J. Org. Chem. 1984, *49*, 1228–1230

Pyrolysis of Organic Compounds. 1. Flash Vacuum Pyrolysis (FVP) of Coal-Model Organo Sulfides and Their *S*-Oxides

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Received August 12, 1983

The primary pyrolysis reaction of sulfides, sulfoxides, and sulfones (**1–3**), in the gas phase at 500–900 °C, is homolytic cleavage of the $C-SO_n$ bond. The order of reactivity, sulfoxide >> sulfone > sulfide, is consistent with the relative stabilities of the radicals produced. At 900 °C a novel and synthetically useful rearrangement of dibenzothiophene 5-oxide (**3b**) to 1-hydroxydibenzothiophene (**5**) was observed.

The synthetic and mechanistic aspects of aliphatic sulfoxide and sulfone pyrolysis have been extensively studied.[1,2] Pyrolysis of these sulfoxides leads to alkenes and sulfenic acids (RSOH),[1,3a] while extrusion of sulfur dioxide (SO_2) from sulfones affords new C–C bonds.[2] Much less is known of the thermal chemistry of the sulfur oxides of diaryl sulfides and condensed thiophenes where analogous reactions cannot and/or are unlikely to occur. An understanding of these thermal chemical processes is also important as part of a general investigation of the chemical desulfurization of coal.[4]

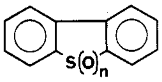
Organic sulfur accounts for between 30% and 70% of the total sulfur in coal. This organic sulfur is comprised of divalent sulfur functions such as sulfides, mercaptans, and condensed thiophenes.[5] The latter are reasonably assumed to be the most refractory sulfur functions in coal. Many of the most effective coal desulfurization processes utilize a coal pyrolysis step under oxidative conditions where coal sulfoxides and coal sulfones are likely to be formed.[4]

$Ph-S(O)_nCH_2Ph$

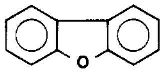
1

$Ph-(O)_nPh$

2



3



4

a, n = 0
b, n = 1
c, n = 2

Typical model compounds for organo sulfur functionalities in coal include phenyl benzyl sulfide (**1a**), diphenyl sulfide (**2a**), and dibenzothiophene (**3a**).[6] Diphenyl sulfide (**2a**) at 0.5–1 atm of pressure for 3–4 h at 525 °C has been reported to give benzene, H_2S, and dibenzothiophene (**3a**).[7] Under similar conditions diphenyl sulfoxide (**2b**) and sulfone (**2c**) gave benzene and SO_2.[7] In benzene over iron catalysts at 600–800 °C, both *p*-tolyl sulfide and sulfone gave *p,p'*-bitoly.[8] In a flow system, in the presence of toluene at 600 °C methyl benzyl sulfide ($PhCH_2SMe$) afforded methyl mercaptan, H_2S, and 1,2-diphenylethane.[9] While dibenzothiophene (**3a**), in a nitrogen flow system was stable to temperatures in excess of 900 °C,[10] dibenzothiophene 5,5-dioxide (**3c**), over Vycor chips at 690 °C and contact times of 15 s, gave a 6:1 mixture of dibenzofuran (**4**) and **3a**, in 95% yield.[11] The formation of an intermediate biphenylene sultine was recently shown

Table I. Flash Vacuum Pyrolysis (FVP) of Organo Sulfur Compounds 1-3

entry	compd	FVP temp, °C	products (% yield)
1	$PhSCH_2Ph$ (**1a**)	800	$PhCH_2CH_2Ph$ (53), PhSSPh (58), **1a** (28)
2		900[a]	$PhCH_2CH_2Ph$ (40), PhSSPh (32), **1a** (29)
3	$PhS(O)CH_2Ph$ (**1b**)	500	$PhCH_2CH_2Ph$ (74), $PhSO_2SPh$ (84)
4	$PhSO_2CH_2Ph$ (**1c**)	550	no reaction
5		800	$PhCH_2CH_2Ph$ (31), $PhCH_2Ph$ (28), Ph-Ph (6)
6	Ph-S-Ph (**2a**)	900	no reaction
7	PhS(O)Ph (**2b**)	700	$PhSO_2SPh$ (40), PhSSPh (12), PhPh (6), PhOH (4), **2a** (7), **2b** (11)
8		900[a]	$PhSO_2SPh$ (10), PhSSPh (12), Ph-Ph (12), PhOH (trace), **2a** (12)
9	$PhSO_2Ph$ (**2c**)	700	no reaction
10		900	Ph-Ph (10), **2c** (80)
11	**3a**	900	no reaction
12	**3b**	700	**4** (3), **5** (34), **3a** (21), **3b** (28)
13		900	**4** (6), **5** (55), **3a** (15), **3b** (trace)
14	**3c**	700	no reaction
15		900[b]	**4** (20), **3a** (3), **3c** (70)

[a] Considerable charring was noted. [b] Reference 12.

[†] Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining, WPAS-AA-75-05-05.

(1) For leading references on aliphatic sulfoxide pyrolysis see: Davis, F. A.; Friedman, A. J.; Nadir, U. K. *J. Am. Chem. Soc.* **1978**, *100*, 2844. Jones, N. D.; Hill, D. R.; Lewton, D. A.; Sheppard, C. *J. Chem. Soc. Perkin Trans. 1* **1977**, 1574.

(2) For a review of aliphatic sulfone pyrolysis see: Vogtle, F.; Rossa, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 515.

(3) (a) Davis, F. A.; Jenkins, Jr., R. H.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3467. (b) Franz, J. A.; Camaioni, D. M. *Ibid.* **1980**, *45*, 2928. (c) Trahanovsky, W. W.; Swenson, K. E. *Ibid.* **1981**, *46*, 2928.

(4) For general references on coal desulfurization prior to combustion see: (a) Eliot, R. C., Ed. "Coal Desulfurization Prior to Combustion"; Noyes Data Corporation: Park Ridge, NJ, 1978. (b) Meyers, R. A. "Coal Desulfurization"; Marcel Dekker: New York, 1977. (c) Whitehurst, D. D. *ACS Symp. Ser.* **1978**, *71*, 1. (d) Bunger, J. W.; Thomas, K. P.; Dorrence, S. M. *Fuel* **1979**, *58*, 183.

(5) Attar, A.; Dupuis, F. *Preps. Pap. Am. Chem. Soc., Div. Fuel Chem.* **1978**, *23*, 44.

0022-3263/84/1949-1228$01.50/0

by us to be involved in this transformation.[12]

The notable lack of a systematic study of the thermal chemistry of these sulfur functionalities has prompted this investigation.

Results and Discussion

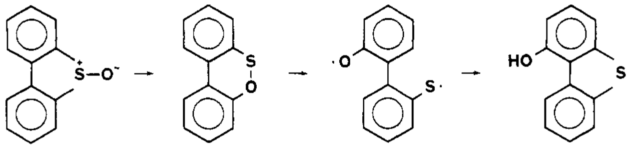
The flash vacuum pyrolysis (FVP) technique was employed to investigate the pyrolysis chemistry of coal-model sulfur compounds **1–3**. FVP simplifies complex pyrolysis reactions because of the manner in which the pyrolyses are carried out (gas phase) and the temperatures at which the products are collected (–196 °C).[13] The value of the FVP method in elucidating complex pyrolysis chemistry has been demonstrated by Davis et al. in the study of sulfenic acids (RSOH)[3a] and by Franz[3b] and Trahanovsky[3c] in studies of coal H-donor solvents.

The gas phase FVP of coal-model organosulfur compounds **1–3** is summarized in Table I. The minimum FVP temperature at which most of the substrate was consumed was determined by trial and error. Products were separated by preparative TLC and flash chromatography (silica gel) and were identified by gas chromatography by comparison with authentic materials.

Generally, the sulfides were the least reactive species. Diphenyl sulfide (**2a**) and dibenzothiophene (**3a**) were unreactive at FVP temperatures of 900 °C (entries 6 and 11); essentially all of the starting materials were recovered. Phenyl benzyl sulfide (**1a**) was somewhat more reactive giving, at 900 °C, 1,2-diphenylethane ($PhCH_2CH_2Ph$), diphenyl disulfide (PhSSPh), and starting material (28%) (entries 1 and 2).

Phenyl benzyl sulfoxide (**1b**), at 500 °C, gave $PhCH_2CH_2Ph$ and phenyl benzenethiosulfinate ($PhSO_2SPh$) as principal products. FVP of diphenyl sulfoxide (**2b**) at 700 °C afforded $PhSO_2SPh$ and PhSSPh as major products with minor amounts of biphenyl (Ph–Ph) (**2a**) and phenol (PhOH) (entry 7). When the temperature was raised to 900 °C considerable charring was noted and the principal products were **2a**, $PhSO_2SPh$, PhSSPh, and biphenyl (entry 8).

Unexpectedly, dibenzothiophene 5-oxide (**3b**) at 700 °C gave 1-hydroxydibenzothiophene (**5**) in 34% isolated yield in addition to dibenzothiophene (**3a**). The yield of **5** was increased to 55% at 900 °C (entries 12 and 13). 1-Hydroxydibenzothiophene (**5**) has previously been prepared from **3a** in seven steps (5 % overall yield)[14] and was identified by comparison of its infrared and NMR spectra with those of an authentic sample.



3b 6 5

Intermediate in reactivity are the sulfones. Phenyl benzyl sulfone (**1c**), diphenyl sulfone (**2c**), and dibenzothiophene 5,5-dioxide (**3c**) were unreactive in the temperature range 550–700 °C (entries 1, 9 and 7). At 700–800 °C **1c** gave bibenzyl, diphenylmethane, and biphenyl, while **2c** gave low yields of biphenyl (entries 5 and 10). Minor amounts of dibenzofuran (**4**) and dibenzothiophene (**3a**) were obtained on FVP of **3c** at 900 °C (entries 14 and 15).[11]

Under the FVP conditions the order of reactivity was sulfoxides (**1b–3b**) >> sulfones (**1c–3c**) > sulfides (**1a–3a**) (Table I). The $C–S(O)_n$ bond dissociation energies of organosulfur compounds decrease in the order: $R_2SO > R_2SO_2 > R_2S$.[15] Thus, the primary pyrolysis reactions of organosulfur compounds **1–3** can be interpreted in terms of an initial homolytic cleavage of a $C–S(O)_n$ bond (eq 1).

$$\mathrm{R{-}S(O)}n\mathrm{{-}R} \rightarrow \mathrm{R{-}SO}_n\cdot + \mathrm{R}\cdot \qquad (1)$$

The stability of the sulfinyl radical (RSO·) is undoubtedly responsible for the greater reactivity of sulfoxides compared to sulfones and sulfides.[16,17] Similarly, the higher reactivity of phenyl benzyl sulfide (**1a**) compared to **2a** and **3a** is consistent with the greater stability of benzyl vs. phenyl radicals.

Homolytic cleavage of the C–S bond in phenyl benzyl sulfide (**1a**) affords benzyl and phenyl thiyl radicals which recombine (eq 2 and 3) to give 1,2-diphenylethane and

$$2\mathrm{R}\cdot \rightarrow \mathrm{R{-}R} \qquad (2)$$

$$2\mathrm{RS}\cdot \rightarrow \mathrm{RS{-}SR} \qquad (3)$$

di-phenyl disulfide, respectively. The fact that 1,2-diphenylethane is a major product of the pyrolysis of **1c** suggests radical (eq 1) rather than concerted extrusion of SO_2 from sulfones **1c** and **2c**.

Phenylsulfinyl (PhSO·), benzyl, and aryl radicals are formed on pyrolysis of **1b** and **2b** as evidenced by the formation of $PhSO_2SPh$. The coupling of sulfinyl radicals, probably though sulfenyl sulfinates, has been described (eq 4).[13,16] The most likely source of phenol and diphenyl

$$2\mathrm{PhSO}\cdot \rightarrow [\mathrm{PhS(O){-}O{-}SPh}] \rightarrow \mathrm{PhSO_2SPh} \qquad (4)$$

disulfide observed in the pyrolysis of **2b** is via PhS and PhO radicals. A possible source of these radicals is from an intermediate sulfenate ester (PhS–O–Ph) formed, in the gas phase, from the sulfoxide (**2b**) (eq 5 and 6). The

$$\mathrm{Ph{-}S(O)Ph} \rightarrow \mathrm{Ph{-}S{-}O{-}Ph} \qquad (5)$$

$$\mathrm{Ph{-}S{-}O{-}Ph} \rightarrow \mathrm{Ph{-}S}\cdot + \mathrm{Ph{-}O}\cdot \qquad (6)$$

[2,3]-sigmatropic rearrangement of allylic sulfoxides to sulfenate esters is known,[18] and sulfenate intermediates have been proposed in the rearrangements of certain sulfoxides.[19]

In accord with this hypothesis is the rearrangement of dibenzothiophene 5-oxide (**3b**) to 1-hydroxydibenzothiophene (**5**). Homolytic cleavage of the weak S–O bond in sulfenate ester (sultene) **6** affords arylthiyl (ArS·) and aryloxy (ArO·) radicals. The more aromatic dibenzothiophene (**3a**) is formed in preference to dibenzofuran (**4**) by combination of the arylthiyl radical with the adjacent aromatic ring. The involvement of sulfinate esters (**6**)

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(6) (a) LaCount, R. B.; Friedman, S. *J. Org. Chem.* **1977**, *42*, 2751. (b) Van Buren, R. L.; Baltixberger, R. J.; Woolsey, N. F.; Senberg, V. I. *Ibid.* **1982**, *47*, 4107.

(7) Levy, A.; Ambrose, C. J. "Report 161498". *U.S. Dept. Com., Office Tech. Serv.* PB 1959; *Chem. Abstr.* **1961**, *55*, 27177d.

(8) Heldt, W. Z. *J. Org. Chem.* **1965**, *30*, 3897.

(9) Braye, E. H.; Sehon, A. H.; Darwent, B. DeB. *J. Am. Chem. Soc.* **1955**, *77*, 5282.

(10) Aitken, J.; Heeps, T.; Steedman, W. *Fuel* **1968**, *47*, 353.

(11) Fields, E. K.; Meyerson, S. *J. Am. Chem. Soc.* **1966**, *88*, 2836.

(12) Squires, T. G.; Venier, C. G.; Hodgson, B. A.; Chang, L. W.; Davis, F. A.; Panunto, T. W. *J. Org. Chem.* **1981**, *46*, 2373.

(13) For a recent monograph on the FVP technique see: Brown R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980.

(14) Gronowitz, S.; Hersoloff, M.; Svenson, R.; Bondesson, G.; Magnusson, O.; Stjernostrom, E. E. *Acta Pharm. Suec.* **1978**, *15*, 337.

(15) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(16) Koeliwijn, P.; Berger, H. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1275.

(17) Davis, F. A.; Awad, S. B.; Jenkins, Jr., R. H.; Billmers, R. L.; Jenkins, L. A. *J. Org. Chem.* **1983**, *48*, 3071.

(18) Bickart, P.; Carson, F. Q.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869.

(19) Numat, T.; Oae, S. *Int. J. Sulfur Chem. Part A* **1971**, *1*, 215.

(S═S(O)) in the thermal rearrangement of **3c** to dibenzofuran (4) has been described.[11]

Sulfides **2a** and **3a** are minor products of the FVP of sulfoxide **2b** and **3b** (Table I). At least three sources of these sulfides can be considered: (i) oxygen extrusion from a sulfenate ester intermediate, (ii) direct deoxygenation of the sulfoxide, and (iii) combination of arylthiyl and aryl radicals (eq 7).

$$R\cdot + RS\cdot \rightarrow R\text{–}S\text{–}R \qquad (7)$$

Oxygen extrusion from a sulfenate ester (R–S–O–R) seems unlikely because, in addition to oxygen extrusion, sulfur extrusion would also be expected. Diphenyl ether (Ph–O–Ph) was not detected in the FVP of sulfoxide **2b** and dibenzofuran (4) is a minor product of the FVP of **3b**. Furthermore, an increase in temperature actually gave more sulfide in the case of **2b** but less for **3b** where the sulfenate ester (**6**) must be in greater concentration.

On the basis of available evidence one cannot readily distinguish between direct deoxygenation of the sulfoxide and combination of arylthiyl and aryl radicals (eq 6). However, it should be noted that as the FVP temperature increased from 700 to 900 °C for sulfoxide **2b** both the yield of sulfide (**2a**) and biphenyl increased suggesting deoxygenations of a sulfinyl (PhSO·) radical. Deoxygenation of sulfenic acids (RSOH) and sulfinyl radicals has been proposed.[3a,17] Furthermore, dibenzothiophene (**3a**) observed in the FVP of dibenzothiophene 5,5-dioxide (**3c**) occurs not from the sulfone (**3c**) but rather from the intermediate sultine.[11] Extrusion of molecular oxygen from the sultine, possibly from a thioperoxide intermediate (RS–O–O·), was suggested.

Summary and Conclusions

The initial or primary reaction of organosulfur **1**–**3** under pyrolytic conditions, is homolytic cleavage of the $C{-}SO_n$ bond (eq 1). The order of reactivity was observed to be sulfoxide >> sulfone > sulfide as predicted on the basis of the relative stabilities of the radicals produced. These sulfur and carbon radicals combine regioselectivity to form new sulfur–sulfur and carbon–carbon bonds (eq 2 and 3, respectively).

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H spectra were measured on Varian A60-A and Joel FX 90Q NMR spectrometers. GS/MS data were obtained on a Finnigan 4000 GS/MS using a 6 ft × $^1/_4$ in., 3% OV-17 on Anakorm Q (90/100 mesh), glass column. Gas chromatographic analyses were performed on a Varian 3700 gas chromatograph (FID) with a 6 ft × $^1/_8$ in., 3 % OV-17 on Anakorm Q (90/100 mesh) column. The analyses were determined by comparison of peak areas with standard solutions of the reaction products. Analyses were performed at least twice and the results averaged. Solvents were commercial grade and used without additional purification. Compounds **1a**–**3a**, **1b**, **2b**, and **1c**–**3c** were purchased commercially (Aldrich & Parish Chem. Co.) and used unpurified. Dibenzothiophene 5-oxide (**3b**) was prepared by oxidation of **3a** using ceric ammonium nitrate and purified by flash chromatography on silica gel.[20]

General Flash Vacuum Pyrolysis (FVP) Procedure. FVP was carried out by vaporizing, at 80 °C, 100–150 mg samples of organo sulfur compounds **1**–**3** into a 1.5 × 20 cm quartz pyrolysis chamber at 10^{-2}–10^{-3} torr.[21] The pyrolyzate was collected on a cold finger cooled to −196 °C with liquid N_2. The temperature of the pyrolysis was monitored at the center of the pyrolysis chamber using a Barber-Coleman thermocouple, the accuracy of which is estimated to be ±10 °C. After completion of the FVP experiment the vacuum was disengaged and the system flushed with dry nitrogen gas. After warming to room temperature the products, which had collected on the cold finger, were washed into a receiver and separated by flash chromatography or preparative TLC. The products were analyzed by gas chromatography. The FVP experiments were performed at least twice and the results averaged (Table I).

1-Hydroxydibenzothiophene (5). FVP of dibenzothiophene 5-oxide (**3b**), 0.5 g (0.0025 mol), at 900 °C gave a dark solid on the cold finger condenser. After thawing the cold finger condenser, the deposited solid was dissolved in chloroform and treated once with decolorizing charcoal. After removing the solvent under vacuum the residue was purified by flash chromatography (Silica gel) eluting with 1:1 ether/*n*-pentane to give 0.28 g (55%) of a white solid, mp 141–142 °C (lit.[14] 142–143 °C), identified as **5** by comparison of its IR and NMR spectra with values recorded in the literature.[14]

Acknowledgment. This investigation was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining, WPAS-AA-75-05-05.

Registry No. **1a**, 831-91-4; **1b**, 833-82-9; **1c**, 3112-88-7; **2a**, 139-66-2; **2b**, 945-51-7; **2c**, 127-63-9; **3a**, 132-65-0; **3b**, 1013-23-6; **3c**, 1016-05-3.

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[20] Tse-Lok, H.; Wong, C. M. *Synthesis* **1972**, 561.

[21] For a description of the flash vacuum pyrolysis apparatus see ref 3a and the references cited therein.

Reactions of 3-Hydroxyvinyl Selenones with Alkoxides. Oxetane Formation and Fragmentation Reactions[1,2]

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Received August 24, 1983

3-Hydroxyvinyl phenyl selenones are prepared and their behavior as conjugate addition acceptors has been investigated. As a result, a selenonyl group has been found to activate the C═C bond for conjugate addition of nucleophiles and further to behave as an excellent leaving group. According to such characteristic features, acyclic 3-hydroxyvinyl selenones undergo an addition reaction of alkoxides followed by an internal substitution reaction with a 3-hydroxy group to give the corresponding 3-alkoxyoxetanes. On the other hand, cyclic ones afford the corresponding ring-opened product, alkoxyethylenic or acetylenic ketones, via an addition–fragmentation or a direct fragmentation reaction. Application of this addition–fragmentation process to an intramolecular system has also been described.

From numerous reports[3] it is known that vinyl sulfones are more reactive than vinyl sulfoxides toward conjugate addition of nucleophiles. By analogy, vinyl selenones are expected to be more efficient acceptors of nucleophiles

0022-3263/84/1949-1230$01.50/0