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Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 28.¹ Reactions of Aryl Sulfoxides and Sulfones in Sub- and Supercritical Water at 200–460 °C

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Diphenyl and methyl phenyl sulfones and sulfoxides and dibenzothiophene sulfone were treated at 460 °C with water, 15% aqueous formic acid, and 15% aqueous sodium formate. Thermal comparisons were run in cyclohexane, and for those compounds and conditions that resulted in fast conversion after 7 min at 460 °C, also at lower temperatures. Sulfoxides are highly reactive, sulfones less so. Reactivity is greatest in 15% aqueous sodium formate followed by formic acid for the sulfones; this reactivity order is inverted for the sulfoxides. In all of the aqueous media, ionic reactions dominate. The sulfoxides are mainly deoxygenated to the corresponding sulfides, while C–S bond cleavage is more important for the sulfones. Product slates are identified and analyzed, and reaction pathways are suggested for the transformations found.

Introduction

The reactions of a wide range of organic compounds in aqueous solutions at temperatures between 200 and 350 °C have been previously described by us.^{2,3} The significance of these results to our understanding of potential processes for the treatment of resource materials prompted us to extend the work to temperatures above the critical point of water (374.2 °C), as we have recently reported.^{4,5} The temperature employed (460 °C) was carefully chosen to allow high reaction rates at shorter reaction times.

We have now extended this study of supercritical water reactions to encompass a set of aryl sulfoxides and sulfones. The work is of relevance to the possibility of desulfurization of resource materials via initial oxidation of the sulfur compound to sulfoxides and/or sulfones.

Studies by other research groups have previously focused attention on the aquathermolysis of several organosulfur compounds, namely thiophene, tetrahydrothiophene, and dibenzothiophene.^{6–8} Subcritical neutral aquathermolyses of thiophene and tetrahydrothiophene resulted in very slow reaction,⁶ whereas acidic media at 350 °C gave much more rapid conversion⁷ to hydrogen sulfide and low molecular weight hydrocarbons. One study⁸ in the supercritical range found dibenzothiophene to be essentially unreactive after 4 h in water at 550 °C. Clark found that aqueous solutions of first-row transition metals and aluminum cations at 240 °C for 28 days resulted in some desulfurization of thiophene and tetrahydrothiophene to give complex mixtures of organic products.⁹ Our own studies confirmed the unreactive nature of thiophene, tetrahydrothiophene, 2,5-dimethylthiophene, benzo[*b*]thiophene, and dibenzothiophene under neutral aquathermolysis conditions up to 350 °C. In the presence of 10% phosphoric acid at 350 °C only benzo[*b*]thiophene was desulfurized to any extent (60%).¹⁰

To our knowledge, sulfoxides and sulfones have not previously been used as substrates in aquathermolysis reactions designed to investigate the possible desulfu-

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Table 1. Structure and Identification of Starting Materials and Products

no. factor	t_R , min	structure	mol wt	equiv wt ^a	identification ^b	response basis
1	0.44	benzene	78	78	Table 2	1.00
2	0.66	toluene	92	92	Table 2	0.96
3	1.07	cyclohexanol	100	100	Table 2	0.79
4	1.19	cyclohexanone	98	98	Table 2	0.79
5	1.24	ethylbenzene	106	106	Table 2	0.96
6	1.89	propylcyclohexane	126	126	Table 3	0.95
7	2.08	thiophenol	110	110	Table 3	0.72
8	2.49	phenol	94	94	Table 2	0.79
9	3.12	butylcyclohexane	140	140	Table 3	0.95
10	3.61	methyl phenyl sulfide	124	124	Table 3	0.70
11	4.82	naphthalene	128	128	Table 2	0.95
12	6.07	methyl phenyl disulfide	156	156	Table 3	0.45
13	6.24	bicyclohexyl	166	83	Table 3	0.94
14	6.44	2-methylnaphthalene	142	142	Table 3	0.94
15	6.80	cyclohexylbenzene	160	160	Table 3	0.94
16	6.87	methyl phenyl sulfoxide	140	140	Table 2	0.58 ^c
17	7.50	methyl phenyl sulfone	156	156	Table 2	0.32 ^c
18	7.53	biphenyl	154	77	Table 3	0.94
19	7.79	2-methylbiphenyl	168	168	Table 3	0.93
20	9.05	2-phenylphenol	170	170	Table 2	0.76
21	9.10	2-phenylphenyl mercaptan	186	93	Table 4	0.69
22	9.18	4-phenylphenyl mercaptan	186	93	Table 4	0.69
23	10.02	9H-fluorene	166	166	Table 2	0.93
24	10.13	diphenyl sulfide	186	186	Table 3	0.68
25	10.20	9-methylfluorene	180	180	Table 3	0.93
26	11.62	dibenzothiophene	184	184	Table 3	0.68
27	12.04	anthracene	178	178	Table 2	0.93
28	12.74	diphenyl disulfide	186	186	Table 3	0.42
29	13.00	2-cyclohexylbiphenyl	236	236	Table 4	0.91
30	13.09	4-cyclohexylbiphenyl	236	236	Table 4	0.91
31	13.18	diphenyl sulfoxide	202	202	Table 2	0.25 ^c
32	13.20	2-cyclohexenylbiphenyl	234	234	Table 4	0.91
33	13.33	<i>o</i> -terphenyl	230	76.7	Table 3	0.91
34	13.54	9-methylanthracene	192	192	Table 3	0.92
35	13.72	diphenyl sulfone	218	218	Table 2	0.18 ^c
36	14.37	9-ethylanthracene	206	206	Table 3	0.92
37	14.88	hexahydrotriphenylene	234	234	Table 4	0.91
38	14.94	diphenyl trisulfide	250	250	Table 4	0.17
39	15.06	3-cyclohexenylbiphenyl	234	234	Table 4	0.91
40	15.35	dibenzothiophene sulfone	216	216	Table 2	0.63 ^c
41	15.69	<i>m</i> -terphenyl	230	76.7	Table 3	0.91
42	15.78	4-phenylphenyl phenyl sulfide	262	262	Table 4	0.65
43	16.01	<i>p</i> -terphenyl	230	76.7	Table 3	0.91
44	16.08	4-cyclohexenylbiphenyl	234	234	Table 4	0.91
45	16.22	9-butylanthracene	234	234	Table 3	0.91
46	17.23	3-phenylphenyl phenyl sulfide	262	262	Table 4	0.65
47	17.74	2-phenylphenyl phenyl sulfide	262	262	Table 4	0.65
48	17.92	<i>o,o</i> -quaterphenyl	306	76.5	Table 3	0.88
49	18.04	1,2,3,4-tetrahydrotriphenylene	232	232	Table 3	0.82
50	18.23	triphenylene	228	228	Table 3	0.91
51	19.90	<i>o,m</i> -quaterphenyl	306	76.5	Table 3	0.88
52	20.41	<i>o,p</i> -quaterphenyl	306	76.5	Table 3	0.88
53	21.33	1,4-bis(phenylthio)benzene	294	294	Table 3	0.42
54	8.20	diphenylmethane	168	168	Table 3	0.93
55	16.32	hexahydrotriphenylene (<i>cis</i> or <i>trans</i> isomer of 37)	234	234	Table 4	0.91
56	14.75	4-methylphenyl phenyl disulfide	232	232	Table 4	0.42
57	4.95	1-methyl-4-(methylthio)benzene	138	138	Table 3	0.71

^a The equivalent weight expresses the number of moles of molecules of product which could be expected to be formed for one molecule of reactant: in most cases it is the molecular weight; however, for dimeric products the equivalent weight of the product would be MW ÷ 2, whereas for certain fragment products the equivalent weight is MW × 2. ^b Tables 2, 3, and 4 are Supporting Information. ^c Experimentally measured RF data.

rization of resource materials, although these functional groups have been subjected to biochemical investigations for this same purpose;^{11,12} the corresponding sulfoxides and sulfones have been suggested as intermediates in the biodesulfurization of both dibenzothiophene and benzyl methyl sulfide.¹³

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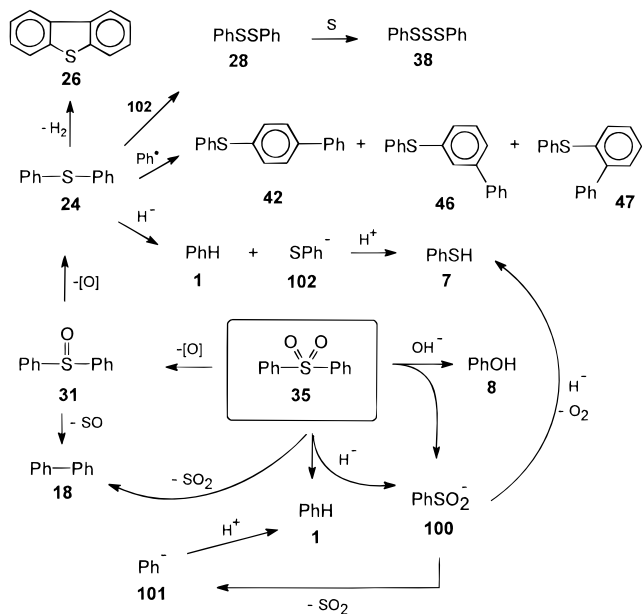
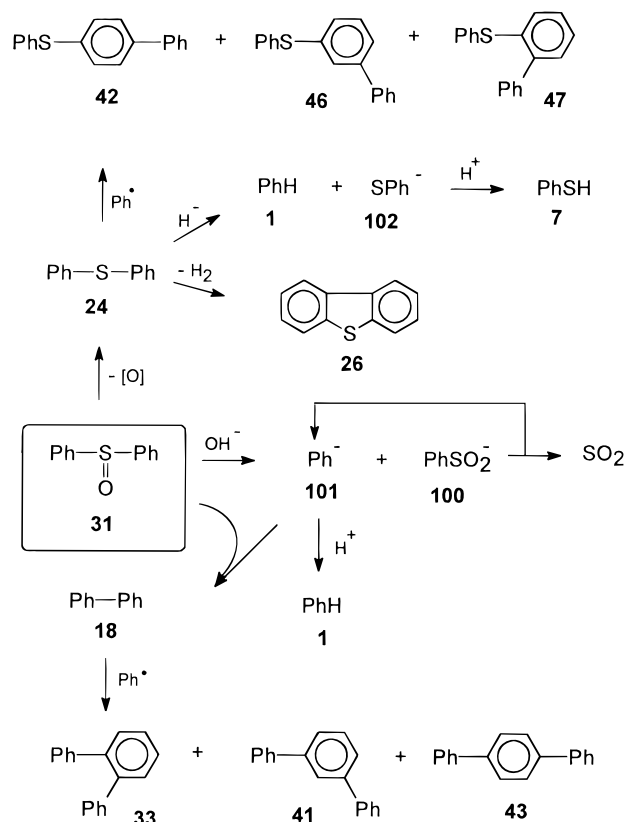
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As before, our reactions in this current study were conducted at 460 °C and each compound was heated in water alone, in 15% aqueous formic acid, and in 15% aqueous sodium formate. Formic acid was chosen for three reasons: to enhance any acid-catalyzed reactions, because of the inherent hydride ion transfer reducing properties, and because on decomposition it simulates CO/H₂O treatments.^{14–17} Sodium formate increases the

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Table 5. Reaction of Diphenyl Sulfone (35)

no.	structure	cyclohexane		H ₂ O		HCO ₂ H (15%)			HCO ₂ Na (15%)				
		460 °C, 7 min	460 °C, 60 min	460 °C, 7 min	460 °C, 60 min	460 °C, 7 min	460 °C, 15 min	460 °C, 60 min	300 °C, 30 min	350 °C, 7 min	350 °C, 60 min	460 °C, 7 min	460 °C, 60 min
1	benzene	2.6	1.2	0.6	2.0	9.5	41.5	83.9	12.6	39.7	55.6	24.3	74.6
7	thiophenol		0.4				2.5	6.7		19.9	33.0	8.7	5.4
8	phenol											0.7	
13	bicyclohexyl		5.5										
15	cyclohexylbenzene	2.4	32.3										
18	biphenyl		0.7			0.1	1.2	2.2	0.9	3.9	5.6	1.6	3.5
24	diphenyl sulfide		9.7				14.1	7.0			4.2	55.6	13.9
26	dibenzothiophene		0.4					0.1			0.1	0.3	0.5
28	diphenyl disulfide						0.7	0.1			0.2	5.0	1.4
35	diphenyl sulfone	95.0	49.8	99.4	98.0	90.4	40.0		86.5	36.5	1.3		
38	diphenyl trisulfide											1.1	0.1
42	4-phenylphenyl phenyl sulfide											0.5	0.1
46	3-phenylphenyl phenyl sulfide											1.2	0.3
47	2-phenylphenyl phenyl sulfide											1.0	0.2

Scheme 1**Scheme 2**

pH of an aqueous solution and is also a powerful hydride donor. Each substrate was also heated in cyclohexane at 460 °C to compare the course of the aquathermolyses with that of purely thermal breakdown. Runs were initially carried out for 7 min and for 1 h; where essentially complete reaction occurred under these conditions, the behavior at lower temperatures was also examined.

Experimental Section

Methyl phenyl sulfoxide (16), diphenyl sulfoxide (31), methyl phenyl sulfone (17), diphenyl sulfone (35), and dibenzothiophene sulfone (40) were obtained from Aldrich. The purities of all the starting materials were checked by gas chromatography (GC) prior to use, and they were purified to >97% when necessary. Water, 15% aqueous formic acid, 15% aqueous sodium formate, and cyclohexane were deoxygenated with nitrogen for 1 h just before use. All of the GC analyses were carried out on a Hewlett-Packard 5890 gas chromatograph

operated in the split injection mode (30:1 ratio) and equipped with a flame ionization detector (FID). A 15 m capillary column (SPB-1) was used, and the oven temperature was programmed from 50 to 250 °C with the initial time set at 1 min and a subsequent rate of 10 °C/min. GC/MS analyses of all compounds were performed either on a Varian 3400 gas chromatograph with a Finnegan MAT 700 ion trap detector or on a Hewlett-Packard 5890 Series II gas chromatograph with a Hewlett-Packard 5972 Series mass selective detector.

General Procedure. The model compound (0.16 g) and the solvent (1.14 mL) were charged into a nitrogen-blanketed stainless steel Swagelok bomb (capacity 4 mL) which was then sealed. The reactor was kept, without agitation, in a Techno fluidized sandbath (Model SBS-4) set at 460 °C using a Techno temperature controller (TC-8D) for 7 min or 1 h. The temperature profile was measured by a Barnant 115 thermocouple thermometer (type J) placed in the sandbath adjacent to the reaction vessel. At 460 °C and a water density of 0.285 g/mL, the reaction pressure due to supercritical water alone (exclud-

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Table 6. Reaction of Diphenyl Sulfoxide (31)

no.	structure	cyclohexane					H ₂ O		
		350 °C, 7 min	350 °C, 20 min	350 °C, 60 min	460 °C, 7 min	460 °C, 60 min	350 °C, 60 min	460 °C, 7 min	460 °C, 60 min
1	benzene						7.2	22.4	19.1
2	toluene		0.1			1.2			
7	thiophenol		0.8	5.9	22.1	19.8			
8	phenol					0.6			0.3
13	bicyclohexyl		0.1	0.2	1.6	1.6			
15	cyclohexylbenzene	0.3	0.5	1.1	2.4	2.9			
18	biphenyl	-	0.2	1.4	2.0	4.5	1.5	3.8	5.7
24	diphenyl sulfide	3.8	21.2	89.3	71.9	66.3	47.0	48.7	49.4
26	dibenzothiophene					1.6	0.1	1.5	4.5
28	diphenyl disulfide		0.4						0.3
31	diphenyl sulfoxide	95.9	76.7	2.1			34.8		
33	<i>o</i> -terphenyl							0.5	0.4
41	<i>m</i> -terphenyl							0.9	0.9
42	4-phenylphenyl phenyl sulfide					0.3	2.7	5.7	1.0
43	<i>p</i> -terphenyl							0.7	1.1
46	3-phenylphenyl phenyl sulfide					0.6	3.4	8.3	8.9
47	2-phenylphenyl phenyl sulfide					0.6	3.3	6.9	7.9
53	1,4-bis(phenylthio)benzene							0.60.5	

no.	structure	HCO ₂ H (15%)				HCO ₂ Na (15%)				
		200 °C, 20 min	300 °C, 30 min	460 °C, 7 min	460 °C, 60 min	300 °C, 30 min	350 °C, 7 min	350 °C, 60 min	460 °C, 7 min	460 °C, 60 min
1	benzene		5.2	12.9	91.9	3.1	13.9	18.7	25.6	27.0
2	toluene	0.3								
7	thiophenol					2.8	8.2	10.5	12.4	13.0
18	biphenyl			0.9	0.9		0.9	1.1	1.1	1.6
24	diphenyl sulfide	95.5	94.1	86.2	7.2	12.8	61.9	65.5	57.4	56.0
28	diphenyl disulfide					0.4	1.9			
31	diphenyl sulfoxide	4.2	0.7			80.5	10.0			
33	<i>o</i> -terphenyl					0.4				
42	4-phenylphenyl phenyl sulfide						0.5	0.9		
43	<i>p</i> -terphenyl								0.6	0.4
46	3-phenylphenyl phenyl sulfide						1.5	1.8	1.4	1.0
47	2-phenylphenyl phenyl sulfide						1.2	1.5	1.5	1.0

ing model compounds and reaction products) is about 6200 ± 200 psi.¹⁸ After the appropriate time period, each reaction was quenched by cooling the reactor with cold air and then with dry ice, and the reactors were carefully opened while the contents were still solid to vent gases with minimal loss of material. The reactors were then resealed, allowed to warm up to 0 °C in ice, and carefully vented once again. Gaseous products were not analyzed, and all conversion calculations were done on a gas-free basis. All conversions and yields were used to quantify conversion of the starting material, and GC peak areas were corrected by response factors and then renormalized to omit material present in <0.1% conversion. Details on estimation of FID response factors are described elsewhere.^{3,19} The conversion of the GC areas to molar units was done by use of an equivalent weight factor (Table 1). The reaction mixtures were worked up as previously described.³

The GC behaviors of all compounds included in the present paper (starting materials and products) are collected in Table 1. Table 2 records the source and mass spectral fragmentation patterns 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 fragmenta-

tion pattern (Table 4). Compounds with numbers ≥100 are postulated intermediates not detected as products by the GC/MS system. Tables 2–4 along with the details of the mass spectral analyses have been deposited as Supporting Information (see paragraph at the end of this paper).

Results and Discussion

Diphenyl Sulfone (35) (Table 5, Scheme 1). Diphenyl sulfone (35) showed conversions of around 5%, 1%, and 10% after 7 min at 460 °C in cyclohexane, water, and 15% aqueous formic acid, respectively. When the reaction time was extended to 1 h in cyclohexane, a 50.2% conversion was observed to give cyclohexylbenzene (15, 32.3%), diphenyl sulfide (24, 9.7%), and bicyclohexyl (13, 5.5%) with benzene (1), thiophenol (7), and dibenzothiophene (26) as minor products. Compounds 13 and 15 are derived by radical coupling reactions with the solvent.

After heating in water for 1 h at 460 °C, diphenyl sulfone (35) remained unreactive (98.0% recovered). In 15% aqueous formic acid 35 was 60.0% converted at 460 °C after 15 min and 100% converted after 1 h: the major product was benzene (1, up to 83.9%), together with thiophenol (7, up to 6.7%). Biphenyl (18, 2.2%) was also observed, while the amount of diphenyl sulfide (24) produced peaked at 14.1% after 15 min and dropped to

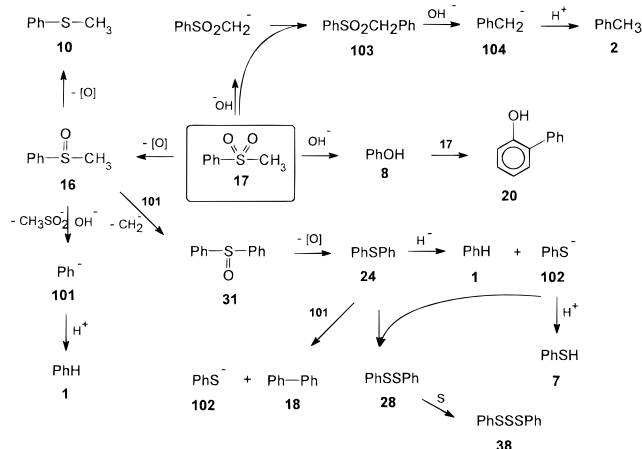
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Table 7. Reaction of Methyl Phenyl Sulfone (17)

no.	structure	cyclohexane		H ₂ O		HCO ₂ H (15%)		NCO ₂ Na (15%)		
		460 °C, 7 min	460 °C, 60 min	460 °C, 7 min	460 °C, 60 min	460 °C, 7 min	460 °C, 60 min	300 °C, 60 min	460 °C, 7 min	460 °C, 60 min
1	benzene	13.4	37.8	0.8	4.0	3.0	29.6	27.2	56.8	54.4
2	toluene	0.2	1.6	1.0	4.7	0.2	1.1	0.2	1.6	2.4
5	ethylbenzene	0.2	2.0						0.3	0.5
7	thiophenol			0.1		0.2	29.4	2.5	15.9	25.8
8	phenol			0.2					1.2	2.3
10	methyl phenyl sulfide							52.0	10.5	6.7
13	bicyclohexyl	0.4	4.2							
15	cyclohexylbenzene	4.7	15.2							
17	methyl phenyl sulfone	81.1	36.8	97.6	87.6	94.2	5.0	18.1	2.6	
18	biphenyl		1.2				0.2		1.4	
20	2-phenylphenol			0.1	3.1				-	
24	diphenyl sulfide		1.2	0.1	0.5	2.0	34.3		8.6	7.9
26	dibenzothiophene						0.3			
28	diphenyl disulfide					0.4	0.1		1.1	
38	diphenyl trisulfide			0.1	0.1					

Scheme 3



7.0% after 1 h. Previous studies have demonstrated that both **7** and **24** are converted to benzene under these conditions.⁴

In 15% aqueous sodium formate, diphenyl sulfone (**35**) was completely consumed even after 7 min at 460 °C to give mainly diphenyl sulfide (**24**, 55.6%) and benzene (**1**, 24.3%); in the 1 h run **24** reacted further and the products were benzene (**1**, 74.6%), diphenyl sulfide (**24**, 13.9%), thiophenol (**7**, 5.4%), and biphenyl (**18**, 3.5%). Fifteen percent aqueous sodium formate reacted significantly with diphenyl sulfone (**35**) at 300 °C and quite rapidly at 350 °C to give initially thiophenol (**7**) and benzene (**1**) and later biphenyl (**18**) and diphenyl sulfide (**24**).

The very low reactivity (<2%) of diphenyl sulfone (**35**) in water demonstrates its thermal stability. The reaction pathway in cyclohexane indicates loss of oxygen to give diphenyl sulfide (**24**) as the main product with substantial amounts of bicyclohexyl (**13**) and cyclohexylbenzene (**15**) formed by oxidation of the solvent. Isomeric phenylphenyl phenyl sulfides (**42**, **46**, and **47**) probably arise from phenyl radical attack on **24**.

In 15% aqueous formic acid and 15% aqueous sodium formate, in addition to deoxygenation to diphenyl sulfide (**24**, 56% formed after 7 min at 460 °C in HCO₂Na), the alternative pathway of hydride ion cleavage of **35** to benzene (**1**) and benzenesulfinic acid (**100**) appears to compete strongly, especially at lower temperatures. Benzenesulfinic acid (**100**) decomposes into SO₂ and more benzene (**1**), or it is reduced to thiophenol (**7**). At

higher temperatures and shorter times **7** and **24** react further (as already shown⁴) and, indeed, we found diphenyl disulfide (**28**) and diphenyl trisulfide (**38**). Biphenyl (**18**) is also formed in some quantities, possibly via diphenyl sulfoxide (**31**) by SO extrusion (see later).

Studies on diphenyl sulfide (**24**) as a substrate under identical reaction conditions to this current study have been reported by us.⁴ In these previous studies, up to 4.3% of biphenyl (**18**) was produced in cyclohexane (via radical mediated processes) after 1 h at 460 °C. In 15% aqueous formic acid, only 1% of biphenyl was generated from **24** under the same reaction conditions, and in both water and 15% aqueous sodium formate no biphenyl was produced. In the current study on diphenyl sulfone (**35**), conversions to biphenyl (**18**) after 1 h at 460 °C of only 0.7% in cyclohexane and 0% in water, but 2.2% in 15% aqueous formic acid and up to 5.6% in 15% aqueous sodium formate, were observed; it is clear that a reaction pathway different from that for diphenyl sulfide as a substrate is being followed. The direct extrusion of SO₂ from diphenyl sulfone (**35**) or the intermediacy of sulfoxide (**31**) via extrusion of SO therefore seems likely in the production of biphenyl (**18**).

Diphenyl Sulfoxide (31) (Table 6, Scheme 2). Diphenyl sulfoxide (**31**) is much more reactive than the sulfone **35** and was completely converted in all four media after just 7 min at 460 °C. In cyclohexane at 460 °C for 7 min, the main products were diphenyl sulfide (**24**, 71.9%) and thiophenol (**7**, 22.1%). After 1 h, further reaction of these two products led to increasing yield of biphenyl (**18**, 4.5%).

Diphenyl sulfoxide (**31**) in water at 460 °C after 7 min was completely converted with formation of high molecular weight compounds (terphenyls **33**, **41**, and **43** and 2-, 3-, or 4-phenylphenyl phenyl sulfides **42**, **46**, and **47**) together with diphenyl sulfide (**24**, 48.7%), benzene (**1**, 22.4%), and biphenyl (**18**, 3.8%). After diphenyl sulfoxide (**31**) was heated for 1 h, there were few significant changes in the product slate except that the amounts of **42** decreased and **26** increased.

In 15% aqueous formic acid after 7 min at 460 °C, the major products were diphenyl sulfide (**24**, 86.2%), benzene (**1**, 12.9%), and biphenyl (**18**, 0.9%), as expected because **24** is known to go to **1**.⁴ After 1 h, benzene (**1**, 91.9%) was a dominant product together with biphenyl (**18**, 0.9%) and as yet unreacted diphenyl sulfide (**24**, 7.2%). Diphenyl sulfoxide (**31**) was rapidly reduced to diphenyl sulfide (**24**) even after 20 min at 200 °C.

Table 8. Reaction of Methyl Phenyl Sulfoxide (16)

no.	structure	cyclohexane					H ₂ O					
		250 °C, 20 min	300 °C, 7 min	300 °C, 30 min	460 °C, 7 min	460 °C, 60 min	250 °C, 7 min	250 °C, 20 min	300 °C, 7 min	300 °C, 30 min	460 °C, 7 min	460 °C, 60 min
1	benzene					30.9		3.3	6.9	8.0	12.7	27.6
2	toluene		0.3	0.7	3.0	6.3			0.3	0.2	5.8	13.5
5	ethylbenzene			0.2		1.0						
7	thiophenol		4.2	17.3	37.2	15.5				5.4	24.8	26.7
8	phenol										0.3	0.6
10	methyl phenyl sulfide	4.5	15.0	20.1	13.1	3.0	2.6	48.9	64.0	65.6	11.9	4.8
12	methyl phenyl disulfide		0.9		0.2				0.5		0.1	
13	bicyclohexyl			0.8	1.0	1.4						
15	cyclohexylbenzene			0.1	3.6	2.4						
16	methyl phenyl sulfoxide	93.3	27.6	0.2			97.4	39.2	4.3	0.4		
18	biphenyl			0.2	3.7	5.1			0.7	0.7	1.8	2.4
20	2-phenylphenol										0.2	
21	2-phenylphenyl mercaptan										0.4	
24	diphenyl sulfide		13.4	23.3	33.8	30.4		2.4	2.8	4.7	34.5	22.4
26	dibenzothiophene					0.7					2.3	1.4
28	diphenyl disulfide	2.2	38.6	25.0	4.4	3.0		6.2	13.2	6.9	1.5	
38	diphenyl trisulfide			0.3						1.0	0.8	
46	3-phenylphenyl phenyl sulfide					0.1			3.7	3.6	1.5	
47	2-phenylphenyl phenyl sulfide					0.1			3.6	3.5	1.1	
54	diphenylmethane			0.7		0.1					0.3	0.6
56	4-methylphenyl phenyl disulfide			11.1								

no.	structure	HCO ₂ H (15%)					HCO ₂ Na (15%)					
		200 °C, 7 min	250 °C, 7 min	300 °C, 30 min	460 °C, 7 min	460 °C, 60 min	250 °C, 7 min	250 °C, 20 min	300 °C, 7 min	300 °C, 30 min	460 °C, 7 min	460 °C, 60 min
1	benzene	0.3	1.9	5.2	34.7	84.8			0.3	0.2	6.0	10.4
2	toluene				5.2	7.9					3.1	11.5
5	ethylbenzene											0.2
7	thiophenol		1.0	4.8	0.1	1.3		2.0	16.4	13.7	21.1	13.8
8	phenol											0.6
10	methyl phenyl sulfide	52.0	90.9	84.8	47.7	4.9	9.2	85.5	80.9	82.0	61.6	34.2
12	methyl phenyl disulfide				0.1							
16	methyl phenyl sulfoxide	47.7					90.8	4.4				
18	biphenyl				0.1							0.2
20	2-phenylphenol				0.4							0.1
24	diphenyl sulfide		3.5	4.2	8.0	1.1				0.6	7.8	22.7
26	dibenzothiophene				0.1							0.3
28	diphenyl disulfide		2.7	1.0	2.7			8.1	0.8	2.2	0.3	4.9
38	diphenyl trisulfide				0.8					0.3		0.4
54	diphenylmethane				0.1							
56	4-methylphenyl phenyl disulfide								1.6	1.0		
57	1-methyl-4-(methylthio)benzene										0.1	0.7

In 15% aqueous sodium formate after 7 min at 460 °C, the major products included diphenyl sulfide (**24**, 57.4%), benzene (**1**, 25.6%), and thiophenol (**7**, 12.4%). The same product slate with similar quantities was observed after the reaction time was extended to 1 h. Decreasing the reaction temperature to 300–350 °C allowed us to observe the generation of diphenyl sulfide (**24**) as the first step in the reaction sequence.

In cyclohexane and water, diphenyl sulfoxide (**31**) began to lose oxygen at 350 °C. In 15% aqueous formic acid, diphenyl sulfide (**24**, 95.5%) was observed at 200 °C after 20 min. Heating at 300 °C for 30 min in 15% aqueous sodium formate showed 19.5% conversion into mainly diphenyl sulfide (**24**, 12.8%), benzene (**1**, 3.1%), and thiophenol (**7**, 2.8%).

Comparison of diphenyl sulfone (**35**) and diphenyl sulfoxide (**31**) shows that the latter is much more reactive and loses its single oxygen much more rapidly to give diphenyl sulfide (**24**). Also, comparison of the product slates of diphenyl sulfoxide (**31**) and diphenyl sulfide (**24**) indicates that **24** is obviously an intermedi-

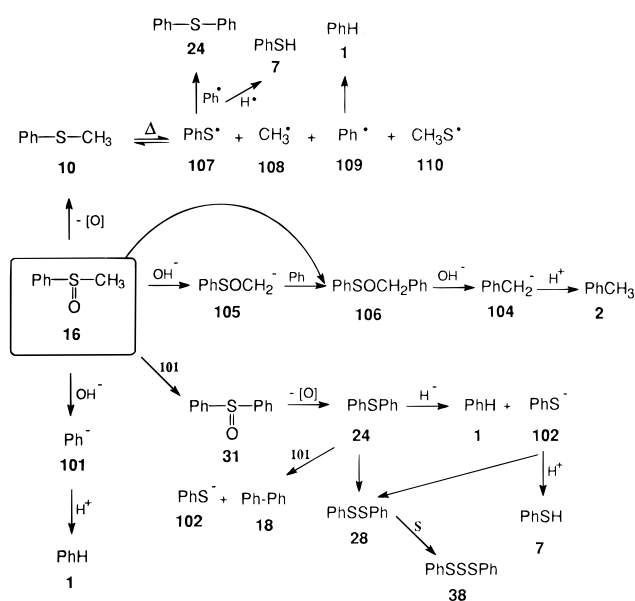
ate in the conversion of diphenyl sulfoxide (**31**). Diphenyl sulfoxide (**31**) is converted to large amounts of diphenyl sulfide (**24**); as reaction times increase, the amount of diphenyl sulfide observed decreases. This decrease is accompanied by a significant increase in the complexity of the product slate; the main products are thiophenol (**7**) and benzene (**1**). This conversion of diphenyl sulfide to mainly thiophenol (**7**) and benzene (**1**) under identical reaction conditions is indeed mirrored in our previous studies on this compound.⁴

A major difference from diphenyl sulfone (**35**) is that diphenyl sulfoxide (**31**) forms small amounts of terphenyls (**33**, **41**, and **43**). The fact that terphenyl derivatives are not observed under identical reaction conditions using diphenyl sulfide (**24**) as a substrate⁴ suggests that **24** is not an intermediate in terphenyl formation (routes to which are not immediately apparent).

Methyl Phenyl Sulfone (17) (Table 7, Scheme 3). In cyclohexane at 460 °C, an 18.9% conversion was observed after 7 min mainly to benzene (**1**, 13.4%) and cyclohexylbenzene (**15**, 4.7%). Extending the reaction

Table 9. Reaction of Dibenzothiophene Sulfone (40)

no.	structure	cyclohexane		H ₂ O		HCO ₂ H (15%)		HCO ₂ Na (15%)	
		460 °C, 7 min	460 °C, 60 min	460 °C, 7 min	460 °C, 60 min	460 °C, 7 min	460 °C, 60 min	460 °C, 7 min	460 °C, 60 min
1	benzene	5.2	35.8				0.9		1.0
2	toluene		0.1						0.5
3	cyclohexanol	0.1	0.9						
4	cyclohexanone	0.1	0.4						
5	ethylbenzene		0.2						
7	thiophenol		0.1						
9	butylcyclohexane		0.6						
11	naphthalene								0.5
13	bicyclohexyl		1.7						
14	2-methylnaphthalene								0.4
15	cyclohexylbenzene		0.2						
18	biphenyl		2.7		0.5	1.1	9.6	26.5	30.1
19	2-methylbiphenyl		0.7						
20	2-phenylphenol		0.2		12.0		3.7	28.2	31.2
23	9H-fluorene		0.9				0.2	0.1	0.1
24	diphenyl sulfide		0.5			0.3		0.6	
25	9-methylfluorene		3.8						
26	dibenzothiophene	0.7	11.9		2.1	9.4	45.1	23.7	34.0
27	anthracene		3.1						
28	diphenyl disulfide		0.4						
29	2-cyclohexylbiphenyl	0.9							
30	4-cyclohexylbiphenyl	0.2	2.3						
32	2-cyclohexenylbiphenyl	0.7							
33	<i>o</i> -terphenyl		2.2						
34	9-methylanthracene		7.6						
36	9-ethylanthracene		2.1						
37	hexahydrotriphenylene	8.1	0.8						
40	dibenzothiophene sulfone	81.4	12.9	100	84.9	89.2	39.1	20.1	
45	9-butylantracene	1.4	2.9						
48	<i>o,o</i> -quaterphenyl				0.1			0.4	0.8
49	1,2,3,4-tetrahydrotriphenylene	0.2	0.5						
50	triphenylene		4.5				0.9		
51	<i>o,m</i> -quaterphenyl				0.3		0.5	0.2	0.7
52	<i>o,p</i> -quaterphenyl				0.1			0.2	0.7
55	hexahydrotriphenylene (<i>cis</i> or <i>trans</i> isomer of 37)	1.0							

Scheme 4

time in cyclohexane to 1 h led to an increased thermal conversion (63.2%) of methyl phenyl sulfone (17), again mainly to benzene (1, 37.8%), cyclohexylbenzene (15, 15.2%) (obviously formed by reaction with the solvent), and toluene (2, 1.6%).

In water at 460 °C, methyl phenyl sulfone (17) was 2.4% reacted after 7 min, whereas after 1 h a 12.4% conversion was observed to give toluene (2, 4.7%), benzene (1, 4.0%), and 2-phenylphenol (20, 3.1%) to-

gether with minor products including diphenyl sulfide (24, 0.5%) and diphenyl trisulfide (38, 0.1%).

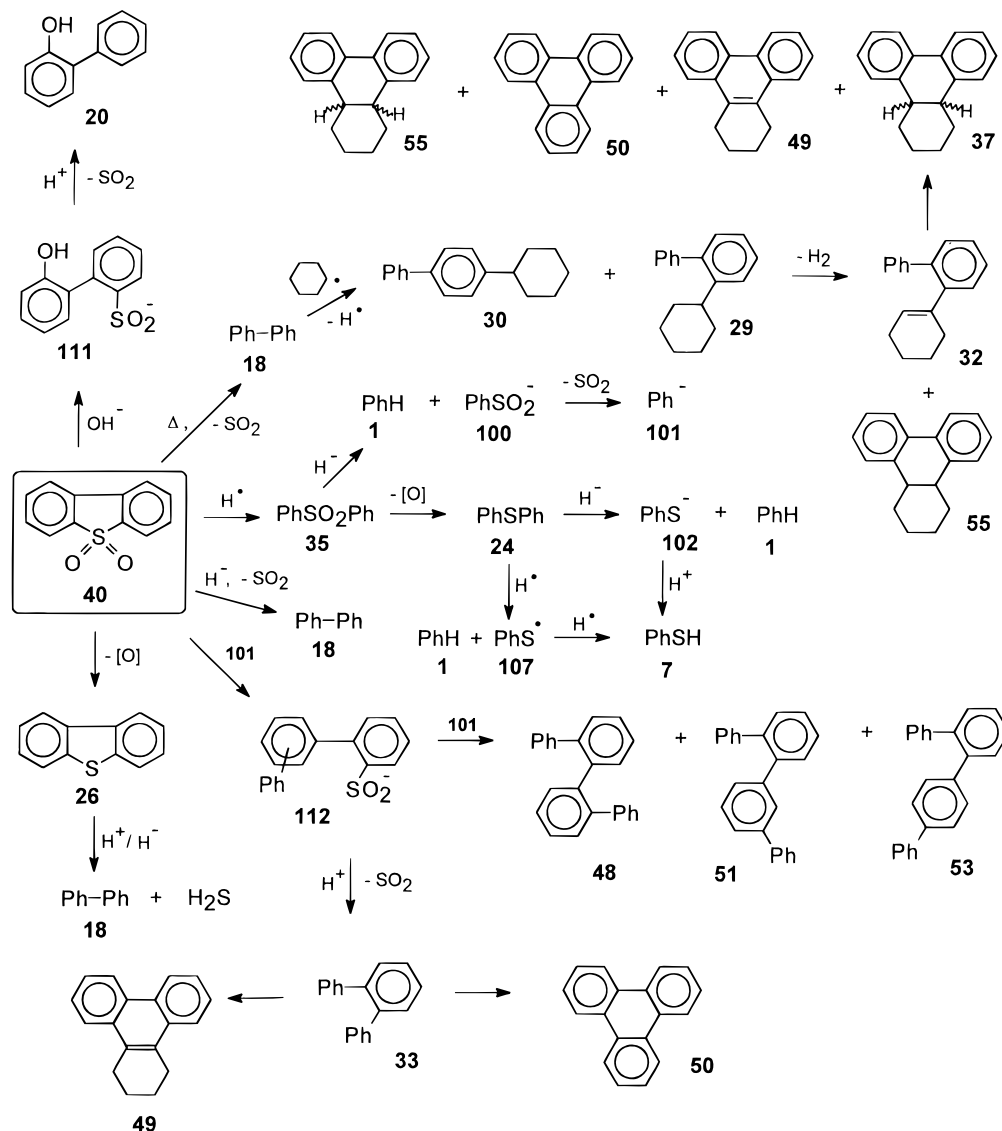
That smaller amounts of toluene (2) are formed in cyclohexane than in water suggests either an ionic pathway in water (see Scheme 3) or capture of Me and Ph radicals by other radicals in cyclohexane.

In 15% aqueous formic acid, methyl phenyl sulfone (17) showed a conversion of only 5.8% at 460 °C after 7 min, but at 460 °C after 1 h, a 95.0% conversion was observed mainly to diphenyl sulfide (24, 34.3%), benzene (1, 29.6%), and thiophenol (7, 29.4%).

Methyl phenyl sulfone (17) was highly reactive at 460 °C in 15% aqueous sodium formate, showing a 97.4% conversion after just 7 min at 460 °C; the major products were benzene (1, 56.8%), thiophenol (7, 15.9%), methyl phenyl sulfide (10, 10.5%), and diphenyl sulfide (24, 8.6%). After 1 h, complete reaction occurred, giving a similar product slate with an increased amount of thiophenol (7). Even at 300 °C after 1 h, 81.9% was reacted in 15% aqueous sodium formate to give methyl phenyl sulfide (10, 52.0%), benzene (1, 27.2%), and thiophenol (7, 2.5%).

Benzene (1) was a dominant product in both formic acid and sodium formate, probably formed by hydride ion donation. However, the large quantities of methyl phenyl sulfide (10) formed in sodium formate at 300 °C indicate here that loss of oxygen occurs first. Our belief that methyl phenyl sulfoxide (16) is an intermediate in this process is supported by the similarity to the product slate of 16 and 17 (see below). The subsequent reactions of methyl phenyl sulfide (10) at lower temperatures

Scheme 5



have previously been documented by us;²⁰ in cyclohexane at 250 °C, methyl phenyl sulfide (**10**) was almost unreactive after 5 days. Only a 2.9% conversion was observed to diphenyl sulfide (**24**, 1.3%), diphenyl disulfide (**28**, 1.1%), and biphenyl (**18**, 0.5%). In water at 250 °C, methyl phenyl sulfide (**10**) was only 1.7% converted after 5 days. The two products observed were diphenyl sulfide (**24**, 0.9%) and biphenyl (**18**, 0.8%). Since water had relatively little influence on the reactivity of methyl phenyl sulfide (**10**) at 250 °C, it was assumed that the minor conversions noted were the result of radical-mediated processes.

Methyl Phenyl Sulfoxide (16) (Table 8, Scheme 4). Methyl phenyl sulfoxide (**16**) was highly reactive after just 7 min at 460 °C in all four media. In fact, **16** began to lose oxygen even at 250 °C after 7 min in water and in 15% aqueous sodium formate and after 20 min in cyclohexane. In 15% formic acid, conversion into methyl phenyl sulfide (**10**, 52.0%) was observed already at 200 °C after 7 min.

In cyclohexane after 7 min at 460 °C, the main products were thiophenol (**7**, 37.2%), diphenyl sulfide

(**24**, 33.8%), and methyl phenyl sulfide (**10**, 13.1%). Benzene (**1**, 30.9%) and diphenyl sulfide (**24**, 30.4%) became the major products after 1 h, after which time decreased amounts of thiophenol (**7**, 15.5%) and methyl phenyl sulfide (**10**, 3.0%) were observed.

However, the runs at lower temperatures suggest that the initial reaction is mutual oxidation–reduction to give methyl phenyl sulfide (**10**) as the reduction product and diphenyl disulfide (**28**) as the oxidation product. At higher temperatures and longer times, both of these products react further. After 1 h at 460 °C, an extensive product slate was observed; in addition to benzene (**1**), thiophenol (**7**), and diphenyl disulfide (**28**) as the main products, small amounts of toluene (**2**, 6.3%), biphenyl (**18**, 5.1%), methyl phenyl sulfide (**10**, 3.0%), and diphenyl disulfide (**28**, 3.0%) were observed.

The previous results of methyl phenyl sulfide (**10**) thermolysis in cyclohexane at the lower temperature of 250 °C are reviewed above (see Methyl Phenyl Sulfone).¹⁴ The conversion of diphenyl disulfide (**28**) in cyclohexane at 250 °C for a reaction time of 5 days has also been previously reported by us;¹⁴ it was noted in these studies that under both thermal and aquathermolysis conditions at 250 °C, **28** forms similar product

(20) Katritzky, A. R.; Lapucha, A. R.; Greenhill, J. V.; Siskin, M. *Energy Fuels* **1990**, *4*, 562.

Table 10. Summary of Reactivity of Sulfoxides and Sulfones at 460 °C

	<i>t</i> (min)	medium	% convrn	major products ^a	comments
diphenyl sulfone	60	CyC ₆	50.2	CyC ₆ Ph (32.3%), PhSPh (9.7%), (CyC ₆) ₂ (5.5%)	thermal reactions with solvent predominate 86.1% desulfurization ^b 78.1% desulfurization
	60	H ₂ O	2.0	PhH (2.0%)	
	60	15% HCO ₂ H	100	PhH (83.9%), PhSPh (7.0%), PhSH (6.7%)	
	60	15% HCO ₂ Na	100	PhH (74.6%), PhSPh (13.9%), PhSH (5.4%)	
diphenyl sulfoxide	7	CyC ₆	100	PhSPh (71.9%), PhSH (22.1%)	92.8% desulfurization (86.2% PhSPh after 7 min) no change after 1 h thermal
	7	H ₂ O	100	PhSPh (48.7%), PhH (22.4%), phenylphenyl phenyl sulfides (20.9%), PhPh (3.8%), terphenyls (2.1%)	
	60	15% HCO ₂ H	100	PhH (91.9%), PhSPh (7.2%)	
	7	15% HCO ₂ Na	100	PhSPh (57.4%), PhH (25.6%), PhSH (12.4%)	
methyl phenyl sulfone	60	CyC ₆	3.2	PhH (37.8%), CyC ₆ Ph (15.2%)	61.3% desulfurization
	60	H ₂ O	12.4	PhCH ₃ (4.7%), PhH (4.0%), 2PhPhOH (3.1%)	
	60	15% HCO ₂ H	95.0	PhSPh (34.3%), PhH (29.6%), PhSH (29.4%)	
	7	15% HCO ₂ Na	97.4	PhH (56.8%), PhSH (15.9%), CH ₃ SPh (10.5%), PhSPh (8.6%)	
methyl phenyl sulfoxide	60	CyC ₆	100	PhH (30.9%), PhSPh (30.4%), PhSH (15.5%)	47.2% desulfurization 44.7% desulfurization 92.7% desulfurization 23.0% desulfurization
	60	H ₂ O	100	PhH (27.6%), PhSH (26.7%), PhSPh (22.4%), PhCH ₃ (13.5%)	
	60	15% HCO ₂ H	100	PhH (84.8%), PhCH ₃ (7.9%), CH ₃ SPh (4.9%), PhSH (1.3%), PhSPh (1.1%)	
	60	15% HCO ₂ Na	100	CH ₃ SPh (34.2%), PhSPh (22.7%), PhSH (13.8%), PhCH ₃ (11.5%), PhH (10.4%), PhSSPh (4.9%)	
dibenzothiophene sulfone	60	CyC ₆	87.1	PhH (35.8%), DBT (11.9%), 20 condensed HC products	55.6% desulfurization, 66.0% after 1 h
	60	H ₂ O	15.1	2PhPhOH (12.0%), DBT (2.1%)	
	60	15% HCO ₂ H	60.9	DBT (45.6%), PhPh (9.6%), 2PhPhOH (3.7%)	
	7	15% HCO ₂ Na	79.9	2PhPhOH (28.2%), PhPh (26.5%), DBT (23.7%)	

^a CyC₆Ph, cyclohexylbenzene; (CyC₆)₂, bicyclohexyl; PhSPh, diphenyl sulfide; PhH, benzene; PhCH₃, toluene; PhSH, thiophenol; CH₃SPh, methyl phenyl sulfide; PhSSPh, diphenyl disulfide; PhPh, biphenyl; DBT, dibenzothiophene; 2PhPhOH, 2-phenylphenol. ^b Percentage of sulfur-free products.

slates. The reaction progressed further in cyclohexane than in water. In cyclohexane at 250 °C, an 89.7% conversion of **28** was observed after 5 days mainly to thiophenol (**7**, 51.5%) and diphenyl sulfide (**24**, 36.7%). In water at 250 °C, a 33.6% conversion was observed; the main products were diphenyl sulfide (**24**, 20.5%) and PhSO₂SPh with thiophenol (**7**) produced in only a 3.8% yield.¹⁴

In water at 460 °C, after 7 min, methyl phenyl sulfoxide (**16**) produced diphenyl sulfide (**24**, 34.5%), thiophenol (**7**, 24.8%), benzene (**1**, 12.7%), methyl phenyl sulfide (**10**, 11.9%), and toluene (**2**, 5.8%) as the major products. Further reaction at 460 °C for 1 h showed increasing amounts of benzene (**1**, 27.6%) and toluene (**2**, 13.5%), while the amount of methyl phenyl sulfide (**10**, 4.8%) was observed to decrease. The runs at lower temperatures show methyl phenyl sulfide (**10**) as the dominant initial product, and then benzene (**1**) and diphenyl sulfide (**24**) accompany the diphenyl disulfide (**28**) as further products. Obviously, in water, the phenyl–S bond is much more susceptible to scission to give a phenyl anion equivalent that can form **1** and **24**. The considerable amount of toluene (**2**) may be formed via PhSOCH₂[−] (compare mechanism suggested for the sulfone **17**).

In 15% aqueous formic acid a large product slate was observed. Major products after 7 min at 460 °C were methyl phenyl sulfide (**10**, 47.7%), benzene (**1**, 34.7%), and diphenyl sulfide (**24**, 8.0%). Benzene (**1**, 84.8%) was a dominant product in this medium after 1 h.

In 15% aqueous sodium formate after 7 min, the major products were methyl phenyl sulfide (**10**, 61.6%), thiophenol (**7**, 21.1%), diphenyl sulfide (**24**, 7.8%), benzene (**1**, 6.0%), and toluene (**2**, 3.1%). After 1 h,

again, smaller amounts of methyl phenyl sulfide (**10**, 34.2%) and thiophenol (**7**, 13.8%) were seen, while the yields of diphenyl sulfide (**24**, 22.7%), toluene (**2**, 11.5%), benzene (**1**, 10.4%), and diphenyl disulfide (**28**, 4.9%) were found to increase.

Dibenzothiophene Sulfone (40) (Table 9, Scheme 5). Dibenzothiophene sulfone (**40**) showed an 18.6% conversion in cyclohexane at 460 °C after 7 min, when the formation of benzene (**1**, 5.2%) and polyaryl derivatives (**29**, **30**, **32**, **37**, **55**) was observed. Extending the reaction time to 1 h led to major conversion (87.1%) with a large product slate and increased quantities of benzene (**1**, 35.8%), dibenzothiophene (**26**, 11.9%), and polyaryl derivatives (**30**, **33**, **37**, **49**, **50**, **51**).

Dibenzothiophene sulfone (**40**) was unreactive in water at 460 °C after 7 min but showed a 15.1% conversion after 1 h. The main products were 2-phenylphenol (**20**, 12.0%), dibenzothiophene (**26**, 2.1%), and biphenyl (**18**, 0.5%).

In 15% aqueous formic acid at 460 °C for 7 min, a 10.8% conversion was observed to give dibenzothiophene (**26**, 9.4%), biphenyl (**18**, 1.1%), and diphenyl sulfide (**24**, 0.3%). When the reaction time was extended to 1 h, a 60.9% conversion was seen to dibenzothiophene (**26**, 45.1%), biphenyl (**18**, 9.6%), and 2-phenylphenol (**20**, 3.7%). Clearly, reduction of the sulfone is favored in this medium after 1 h, compared to 7 min, when less conversion was observed.

Dibenzothiophene sulfone (**40**) was highly reactive in 15% aqueous sodium formate at 460 °C after 7 min, showing a 79.9% conversion mainly to 2-phenylphenol (**20**, 28.2%), biphenyl (**18**, 26.5%), and dibenzothiophene (**26**, 23.7%). Isomeric quaterphenyls (**48**, **51**, **52**) were observed in minor amounts. Formation of 2-phenylphe-

nol (**20**, 31.2%) was also seen in 15% aqueous sodium formate at 460 °C after 1 h, when dibenzothiophene sulfone (**40**) was completely converted. The mechanism for the generation of the significant quantity of 2-phenylphenol (**20**) is probably as shown in Scheme 5 via attack of a hydroxyl anion to yield a species that then loses SO₂. Overall, at 460 °C after 1 h in 15% aqueous sodium formate, 66.0% of the products are desulfurized.

Conclusions

Phenyl sulfones undergo cleavage and desulfurization at 460 °C to form benzene as the major product most efficiently in 15% aqueous sodium formate, whereas the corresponding sulfoxides are most reactive in 15%

aqueous formic acid. Other sulfur-containing products in the reaction mixtures, e.g., diphenyl sulfide and phenyl mercaptan, will react to form more benzene at longer reaction times. Even dibenzothiophene sulfone undergoes 55.6% desulfurization in only 7 min, whereas the corresponding unoxidized dibenzothiophene is essentially unreactive. All results are summarized in Table 10.

Supporting Information Available: Mass spectral assignments of the structures and Tables 2–4 listing mass spectral fragmentation patterns (33 pages). Ordering information is given on any masthead page.