

## THE REACTION OF PYRITE WITH DIPHENYL ETHER

Peter A. S. Smith\*, Raphael M. Munavu and Scott R. Gilbertson

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

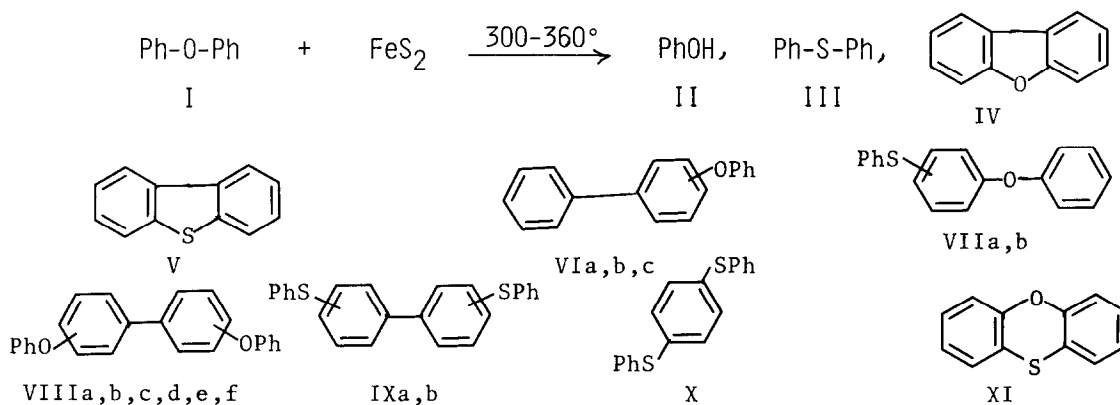
Summary: Diphenyl ether is converted into diphenyl sulfide (largely), dibenzofuran, phenoxybiphenyls, diphenoxybiphenyls, and several other sulfur-containing compounds by reaction with pyrite at 350-360°.

Pyrite,  $\text{FeS}_2$ , is present to some extent in virtually all coal. In the various processes for converting coal to liquid or gaseous fuels, pyrite has traditionally been treated as unreactive toward organic components, although it is reduced to pyrrhotite,  $\text{FeS}_{2-x}$ , in such processes.<sup>1,2</sup> Evidence has accumulated in recent years that pyrite promotes the liquefaction process and may have other catalytic effects.<sup>1,2,3</sup> The possibility that pyrite can be a reactant as well as a catalyst toward organic constituents has been recognized,<sup>2</sup> but it has not been explored. The fragmentary information in the literature is that, apart from catalytic effects, it reacts in unelucidated ways with some halogen and unsaturated compounds,<sup>4</sup> that it oxidizes ore flotation agents, such as xanthates,<sup>5</sup> and that it can be made to react with hot hydrocarbon gases,<sup>6</sup> such as acetylene, to produce thiophene and/or  $\text{CS}_2$ .

We have begun screening representative organic structures for reactivity toward pyrite. Some hydrocarbons, such as diphenylmethane and stilbene, are essentially inert up to temperatures at which they undergo spontaneous decomposition. Diphenyl ether (I), however, ordinarily an unusually stable substance, reacts with pyrite above 300° to give a variety of compounds, some of which contain sulfur. We report our preliminary experiments with it, for they demonstrate, we believe for the first time, the conversion of inorganic, pyritic sulfur to organic sulfur under conditions milder than those obtained in coal liquefaction processes.

Mixtures of pyrite with diphenyl ether, from which the dissolved oxygen had been removed by heating in nitrogen, were kept in sealed pyrex tubes at 360-360° for 20 to 86 h, in duplicate experiments. Both synthetic and ground mineral pyrite were used, with similar results. After cooling, the tubes were opened, and the brown organic material was separated from mineral matter by extraction with methylene chloride. The odor of hydrogen sulfide

was evident. The solutions were analyzed by interfaced GC/MS. The products were identified by matching retention times and mass spectra with those in the library bank of the instrument or with those of authentic samples, or by inference from the mass spectrum fragmentation patterns. Nineteen GC peaks of significant magnitude were obtained, all but two of which (both minor) corresponded to single compounds (II-IX). One of the lesser peaks appeared to be a mixture of dibenzothiophene (V) and phenoxathiin (XI) and one to a mixture of 2,2'-diphenoxybiphenyl (VIIIf) and 1,4-bis(phenylthio)-benzene (X). The major components are shown in Table I; benzene also appeared to be present, but was not determined. When diphenyl ether was heated by itself (360°, 60 h, under N<sub>2</sub>), it was recovered unchanged.



In contrast to our results, diphenyl ether has been previously reported<sup>7</sup> to withstand treatment with pyrite (in the form of a component of low-temperature coal ash) at 450° without detectable reaction. This may be due to the fact that tetralin was also present, and may have reduced the pyrite more rapidly than the latter could react with the diphenyl ether.

We consider the most significant feature of our results to be the fact that diphenyl sulfide (III) was the most abundant product (ca. 15 to 26% of the conversion) and that other sulfur-containing compounds made up an additional ca. 9.4 to 20% of the conversion mixture. This is direct evidence that pyrite is an active reagent toward organic compounds, and has the potential for increasing the organic sulfur content of coal under geologic conditions and of substances derived from coal by industrial processes. (Coal is known to contain aryl ether structures,<sup>1,8</sup> and it is believed that much of the organic sulfur is present in aryl sulfides and thiophenes.<sup>2</sup>)

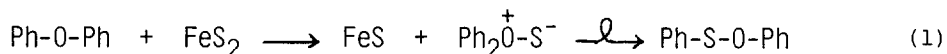
The nature of our products implies the intermediacy of radicals. These may be derived from initial transfer of sulfur to oxygen (Eq. 1).

Table I. Products from the Reaction of Diphenyl Ether with Pyrite.

	Compound	Mass No.	Expt.: I	Composition, <sup>a</sup> %			
				II	III	IV	V
II	Phenol	94	1.50	b	1.88	1.10	a
I	Diphenyl ether	170	78.8	96.7	87.39	92.69	97.0
IV	Dibenzofuran	168	1.69	0.30	0.73	0.66	0.20
III	Diphenyl Sulfide	186	4.05	0.50	3.48	1.57	0.48
VIa	2-Phenoxybiphenyl	246	0.18	0.07	0.07	0.07	0.04
VIIb	4-Phenoxybiphenyl	246	0.40	0.08	0.80	0.27	0.04
VIIc	3-Phenoxybiphenyl <sup>C</sup>	246	0.18	0.04	0.04	0.10	0.09
VIIa	1-Phenoxy-2-(phenylthio)benzene <sup>C</sup>	278	0.76	0.10	1.04	0.25	0.21
VIIb	1-Phenoxy-4-(phenylthio)benzene <sup>C</sup>	278	0.76	0.10	1.04	0.25	0.21
VIIIa	2,3'-Diphenoxybiphenyl <sup>C</sup>	338	2.38	0.45	0.76	0.66	0.31
VIIIb	2,4'-Diphenoxybiphenyl <sup>C</sup>	338	0.62	0.16	0.25	0.25	0.13
VIIIc	3,3'-Diphenoxybiphenyl <sup>C</sup>	338	3.60	0.66	0.86	1.24	0.48
VIIIId	3,4'-Diphenoxybiphenyl <sup>C</sup>	338	2.76	0.55	0.72	0.83	0.37
VIIIe	4,4'-Diphenoxybiphenyl	338	0.26	0.08	0.11	0.07	0.07
IXa	2,2'-Bis(phenylthio)biphenyl <sup>C</sup>	370	0.12	trace	0.18	0.04	0.03
IXb	2,4'-Bis(phenylthio)biphenyl <sup>C</sup>	370	0.15	trace	0.13	0.09	0.03

Conditions: I, 115 mg Ph<sub>2</sub>O, 161 mg FeS<sub>2</sub>, 350°, 40 h; II, 115 mg Ph<sub>2</sub>O, 50 mg FeS<sub>2</sub>, 350°, 40 h; III, 1.50 g Ph<sub>2</sub>O, 2.0 g FeS<sub>2</sub>, 360°, 86 h; IV, 298 mg Ph<sub>2</sub>O, 108 mg FeS<sub>2</sub>, 350°, 20 h; V, 50 mg Ph<sub>2</sub>O, 30 mg FeS<sub>2</sub>, 350°, 300 h.

Footnotes: <sup>a</sup>Uncorrected for differences in the GC response proportionality constants. <sup>b</sup>Not determined. <sup>c</sup>Identity deduced from MS fragmentation and GC retention times in comparison with isomeric model compounds, such as VIa and VIIIe.



Rearrangement of the resulting ylide, analogous to the Stevens rearrangement, would give phenyl benzenesulfenate (XII). Such a reaction is "forbidden" as a concerted process, but could take place by migration of a phenyl radical, either in the coordination sphere of the iron from which the sulfur came, or in a solvent cage. The solvent in our experiments is also the substrate; its interception of a portion of the radicals could readily lead to the higher ethers that were formed. The sulfenate could be a source of PhO· and PhS· radicals by homolysis, and might be the source of diphenyl sulfide by rearrangement to diphenyl sulfoxide and subsequent deoxygenation by the several oxygenophiles present (Eq. 2). Allylic and benzylic sulfenates rearrange to



sulfoxides under mild conditions;<sup>9</sup> it is not unreasonable to suppose that an aryl sulfenyl would do so at 350°.

Diphenyl sulfide has been reported<sup>10</sup> as the product from heating diphenyl ether with elemental sulfur, but since no other products besides black resin were reported, comparison with our results is not possible. However, the possibility that the products from our experiments might have arisen from initial decomposition of pyrite into sulfur and FeS is inconsistent with the fact that pyrite by itself is stable<sup>2,11</sup> up to 470°. It may nevertheless be true that the reactions of sulfur and pyrite have in common the initial step of transfer of a sulfur atom to the ether oxygen.

Acknowledgment. This work was supported in part by the U.S. Department of Energy Grant No. DE-FG02-80ER10125. One of us (R.M.M.) expresses gratitude for a Fulbright-Hayes grant to spend a leave from the University of Nairobi at the University of Michigan. The Finnigan mass spectrometer used in this work was bought with funds provided by the United States National Science Foundation.

#### References

1. (a) J. G. Speight, "The Chemistry and Technology of Coal," Marcel Dekker, Inc., New York, 1983, Chapter 10. (b) J. W. Larsen, "Organic Chemistry of Coal," ACS Symposium Series 71, Am. Chem. Soc., Washington, 1978.
2. A. Attar, Fuel, 57, 201 (1978).
3. R. M. Davidson, "Mineral Effects in Coal Conversion," IEA Coal Research, London, 1983.
4. R. de Fazi and A. Hemmeler, Atti Acad. Lincei, 12, 583 (1930).
5. L. A. Goold, Nat. Inst. Met., Repub. S. Africa, Rep. No. 1439 (1979); N. I. Elizeev, et al., Izv. Vyssh. Uchobn. Zaved., Tsvetn. Metall., 6, 14 (1977) [C.A., 88, 77074 (1978)].
6. W. Steinkopf and J. Harold, Liebigs Ann. Chem., 428, 123 (1922).
7. Y. Kamiya, S. Nagae, and S. Oikawa, Fuel, 62, 30 (1983).
8. A. Attar and G. G. Hendrickson, in "Coal Structure," R. A. Meyers, Ed., Academic Press, New York, 1982, Chapter 5.
9. D. A. Evans and G. C. Andrews, Acc. Chem. Res., 7, 147 (1974).
10. E. Kuhl, Synthesis, 617 (1971).
11. E. Krafft and O. Steiner, Ber. Dtsch. Chem. Ges., 34, 561 (1901).
12. R. Cypres, M. Ghodsi and R. Stocq, Fuel, 60, 247 (1981).

(Received in USA 24 April 1984)