in this thermal medium, homolysis is rapid to give the two stabilized radicals 118 and 105 which abstract hydrogen atoms to give tetralin (30) and thiophenol (22), respectively. Thus, it is clear that 1-phenylthiotetralin (51) is highly reactive in all four solvents and that radical reactions are also very highly favored. It is apparent that in the aqueous systems both radical and ionic reactions occur.

Benzo[*b*]thiophene (33) (Table 11, Scheme 5). This compound (33) has previously been shown to be unreactive at 250 °C after 82 h in an aqueous mixture of sodium bisulfite/sodium sulfite.¹¹ However, after 5 days at 350 °C in 10% phosphoric acid significant reaction (37.5%) was observed, with ethylbenzene and 2,3-dihydrobenzothiophene as the major products along with minor amounts of higher molecular weight products.

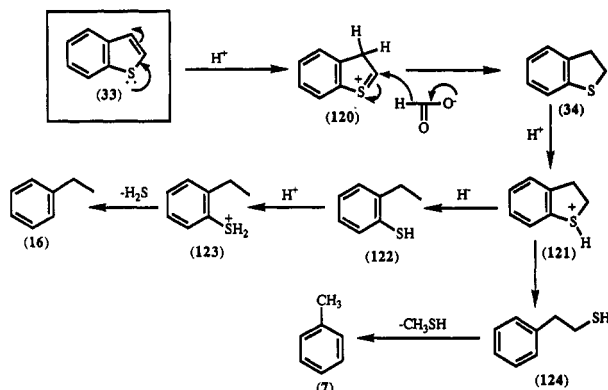
Benzo[*b*]thiophene (33) is now found also to be unreactive at 460 °C for 7 min in all four media. At 460 °C for 1 h, ≤3.5% conversion was seen for all cases. In both aqueous formic acid and aqueous sodium formate a small amount (1.6% in each case) of 2,3-dihydrobenzothiophene (34), from reduction of the starting material, was observed. With aqueous formic acid, ethylbenzene (16, 1.9%) was also observed, presumably generated from a formate induced displacement of hydrogen sulfide from the protonated 2,3-dihydrobenzothiophene (121).

Diocetyl Sulfide (50) (Table 12, Scheme 6). We previously investigated the aquathermolysis and thermolysis of diocetyl sulfide (50) at 250 °C.¹³ Reaction was faster in cyclohexane (73% conversion) than in water (9% conversion) or water at pH 10.5 (19% conversion), all over 5 days. The major products under all three sets of

Table 11. Products Obtained from Benzo[*b*]thiophene (33) Reactions at 460 °C

solvent		cyclohexane		H ₂ O		HCO ₂ H (15%)		HCO ₂ Na (15%)	
no.	structure/time (min)	7	60	7	60	7	60	7	60
7	toluene	—	2.0	—	—	—	—	—	—
16	ethylbenzene	—	—	—	—	—	1.9	—	—
33	benzo[<i>b</i>]thiophene	100	98.0	100	100	100	96.5	100	98.4
34	2,3-dihydrobenzothiophene	—	—	—	—	—	1.6	—	1.1

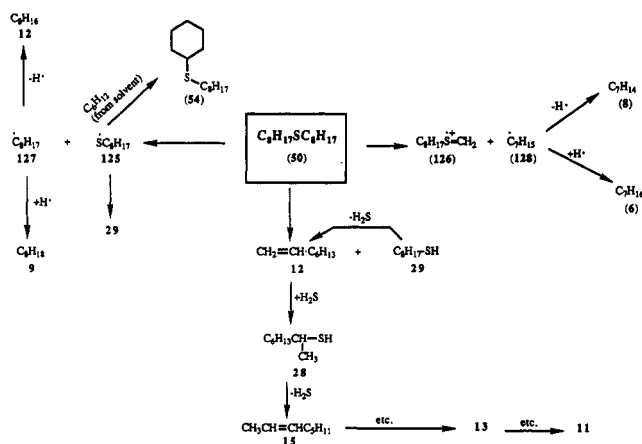
Scheme 5



**Table 12. Products Obtained from Dioctyl Sulfide (50)
Reactions at 460 °C**

solvent		cyclohexane	H ₂ O	HCO ₂ H (15%)	HCO ₂ Na (15%)
no.	structure/time (min)	7	7	7	7
6	heptane	3.6	0.1	0.4	—
8	1-heptene	30.0	38.0	36.1	28.4
9	octane	—	0.1	0.1	0.1
11	4-octene	6.9	0.1	0.2	5.5
12	1-octene	44.5	55.3	59.8	46.5
13	3-octene	3.3	0.1	0.8	2.0
14	ethylcyclohexane	0.1	—	—	—
15	2-octene	1.2	0.2	0.2	0.2
16	ethylbenzene	0.1	—	—	—
20	propylcyclohexane	0.1	—	—	—
27	(2-methyl)- 1-octanethiol	—	—	0.3	0.1
28	2-octanethiol	1.3	0.7	0.6	0.9
29	1-octanethiol	6.1	4.7	1.4	7.2
31	2-(1-butyl)tetra- hydrothiophene	—	0.3	0.1	3.8
50	dioctyl sulfide	1.6	0.4	—	5.3
54	cyclohexyl 1-octyl sulfide	0.1 98.9	—	—	—

Scheme 6



conditions were octane (9), 1-octene (12), and 1-octanethiol (29). With the addition of nontronite to the aqueous systems these products were formed in lower amounts, and the major products were octanal and dioctyl disulfide.

At 300 °C, the reactivity of dioctyl sulfide (50) was similar in neutral water (41 % conversion) and in water at pH 10.5 (33 % conversion). At this temperature nontronite brought about an increase in reactivity in both systems (85 % and 86 % conversion, respectively) and also gave higher levels of hydrogen sulfide gas production. The major products were heptane (6), octane (9), 1-octene (12), 2-octene (15), 1-octanethiol (29).

At 460 °C compound (50) was highly reactive in all four media. Within 7 min complete conversion was seen in aqueous formic acid, and 98.4%, 99.6%, and 94.7% conversions were achieved in cyclohexane, water, and aqueous sodium formate, respectively. In all systems, the major products were 1-heptene (8, 30.0%, 38.0%, 36.1%, 28.4% for cyclohexane, water, aqueous formic acid and aqueous sodium formate, respectively) and 1-octene (12, 44.5%, 55.3%, 59.8%, 46.5%, respectively). Small quantities of 2-octene (15), 3-octene (13), and 4-octene (11) were also detected.

Small amounts of 1-octanethiol (29) and 2-octanethiol (28) were also generated in all four reaction media. Most of the products generated from these reactions were seen in the earlier series of aquathermolysis reactions (subcritical) on compound 50, where the reaction pathways were assumed to proceed *via* radical mechanisms.¹³ Because of the similar product slates, we believe that the same mechanisms are operating under supercritical conditions, although competing ionic mechanisms are also presumed to be occurring in the aqueous media.

Thiophene (5). Previous work in our laboratories has shown thiophene (5) to be inert under all the following conditions: cyclohexane at 250 °C/5 days, water at 250 °C/5 days or 300 °C/3 days, or aqueous buffer (pH 10.5) at 250 °C/5 days. Even when the aqueous systems were re-run after the addition of nontronite clay, no reaction occurred.¹³ However, thiophene did undergo aquathermolysis with 10% H₃PO₄ at 250 °C for 20 h and 4 days to give 13.0% and 31.6% conversions, respectively.¹⁴ Heating at 350 °C for 5 days gave a 71.6% conversion. The major products from this reaction included tetrahydrothiophene (10) and 2-methyltetrahydrothiophene. Mono-, di-, and trimethylthiophenes were also formed in appreciable amounts along with 2-*tert*-butyl- and 5-methyl-2-propylthiophene, ethylbenzene (16), and 1,3,5-trimethylbenzene.

In supercritical water, Klein has shown that dibenzothiophene underwent only very slight aquathermolysis at 550 °C after 5 h; biphenyl and benzene were the products.¹⁶ In the present work, thiophene (5) was completely unreactive in all four media at 460 °C even over 1 h, again attesting to the stability of this aromatic compound.

Tetrahydrothiophene (10). We previously demonstrated that at 250 °C for 5 days tetrahydrothiophene (10) undergoes no reaction in cyclohexane and only a very slight conversion (0.6%) in water to give thiophene.¹³ Similarly, only slight conversions (1.0%) were observed in water at 300 °C for 3 days, and thiophene (5) was the only product.

Employing nontronite clay as a catalyst and using water at higher pH did not lead to any increase in reaction. Even at 350 °C for 5 days in 10% H_3PO_4 tetrahydrothiophene was unreactive.¹⁴

Tetrahydrothiophene (10) was unreactive at 460 °C for 7 min in all four media but was seemingly reactive for the runs after 1 h. The products were assumed to be volatile, low-molecular weight hydrocarbons, arising from the extrusion of sulfur from (10), and they were not identified in this study.

Conclusions

Thiophene (5) and benzo[*b*]thiophene (33) are important model compounds for sulfur-containing impurities in naturally occurring oil resources. Unfortunately, these

were not significantly desulfurized at 460 °C in any of the media employed. However, other model compounds including thiophenols and both alkyl and aryl sulfides could be desulfurized, and of the media examined, 15% aqueous formic acid was the most successful. It is also evident that at 460 °C radical mechanisms become more involved in these reactions. Finally, we conclude that for many heavy oils substantial reductions in sulfur content could be potentially achieved by their treatment with aqueous formic acid under supercritical conditions.

Supplementary Material Available: Mass spectral assignments of the structures and Tables 2, 3, and 4 listing mass spectral fragmentation patterns (8 pages). Ordering information is given on any current masthead page.