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Formic Acid and the High-Temperature Reductive Desulfurization of Aromatic Sulfides

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When diphenyl sulfide is heated with formic acid to 450 °C, it is converted to benzene, toluene, thiophenol, thioanisole, and benzoic acid. By increasing the time of reaction, diphenyl sulfide is converted completely to benzene and toluene. The mechanism of toluene and benzoic acid formation is studied by kinetic data and by comparing CO and CO_2 as possible sources for the extra carbon. It is concluded that PhS· and CO are the precursors to benzoic acid, toluene, thiophenol, and thioanisole. Formic acid reacts primarily via the metal surface of the reactor and most probably with radical initiation.

Formic acid with its decomposition products is now shown to be a desulfurizing agent for aromatic sulfides at temperatures used for coal liquefaction. Formic acid is thermally unstable and decomposes into a mixture of CO, H_2O, CO_2, and H_2. Since these are the components of the shift reaction, this equilibrium reaction is presumed to be forming as the formic acid is heated. It is also this mixture of gases which is known to be effective in reducing a variety of coal model compounds[1-3] and superior to hydrogen for low-rank coal liquefaction.[4-9]

Sulfur compounds, which are present in coals to varying degrees, poison certain types of catalysts and give off SO_2 during combustion. Thus desulfurization during liquefaction is desirable. Sulfur is thought to occur as thiophenes and aryl sulfides within the coal structure.[10] Much data has been generated on the enhancement effects of hydrogen donor solvents during liquefaction; however, one such compound, tetralin, has been shown to be ineffective as a reducing agent for aryl sulfides at liquefaction temperatures.[11,12]

Results and Discussion

Diphenyl sulfide is cleaved at 450 °C in the presence of formic acid to form benzene, toluene, benzoic acid, and thiophenol. The molar ratio of formic acid to diphenyl sulfide directly influences the conversion as illustrated in the data of Table I. Product analyses demonstrates desulfurization is occurring during the reaction. The conversion of diphenyl sulfide into products is increased with increasing temperature by using formic acid (cf. Table II). At lower temperatures, diphenyl sulfide does not react. For example, it is not converted into products when refluxed in formic acid for 24 h at 120 °C. The conversion of diphenyl sulfide caused by formic acid increases with reaction time (cf. Figure 1). By way of comparison, the 5-min reaction of diphenyl sulfide with formic acid gives a larger conversion than tetralin induces at 450 °C for 30 min, i.e., 10.7% conversion into benzene.[12] The results of Table III show, with the exception of dibenzothiophene, that the sulfur compounds of the eight compounds tested are converted in significant yields into products when formic acid is used. The corresponding pyrolysis reactions show no significant conversion of any of these compounds. Formic acid induced products of diphenyl sulfide are interesting since a mechanistic understanding of their formation may answer pertinent questions on the desulfurization of aryl–sulfur compounds.

Table I. Formic Acid Concentration Effect on the Conversion of Diphenyl Sulfide[a-c]

mole ratio of formic acid/ Ph_2S	conversion,[d] %	major products (moles × 10^4)
2:1	15	PhH (5.2), PhSH (2.7)
9:1	57	PhH (18.4), $PhCH_3$ (1.0), PhSH (4.0), PhCOOH (2.9)
18:1	77	PhH (22.1), $PhCH_3$ (2.8), PhSH (2.4), PhCOOH (6.3)

[a] The reactions were run at 450 °C for 32 min with the starting amount of diphenyl sulfide being 23.8 × 10^{-4} mol. [b] All reactions were duplicated within 4%. [c] In each reaction thioanisole formed as a minor product but was less than 1 × 10^{-4} mol. [d] The conversion percentage for this and subsequent tables is defined as equal to 100 × (1 − amount of recovered starting material/initial amount of starting material).

Table II. Effect of Temperature on the Conversion of Diphenyl Sulfide[a-c]

temp, C	conversion, %	major products (moles × 10^4)
250	5	PhH (0.4)
300	12	PhH (2.0), PhCOOH (2.1)
350	18	PhH (5.0), PhCOOH (4.4)
400	39	PhH (12.0), $PhCH_3$ (1.8), PhSH (1.2), PhCOOH (9.6)
450	77	PhH (22.1), $PhCH_3$ (2.8), PhSH (2.4), PhCOOH (6.3)

[a] The molar ratio of formic acid to diphenyl sulfide was 18:1; the reactions were run for 32 min. [b] All reactions were duplicated within 4%. [c] Starting amount of diphenyl sulfide was 23.8 × 10^{-4} mol, and in all reactions except that at 250 °C, thioanisole was formed in amounts less than 1 × 10^{-4} mol.

Of all the compounds in Table III, only diphenyl sulfide and thioanisole yielded carboxylation products when treated with formic acid. Thiophenol was more reactive than diphenyl sulfide and thioanisole. In these three cases,

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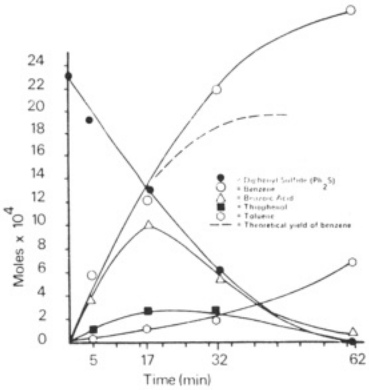


Figure 1. Time dependence of the diphenyl sulfide–formic acid reaction.

Table III. Survey of the Formic Acid Induced Conversions of Model Compounds into Products[a, b]

compd	% conversion formic acid	 thermal
diphenyl sulfide	100	4
thioanisole	99	38
benzothiophene	83	
dibenzothiophene	5	
N,N-dimethylaniline	46	16
diphenyl ether	4	
diphenyl methane	5	
bibenzyl	76	30

[a] The molar ratio of formic acid to the compounds was 18:1 except for dibenzothiophene (36:1); reactions were run at 450 °C for 62 min. [b] All reactions were duplicated within 4%.

the carboxylation product was benzoic acid. Formic acid is thermally unstable: completely decomposes in 5 min at 450 °C and in 17 min at 300 °C, 46% decomposed in 17 min at 250 °C, and 15% decomposed in 32 min and 200 °C. Since formic acid decomposes in 5 min under these conditions and benzoic acid formation continues beyond this time period, the decomposition products of formic acid are responsible for the continuing reaction (Figure 1).

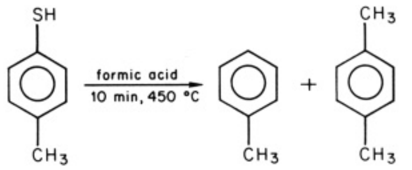
Candidates for the source of the carboxyl group on the product, benzoic acid, are CO and CO$_2$ and for the phenyl group are the phenyl radical and the thiophenol (thiyl) radical. To ascertain the precursors to benzoic acid, we treated diphenyl sulfide with CO (reaction 1) and CO$_2$ (reaction 2), with the rest of the conditions being identical.

$$\mathrm{Ph_2S} \xrightarrow[\text{32 min, 450 °C}]{\mathrm{CO/H_2/H_2O}} \underset{50\%}{\mathrm{PhH}} + \underset{1\%}{\mathrm{PhCH_3}} + \underset{45\%}{\mathrm{PhSH}} + \underset{46\%}{\mathrm{PhCOOH}} \tag{1}$$

$$\mathrm{Ph_2S} \xrightarrow[\text{32 min, 450 °C}]{\mathrm{CO_2/H_2/H_2O}} \underset{113\%}{\mathrm{PhH}} + \underset{30\%}{\mathrm{PhSH}} \tag{2}$$

The quantities are given in mole percent, based on recovered starting material. The conclusion from these two experiments is that CO and not CO$_2$ is a precursor to benzoic acid, and, most probably in the formic acid reactions, the species responsible for benzoic acid formation is CO.

The ipso position on the aromatic ring is where methylation to form toluene and carboxylation to benzoic acid occur. This was determined by treating *p*-thiocresol in accordance with reactions 3 and 4. In reaction 4, the



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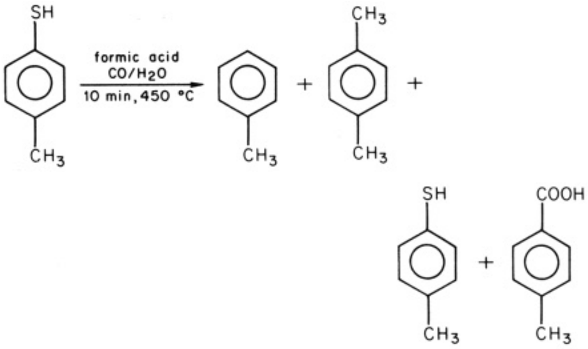

(4)

formic acid to *p*-thiocresol molar ratio (1:2) was lowered from that of reaction 3 (1:18), and CO–H$_2$O was added to enhance *p*-toluic acid formation. The yield of benzoic acid appears to be influenced by the presence of water; cf. reactions 5 and 6.

$$\mathrm{PhSH} \xrightarrow[\text{32 min, 450 °C}]{\mathrm{CO/H_2O}} \underset{57\%}{\mathrm{PhH}} + \underset{2\%}{\mathrm{PhCH_3}} + \underset{15\%}{\mathrm{PhCOOH}} + \underset{15\%}{\mathrm{Ph_2S}} \tag{5}$$

$$\mathrm{PhSH} \xrightarrow[\text{32 min, 450 °C}]{\mathrm{CO}} \underset{31\%}{\mathrm{PhH}} + \underset{3\%}{\mathrm{PhCH_3}} + \underset{2\%}{\mathrm{PhCOOH}} + \underset{3\%}{\mathrm{Ph_2S}} \tag{6}$$

Either phenyl or thiyl radicals, both of which are anticipated decomposition products of diphenyl sulfide, could be the aromatic precursor to benzoic acid and toluene. The most likely candidate would be the thiyl radical since only the aryl sulfides of the compounds tested in Table III gave benzoic acid. Further, the thiyl radical is easily generated[13-15] and has greater stability than the phenyl radical. The thiyl radical is long-lived enough to be detected by UV absorption and ESR spectroscopy.[14] As an analogy to the present reaction, aliphatic sulfur radicals react with free CO followed by removal of sulfur.[16] Holmquist[17] has reported that thioesters (RCOSR) are formed by the reaction of aromatic and aliphatic thiols with CO in the presence of metal carbonyls. Also, CO reacts with thiophenol in the presence of metal carbonyls to form benzoic acid. Since the latter reaction is carried out in the absence of water with good yields of benzoic acid, this reaction must be dependent on the metal carbonyl and not free CO. In confirmation, benzoic acid did not form in the absence of a metal carbonyl. The data reported herein are consistent with the thiyl radical (PhS·) reacting with CO. To evaluate

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Table IV. Comparison of Theoretical and Experimental Yields of Benzene in Formic Acid-Diphenyl Sulfide, Time vs. Conversions[a, b]

time, min	yield, mol × 10^4 experimental	yield, mol × 10^4 theoretical
0	0	0
5	6.4	6.0
17	11.4	12.7
32	22.1	18.2

[a] Theoretical yield calculated from the first-order rate constant for loss of diphenyl sulfide up to 32 min.
[b] Theoretical yield of PhH = starting moles of diphenyl sulfide × $(1 - e^{-kt})$ at anytime t.

PhS· as a precursor for benzoic acid, diphenyl disulfide was pyrolyzed at a temperature of 350 °C in tetralin and with CO–H_2O (reactions 7 and 8). The pyrolysis of diphenyl

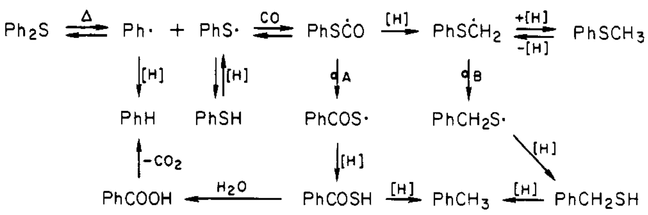
$$Ph_2S_2 \xrightarrow[32\ \text{min},\ 350\ °\text{C}]{\text{tetralin}} PhH\ (0.4\%) \qquad (7)$$

$$Ph_2S_2 \xrightarrow[32\ \text{min},\ 350\ °\text{C}]{CO/H_2O} PhCOOH\ (6\%) \qquad (8)$$

disulfide is known to generate the desired thiyl radicals.[13-15] The benzene yield of reaction 7 represents the maximum amount of thermally generated phenyl radicals, and tetralin is used to quench the radicals by hydrogen atom donation. The benzoic acid yield of reaction 8 exceeds the benzene yield of reaction 7 by 15 times. This indicates that the phenyl radical is not responsible for benzoic acid formation.

Kinetic data from Table IV and Figure 1 give the best evidence that PhS· is the precursor of benzoic acid and toluene. The first-order rate constant for loss of diphenyl sulfide in the presence of formic acid was calculated during the time period of 0–32 min to be $k_{Ph_2S} = 0.045\ \text{min}^{-1}$. This rate constant was then used to calculate the theoretical yields of benzene at 5, 17, and 32 min, as shown in Table IV. The theoretical curve for benzene formation approximates the experimental curve quite well up to 17 min (Figure 1). After 17 min, the theoretical curve falls short of the experimental curve. At this point, the rate of benzoic acid decarboxylation becomes significant, which changes the kinetics for benzene formation. Therefore, in the initial stages of the reaction, the loss of diphenyl sulfide and formation of benzene are essentially equal in rate. This implies that one phenyl-ring portion of the reacted diphenyl sulfide forms benzene and that the second goes to make benzoic acid, thiophenol, toluene, and trace amounts of thioanisole. The stoichiometry illustrated in Table II augments this conclusion. Since the benzoic acid yield approximates the benzene yield up to 400 °C (Table II) and during the initial stages of the 450 °C reaction (Figure 1), it is efficiently formed from its precursor, PhS·. Furthermore, the benzoic acid yield is proportional to that of thiophenol which indicates that the two are formed from a common precursor.

Scheme I



Since conversion of diphenyl sulfide continues after formic acid has decomposed, reactions were run with the formic acid decomposition products (CO, H_2O, CO_2, and H_2) in the ratio which formic acid gives at this temperature. On comparison of reactions 10 and 11 in Table V, formic acid is more effective than the gas mixture at reducing diphenyl sulfide. However, when the radical initiator dibenzoyl peroxide is added to the CO, H_2O, CO_2, and H_2 gas mixture (reaction 12), diphenyl sulfide conversion is enhanced compared to that of reaction 11. For surface effects, diphenyl sulfide was treated with formic acid in both stainless-steel and in sealed Pyrex glass liners (cf. reactions 10 and 13 of Table V). There is a dramatic surface effect on the diphenyl sulfide conversion. When dibenzoyl peroxide is added to the reaction mixture in Pyrex (reaction 14), the conversion is enhanced from that of reaction 13 and approaches the conversions obtained by using CO, H_2O, CO_2, and H_2 with dibenzoyl peroxide (reaction 12) but does not reach the conversion level attained with formic acid in stainless steel (reaction 10). The conversion of diphenyl sulfide with formic acid in the glass liner is increased with time (cf. reaction 15, Table V).

In conclusion, the data presented is consistent with the mechanistic picture outlined in Scheme I. Steps A and B are analogous to the 1,2-rearrangement of the oxygen analogue.[18] Further support of step B is given in reaction 9 whereby thermolysis of thioanisole gives toluene as the

$$PhSCH_3 \xrightarrow[450\ °\text{C},\ 62\ \text{min}]{H_2O} \underset{9\%}{PhH} + \underset{32\%}{PhCH_3} + \underset{23\%}{PhSH} + \underset{16\%}{Ph_2S} \qquad (9)$$

major product. Thiobenzoic acid is not isolated because it is thermally unstable at these temperatures and yields toluene as a product. Evidence that benzoic acid and toluene formation is independent of stainless-steel or Pyrex glass surfaces is found in reaction 15 (Table V). The water requirement for benzoic acid formation is accounted for in Scheme I.

Experimental Section

Batch Autoclave Reactions. All the reactions were done until

Table V. Influence on Diphenyl Sulfide Conversion: Radical Initiators and Surface Effects[a]

reaction	conditions	yield,[c] mol × 10^4 PhH	$PhCH_3$	PhSH	PhCOOH	Ph_2S	conversion, %
10	formic acid	22.1	2.8	2.4	6.3	5.4	77
11	$CO/H_2O/CO_2/H_2$	4.0	0.1	2.6	3.3	16.8	29
12	$CO/H_2O/CO_2/H_2$, dibenzoyl peroxide	NA	NA	3.8	NA	12.4	48
13[b]	formic acid	1.6		1.4		20.0	16
14[b]	formic acid, dibenzoyl peroxide	NA	NA	4.0	NA	14.3	40
15[b]	formic acid; 4 h, 2 min	14.9	0.8	5.2	4.7	6.8	71

[a] The molar ratio formic acid to diphenyl sulfide was 18:1; the reactions were run in a 12-mL stainless-steel autoclave at 450 °C for 32 min unless otherwise noted. The amount of diphenyl sulfide charged was 23.8 × 10^{-4} mol. [b] Reactions were carried out in sealed Pyrex glass liners which fit into the 12-mL stainless-steel autoclaves. [c] NA = not available.

duplication of results was obtained. Mass recoveries of all reactions varied from 85% to 100%. Microautoclaves[19] composed of 316 stainless-steel (12-mL volume) were used. Pyrex glass liners (5-mL volume) were made (0.9 cm × 11.5 cm) to fit into the 12-mL microautoclave reactor tubes. The reaction times and temperatures were varied, but the heat-up time was maintained at 2 min and the cool-down time at 30 s, respectively. At the end of the reactions, gases were vented while the microautoclaves were maintained at dry ice/acetone temperature to ensure minimal loss of volatile liquid products. The workup involved addition of an internal standard and the solvent diethyl ether. The internal standard used most frequently was 1-bromonaphthalene while *n*-decanol was used for the bibenzyl reactions. Between reactions the reactor tubes were cleaned with soapy water, rinsed with distilled water, treated with concentrated nitric acid for 30–60 min, brushed with steel wool, and finally rinsed with acetone.

Product analyses for the microautoclave reactions were done by gas–liquid chromatography with Aerograph Autoprep 700 (Varian) and Varian 2100 instruments. The following column materials were used: 5% OV-17 on 80/100-mesh Chromosorb W (0.25 in. × 6 ft) and 3% OV-17 on Suplecoport A (0.25 in. × 6 ft). The following compounds were identified as indicated. Benzoic acid: GLC retention time; mass spectrum (70 eV), *m/e* (relative intensity) 122 (94), 105 (100), 78 (10), 77 (61), 74 (7), 51 (35), 50 (21), 39 (12), which compares favorably with data for authentic benzoic acid. Toluic acid: GLPC retention time; mp 179–179.5 °C (lit.[20] mp 182 °C); mmp 178–179.5 °C. *p*-Xylene: GLPC retention time; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 6 H), 6.94 (s, 4 H); IR (neat) 2941, 2857, 1887, 1786, 1639, 1492, 1428, 1389, 1205, 1111, 1020, 775 cm^{-1}; these data compare favorably to the NMR and IR of authentic *p*-xylene.

Gas analyses were done at the University of North Dakota Engineering Experimental Station. Analyses were carried out on a Hewlett-Packard F&M Scientific 700 laboratory chromatograph fitted with a fixed-volume gas sample injection loop.

Molar Ratios. For reaction 1, the molar ratio was 1:9:9:9 diphenyl sulfide/$CO/H_2/H_2O$. The rest were as follows: reaction 2, diphenyl sulfide/$CO_2/H_2/H_2O$, 1:9:9:9; reaction 3, *p*-thiocresol/formic acid, 1:18; reaction 4, *p*-thiocresol/formic acid/CO/H_2O, 1:2:3.8:1.5; reaction 5, thiophenol/CO/H_2O, 1:18:18; reaction 6, thiophenol/CO, 1:18; reaction 7, diphenyl disulfide/tetralin, 1:9; reaction 8, diphenyl disulfide/CO/H_2O, 1:18:18.

Gas Analyses. The composition of the products formed on heating formic acid for 5 min at 450 °C in a stainless-steel microautoclave were as follows: CO, 37.5%; H_2, 12.5%; CO_2, 12.5%; the balance being water.

CO, H_2O, CO_2, and H_2 Reactions (Reactions 11 and 12, Table V). The percentages of CO, H_2O, CO_2, and H_2 were the same as those given by the thermal decomposition of formic acid at 5 min and 450 °C. The overall molar ratio of the gas mixture to diphenyl sulfide was 18:1.

Dibenzoyl Peroxide and Diphenyl Sulfide Reactions. The molar ratio of dibenzoyl peroxide to diphenyl sulfide was 1:1.

Formic Acid, Temperature and Time Decomposition. The extent of formic acid decomposition was obtained by titration with a potassium phthalate standardized NaOH solution. Phenolphthalein was used as the indicator.

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Registry No. Diphenyl sulfide, 139-66-2; formic acid, 64-18-6; thioanisole, 100-68-5; benzothiophene, 95-15-8; dibenzothiophene, 132-65-0; *N,N*-dimethylaniline, 121-69-7; diphenyl ether, 101-84-8; diphenylmethane, 101-81-5; bibenzyl, 103-29-7.

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Structure of Altertoxin I, a Mycotoxin from *Alternaria*

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The structure of altertoxin I, a mycotoxin produced by *Alternaria* molds, was established by ^{1}H, two-dimensional, *J*-resolved and ^{13}C polarization transfer NMR spectroscopy. This compound was found to be an unusual perylene derivative, 1,2,7,8,12b-pentahydro-1,4,6b,10-tetrahydroxyperylene-3,9-dione. Decomposition products of this material were tentatively identified by mass spectrometry as mono- and didehydration products.

The *Alternaria* are a group of molds that cause numerous plant diseases and are responsible for significant amounts of food spoilage. They produce a wide array of secondary metabolites, including many with toxic properties.[3] One metabolite, altertoxin I, $C_{20}H_{16}O_6$ (ATX-I), has been reported as toxic to bacteria, HeLa cells, and mice,[4] as well as being mutagenic by the Ames test.[5] In this paper we present the characterization of altertoxin I, **1**, a novel perylene metabolite.

Perylenes previously have been reported as fungal metabolites. *Daldinia concentrica*, a mushroom parasitic on ash trees,[6] and *Bulgaria inquinans* (Fries), a fungus on oak bark,[7] have been reported to produce 4,9-dihydroxyperylene-3,10-quinone, **2**.

Aspergilline, the black pigment of *Aspergillus niger* spores, also contains **2** as a peptide conjugate.[8]

Elsinochromes A, B, and C, **3**, which also contain the perylene quinone system, are produced by the *Elsinoe*, a fungal genus parasitic on leaves and stems of angiosperms.[9]

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