

RETROGRESSIVE ARYL-ALKYL BOND FORMING REACTIONS
FACILITATED BY REACTIONS OF SULFUR-CENTERED FREE RADICALS

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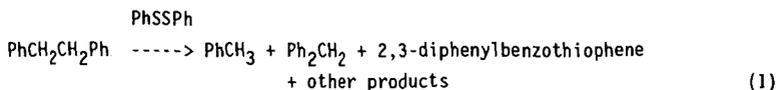
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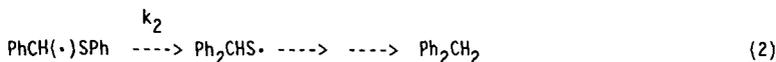
INTRODUCTION

It is well known that additives such as elemental sulfur, pyritic minerals and thiols play a significant role in structural reorganization during the thermal degradation of coals.¹⁻⁴ Studies have shown that the rates for hydrogen atom transfer reactions between benzylic positions of model compounds and coals are increased significantly with higher sulfur content.^{5,6} Displacement reactions of aromatic substituents by thiyl radicals and abstraction reactions by sulfur-centered radicals have long been recognized,⁷⁻¹⁰ and are thought to be important in coal liquefaction. However, the mechanistic aspects of C-C and C-S bond formation and the rearrangement of organic structure in coal facilitated by thiyl radicals is less well understood.

Recently, we have demonstrated the importance of thiyl radicals in the enhancement of the cleavage of strong C-C bonds and in the formation of inert thiophene structures (eq. 1).^{11,12} Products from the pyrolysis of bibenzyl in the presence of PhSSPh are shown in eq. 1. Diphenylmethane is formed in



a sequence of reactions involving the key step of phenyl migration from sulfur to the carbon-centered radical (eq. 2)¹³. Thus, at coal

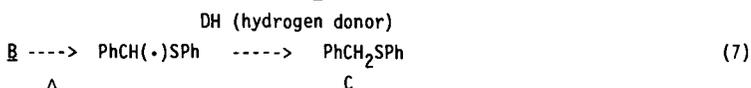
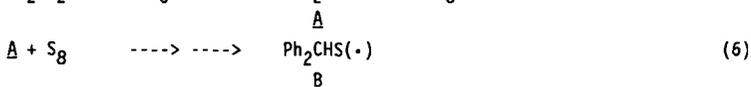
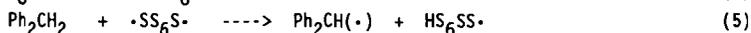


liquefaction temperatures (450°C), reaction (2) proceeds very rapidly and the rate constant of the phenyl migration (k_2) approaches $1.5 \times 10^4 \text{ s}^{-1}$.¹³

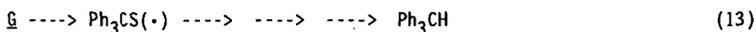
In this paper, we present preliminary results of high-temperature reactions of elemental sulfur with diphenylmethane and triphenylmethane. These results demonstrate the complete reversibility of reaction (2) and provide direct evidence of thiyl radical participation in the cleavage of strong carbon-carbon bonds through a series of abstraction and migration reactions.

RESULTS AND DISCUSSION

Pyrolysis of diphenylmethane in the presence of excess elemental sulfur at $380 \pm 3 \text{ }^\circ\text{C}$ gave toluene, thiophenol and triphenylmethane as the major products along with lesser amounts of PhCH_2SPh , PhSPh , PhSSPh and higher molecular weight products (Table I). The near unity ratio of toluene to thiophenol demonstrates the elementary free radical reactions in eqs. 3-10.



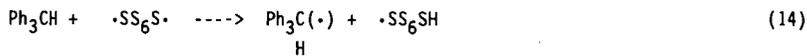
Triphenylmethane is formed via the termination reaction of diphenylmethyl and thiophenoxy radicals followed by hydrogen atom abstraction and phenyl migration reactions (eqs. 11-13). The formation of



The minor products show the origin of termination, displacement, abstraction, and oxidation reactions.¹²

As noted in Table I (compare entries 4 and 2), triphenylmethane was more abundant at low sulfur concentration. Rapid phenyl migration in eq. 13 and the low concentration of thiol donors provide an explanation for the observed result.

Table II gives the product distributions of the pyrolysis reaction of triphenylmethane with elemental sulfur at $380^\circ\text{C} \pm 3$. The formation of thiophenol and diphenylmethane is a consequence of phenyl migration from carbon to a sulfur-centered radical, eqs. 14-19. The production



of toluene and diphenyldisulfide is the result of further reactions of diphenylmethane with sulfur and the termination of thiophenoxy radical respectively. A similar interpretation explains the high yield of Ph_2CH_2 in the presence of low concentration of sulfur (Table II, entry 4). Rapid phenyl

migration, eq. 16, followed by abstraction and further reduction produced the desired product.

SUMMARY

These observations show that the cleavage of strong alkyl-aromatic carbon-carbon bonds can become completely reversible under the influence of thiyl radicals, via a rapid sequence of 1,2-phenyl migration, or neophyl-like rearrangements of thiyl radicals.^{12,13}

EXPERIMENTAL

General. Diphenylmethane, triphenylmethane, and sulfur were purchased from the Aldrich Chemical Co. and used as received. Products were identified by gas chromatography by coinjection with authentic samples. Gas chromatography was carried out using a Hewlett-Packard Model 5890A equipped with an on-column injector and flame-ionization detection. Analyses were performed on a 25-m, 0.32 mm i.d. J&W Scientific DB-5 capillary column.

General procedure for Thermolysis Reactions. To a 0.01-0.05g of diphenylmethane or triphenylmethane was added an appropriate amount of sulfur. The mixture was mixed, freeze-thaw degassed in liquid nitrogen, and sealed under high vacuum. The tubes were introduced to a fluidized sand bath at $380^{\circ}\text{C} \pm 3$ for intervals of 5 and 20 minutes, cooled immediately in tap water, open under nitrogen, and transferred to a degassed solution of CH_2Cl_2 containing naphthalene as an internal G.C. standard.

ACKNOWLEDGEMENT

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Table I

Effect of Sulfur on Product Distributions from Diphenylmethane
Thermolysis at 380 ± 3 °C.^{a,b,c}

| $[\text{Ph}_2\text{CH}_2]/[\text{S}]^{\text{d}}$ | Time (min) | PhCH_3^{e} ($\times 10^{-3}$) | PhSH^{e} ($\times 10^{-3}$) | $\text{Ph}_3\text{CH}^{\text{e}}$ ($\times 10^{-4}$) |
|--|---------------|--|--|---|
| 0.55 | 5 | 0.86 | 0.68 | 1.32 |
| 0.55 | 20 | 1.42 | 1.40 | 1.80 |
| 0.22 | 20 | 0.82 | 1.10 | 0.80 |
| 10.0 ^f | 20 | 1.60 | 1.75 | 8.9 |

a) In the control experiment, the absence of sulfur, Ph_2CH_2 produced trace amounts of PhCH_3 , $\text{PhCH}_2\text{CH}_2\text{Ph}$, Ph_3CH and tetraphenylethane under the reaction conditions. b) % Conversion of $\text{Ph}_2\text{CH}_2 = 10\text{-}20\%$. c) PhCH_2SPh , PhSSPh , PhSPh and higher molecular weight materials were also produced in small amounts. d) Ratio of diphenylmethane to sulfur. e) In mmoles. f) $\text{PhCH}_2\text{CH}_2\text{Ph}$ and Stilbene were also produced.

Table II

Effect of Sulfur on Product Distributions from Triphenylmethane
Thermolysis at 380 ± 3 °C.^{a,b,c}

| $[\text{Ph}_3\text{CH}]/[\text{S}]^{\text{d}}$ | Time (min) | PhCH_3^{e} ($\times 10^{-4}$) | PhSH^{e} ($\times 10^{-3}$) | $\text{Ph}_2\text{CH}_2^{\text{e}}$ ($\times 10^{-3}$) | PhSSPh^{e} ($\times 10^{-3}$) |
|--|---------------|--|--|---|--|
| 0.55 | 5 | 0.30 | 1.0 | 3.63 | 0.45 |
| 0.55 | 20 | 9.7 | 3.38 | 6.55 | 1.2 |
| 0.22 | 20 | 7.15 | 2.20 | 4.03 | 0.20 |
| 10.0 | 20 | 3.0 | 3.20 | 17.7 | 1.75 |

a) In a control experiment in the absence of sulfur, Ph_3CH produced no detectable products. b) % conversion of $\text{Ph}_3\text{CH} = 10\text{-}20\%$. c) Higher molecular weight materials were also produced. d) Ratio of triphenylmethane to sulfur. e) In mmoles.