

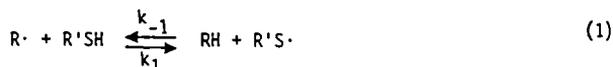
REACTIONS OF THE THIOPHENOXY RADICAL FROM THE
THERMAL AND PHOTOLYTIC DECOMPOSITION OF PHENYLDISULFIDE

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INTRODUCTION

The importance of sulfur-containing constituents or additives on the thermal degradation of coal has been recognized by many investigators.^{1a-d} Stock and co-workers^{1a,c} in a study of the hydrogen atom transfer reactions of tetralin-d₁₂ with coal, diphenylmethane, and other coal model-compounds have shown that sources of thiol radicals such as benzylphenylsulfide significantly accelerate the rate of hydrogen shuttling between benzylic positions of model structures. Studies of deuterium exchange between deuterated donors and coals^{2a} suggest that a higher sulfur content is correlated with a more rapid exchange of benzylic hydrogen with the deuterated donor. Activation barriers for abstraction of hydrogen atoms from thiols



(k_1) are less than a few kcal/mole, with the result that the reverse reaction, abstraction from hydrocarbons by thiol radical (k_{-1}) is very rapid, being limited only by ΔH^0 of the reaction. For example, for R = benzyl and R' = phenyl in (eqn. 1) $\log (k_1/M^{-1}s^{-1}) = (8.27 \pm 0.07) - (3.79 \pm 0.12)/\theta$, $\theta = 2.3RT$ kcal/mole.^{2b} For $\Delta H^0 = -6.5$ kcal/mole,^{2c} $\log (k_{-1}/M^{-1}s^{-1}) = (8.5 \pm 0.5) - (10 \pm 2)/\theta$. Thus, at coal liquefaction temperatures (450°C), k_1 is about $10^7 M^{-1}s^{-1}$ and k_{-1} is $3 \times 10^5 M^{-1}s^{-1}$, resulting in very rapid equilibration of hydrogen between benzylic sites. Rapid, reversible abstraction reactions of sulfur-centered radicals are well documented.³⁻⁸ Hydrogen sulfide, pyrite, elemental sulfur, and organic disulfides have been suggested to play significant roles in promoting the liquefaction of various coals.^{1,9-12} Displacement of aromatic substituents and dehydrogenation of hydroaromatic hydrocarbons facilitated by sulfur-centered radicals in reactions with sulfur and disulfides have been extensively studied.¹³⁻¹⁵

The rapid, reversible reactions of addition of sulfur-centered radicals to aromatic rings and readily reversible abstraction reactions (eqn.1) dominate mechanisms of structural evolution during liquefaction, by virtue of the weak S-S bond strengths of disulfides (54 kcal/mol for PhSSPh)¹⁶ which assure that



the sulfur-centered radicals are present in significant concentrations throughout the coal liquefaction process for any sulfur-containing coal. Although it is well known that sulfur-sulfur bonds in alkyl and aryl disulfides and sulfides readily undergo photolytic or thermal homolysis, and many studies¹⁷⁻²¹ have been devoted to the reactions of thiyl radicals with organic substrates, mechanistic aspects of the incorporation of sulfur into aromatic structure are perhaps less well developed, and detailed pathways of carbon-carbon and carbon-sulfur bond cleavage and formation reactions in the context of the thermal evolution of coal structure during liquefaction are lacking.

Thus, we present preliminary results of high-temperature reactions of phenyldisulfide and benzylphenyl sulfide with organic substrates (9,10-dihydroanthracene, diphenylmethane, bibenzyl, stilbene, and diphenylacetylene) which demonstrate mechanisms for the enhanced cleavage of $\text{sp}^2\text{-sp}^2$, $\text{sp}^2\text{-sp}^3$, and $\text{sp}^3\text{-sp}^3$ bonds mediated by thiophenoxy radical, and a series of addition-elimination, abstraction and rearrangement reactions leading to a series of thiophenes and related structures.

EXPERIMENTAL

General. NMR spectra were obtained with Varian FT-80 or Bruker AM-300 systems. Gas chromatography was performed with a Hewlett-Packard HP5890A instrument equipped with a 25-m, 0.32-mm i.d. J&W Scientific DB-5 capillary column. GC-mass spectrometry was performed with HP-5970 or HP-5992 systems. Products were identified by gc coinjection and comparison of mass spectra of authentic standards.

General Procedure for Thermolysis Reactions. In a typical reaction 0.05-0.10 mmole of phenyldisulfide or benzylphenylsulfide and an appropriate amount of

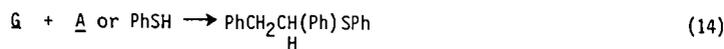
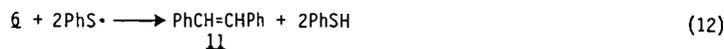
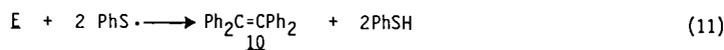
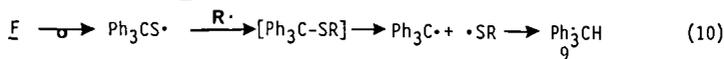
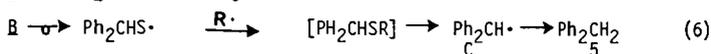
the desired additive were mixed in quartz tubes, freeze-thaw degassed, and sealed. The tubes were heated in a fluidized sand bath at $400 \pm 5^\circ\text{C}$ for 30 min., cooled to room temp, opened under nitrogen, and transferred to a degassed methylene chloride solution containing naphthalene as an internal gc standard.

Thermolysis of Model Compounds in the Presence of Phenyldisulfide or Benzylphenylsulfide. Thermal decomposition of neat PhSSPh at 400°C produced the following products; thiophenol (1), diphenylsulfide (2), and thianthrene (3). Decomposition of neat benzylphenylsulfide produced the following products: toluene (4), 1, diphenylmethane (5), bibenzyl (6), 2, phenyldisulfide (7), 3, 2-phenylbenzothiophene (8), triphenylmethane (9) and tetraphenylethylene (10). The reactions of PhSSPh with additives are presented below, followed by major products in parentheses: PhSSPh + dihydroanthracene (1, 2, and anthracene); PhSSPh + diphenylmethane (1, 2, 4, 9 and 10); PhSSPh + bibenzyl (1, 2, 4, trans-stilbene (11), 8, 2,3-diphenylbenzothiophene (12), and 1,2,3,4-tetraphenylthiophene (13)); PhSSPh + trans-stilbene (1, 2, 4, 5, 8, 12, and 13); and PhSSPh + diphenylacetylene (1, 2, 4, 8, 12, and 13). The products listed accounted for typically 80% or more based on unrecovered starting material, with individual products varying from 5-10% to as high as 50%.

Preparation of 2,3-Diphenylbenzothiophene. Phenyldisulfide (0.50 mmol) and diphenylacetylene (0.50 mmol) were placed in a quartz tube, freeze-thaw degassed, and heated at 400°C for 30 min. The reaction mixture was transferred to hexane/ether solution (97/3 (v/v)) followed by flash liquid chromatography through a short silica column. Several fractions were taken for GC analysis. The fraction containing most of the product was concentrated. The residue was recrystallized from hexane to give 30% yield of 2,3-diphenylbenzothiophene:m.p. $114-115^\circ\text{C}$ (lit.²² 113-114). 300 MHz ^1H NMR (CDCl_3), 7.85 (m, 1H), 7.59 (m, 1H), 7.32 (m, 9H), 7.21 (m, 3H); 75 MHz ^{13}C NMR (CDCl_3), 140.87, 139.53, 138.84, 135.51, 134.22, 133.22, 130.42, 129.59, 128.62, 128.32, 127.67, 127.35, 124.50, 124.41, 123.33, 122.04; GC-MS, m/e (relative intensity) 287 (18, $\text{M}^+ + 1$), 286 (100, M^+), 285 (33), 284 (30), 282 (10), 271 (12), 252 (10), 44 (19).

Results and Discussion

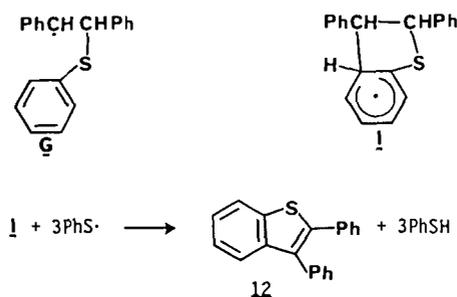
Pyrolysis of neat benzylphenylsulfide produced toluene, thiophenol, Ph_2CH_2 , Ph_2S_2 , Ph_3CH , Ph_2S , 2-phenylbenzothiophene and 2,3-diphenylbenzothiophene. With a central bond strength of $\approx 52 \pm 2$ kcal/mole,¹⁶ benzylphenylsulfide will exhibit a unimolecular half-life of about 5 seconds at 400°C . The elementary free radical reactions in eqns. 2-14 show the origin of abstraction (PhCH_3 , PhSH) rearrangement (Ph_3CH , Ph_2CH_2), and termination/oxidation ($\text{Ph}_2\text{C}=\text{CPh}_2$, $\text{PhCH}=\text{CHPh}$) products.



As noted, radical forming reactions for the weak C-S bonds (eqn. 2) are very rapid at 400°C resulting in the facile equilibria of eqns. 2 and 4. Ph_3CH and Ph_2CH_2 both must occur via 1,2-aryl migration of phenyl from sulfur to carbon (equations 6,10), since an alternate mechanism of ipso displacement by benzyl radical on benzylphenylsulfide has been rendered unlikely based on other model studies.^{15,23} Tetraphenylethylene (10) and stilbene (11) result from radical oxidation of the parent hydrocarbons $\text{Ph}_2\text{CHCHPh}_2$ and $\text{PhCH}_2\text{CH}_2\text{Ph}$.

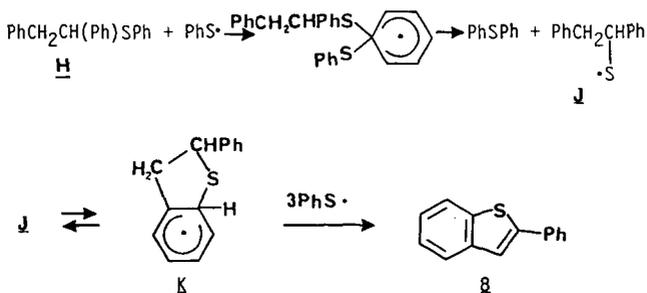
The formation of 2,3-diphenylbenzothiophene is a straightforward consequence of the formation of stilbene. Rapid, reversible addition of $\text{PhS}\cdot$ to stilbene followed by cyclization and oxidation provides the observed product as shown in Scheme I.

Scheme I



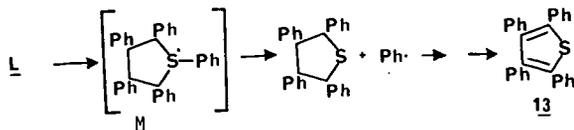
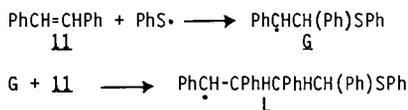
The formation of 2-phenylbenzothiophene must involve a displacement by the thiophenoxy radical on H as depicted in Scheme II.

Scheme II



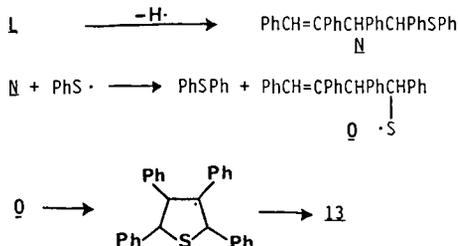
Oxidation of the intermediate hydrocarbons and radicals separating **K** and **Q** will occur in straightforward fashion. The by-product Ph_2S was detected as a significant product accompanying the formation of **Q**. The mechanisms of Schemes I and II were supported by products from reactions of stilbene and bibenzyl with PhSSPh at 400°C . Both reagents gave substantial yields of **12**. In addition, the reaction of stilbene and PhSSPh produced 1,2,3,4-tetraphenylthiophene (**13**). Scheme III depicts a plausible route for the formation of **13**. Displacement of a phenyl radical by the benzylic radical may proceed

Scheme III

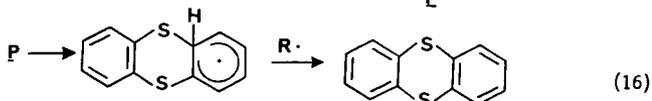
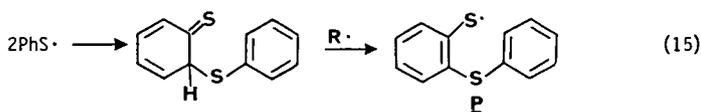


via the hypervalent 9-S-3 intermediate **M** lying in a shallow well of perhaps 3 kcal/mole,²⁴ or it may be merely a transition state. However, since displacement (although feasible at 400°C) of the phenyl radical would be substantially endothermic, an alternate mechanism (Scheme IV) seems more likely.

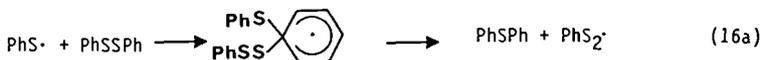
Scheme IV



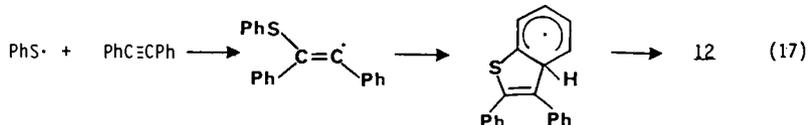
The displacement reaction of $\text{PhS}\cdot$ with **11** will be rapid at these temperatures (cf. the photolysis of Ph_2S_2 at 25°C efficiently produces Ph_2S as the major product), providing an unambiguous route to **13**. The thermolysis of neat phenyldisulfide provides thianthrene and phenylsulfide, the former product by a termination pathway (eqns. 15,16),



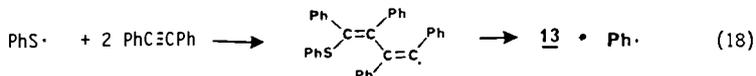
and the latter via direct displacement (eqn.16a).



The reaction of diphenylacetylene and Ph_2S_2 produced 2,3-diphenylbenzothiophene in synthetically useful yields, along with **13**. Production of 2,3-diphenylbenzothiophene (**12**) occurs in straightforward fashion (eqn. 17).

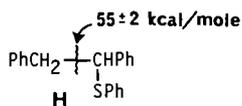


The formation of **13** is difficult to explain without proposing displacement by an intermediate vinylic radical at sulfur (eqn. 18). The displacement of



phenyl radical would be nearly thermoneutral in this case, and the 9-S-3 intermediate (or transition state) is quite plausible.

Finally, we note that significant yields of toluene were produced in reactions of stilbene and bibenzyl. The intermediacy of **H** is suggested.



The thermal C-C cleavage in H to produce $\text{PhCH}_2\cdot$ and species B is expected to be rapid since the estimated bond dissociation energy is comparable to that of PhSSPh (55 ± 2 kcal/mol). The net effect of the thiophenoxy radical in these reactions will have been to substantially enhance the cleavage of $\text{sp}^2\text{-sp}^2$ and $\text{sp}^3\text{-sp}^3$ bonds in these otherwise refractory systems.

Conclusions

The disulfide \rightleftharpoons thiophenoxy radical equilibrium, which models an important family of equilibrating sulfur-center radicals present during liquefaction of sulfur-containing coals, provides facile mechanisms for rapid hydrogen transfer, displacement and condensation reactions leading to enhanced cleavage of aralkyl structure on the one hand, and retrograde formation of nearly inert thiophene structures on the other hand. Further work is underway in this laboratory to determine the kinetics of 1,2-aryl migrations of phenyl from sulfur to carbon and to detect the intermediacy (if any), of 9-S-3 sulfur-centered radicals involved in radical displacement reactions at sulfur.

Acknowledgment

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