

## ABSTRACT

### Pyrolysis of phenyl benzoate

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The thermal degradation of diaryl esters currently is of interest. However, the low temperature pyrolysis of diaryl esters has not been studied in great detail. Here the pyrolysis of phenyl benzoate was studied neat and diluted in naphthalene at 400 °C. The major products from the pyrolysis of the neat substrate were benzene, phenol, and benzoic acid, while smaller amounts of biphenyl, benzophenone, phenyl biphenylcarboxylate, and phenyl benzoylbenzoate were observed. Surprisingly, the reaction rate increased ca. 30% when phenyl benzoate was diluted 10-fold in naphthalene and 1- and 2-phenylnaphthalene ( $12.8 \pm 2.1$  mol%) were formed at the expense of phenyl biphenylcarboxylate. Although C-O homolysis (bond dissociation energy=70 kcal/mol), should not occur to an appreciable extent at 400 °C, these products indicate that phenyl radicals are produced in the reaction. Phenyl radicals could be produced from the decomposition of benzoic anhydride, formed from the condensation of benzoic acids, but the addition of water (10-20 mol%) reduced the formation of phenyl biphenylcarboxylate ca. 40-58%. The mechanistic origins of the products will be discussed in the presentation.

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## Extended Abstract

### Pyrolysis of Phenyl Benzoate

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#### Introduction

It has been proposed that oxygen functional groups (i.e., carboxylic acids, phenols, and ethers), prevalent in low-rank coals, are responsible for cross-linking reactions that inhibit the efficient conversion of low-rank coals to liquid fuels.<sup>i</sup> In previous studies, the thermal decomposition of aromatic carboxylic acids was investigated to determine if decarboxylation leads to cross-linking.<sup>ii</sup> Although carboxylic acids predominately undergo decarboxylation by an acid promoted ionic pathway at 400 °C, small amounts (<5 mol%) of cross-linked products (i.e., arylated products) were formed by formation and radical induced decomposition of anhydrides. Anhydride formation and cross-linking reactions were enhanced by incorporating the aromatic carboxylic acids in a polymer (poly(*m*-xylylene)-*co*-(5-carboxy-*m*-xylylene) at concentrations similar to those found in low rank coal (ca. 2.4 carboxyls per 100 carbons).<sup>iii</sup> Since condensation reactions appear to readily occur under the reaction conditions used in these studies, which are similar to the temperatures found in the thermal processing of coal (350-425 °C). This opens the possibility for another type of cross-linking reaction from the condensation of carboxylic acids and phenols to make aryl esters. Since phenols are 1-5 times more concentrated than carboxylic acids in low rank coal, aryl esters, which are not native to coal, could form from condensation reactions. Aryl esters are predicted to be thermally stable up to temperatures of 650 °C based on the Arrhenius parameters reported for the C-O homolysis of phenyl acetate ( $\log k \text{ (s}^{-1}\text{)} = 15.3 - 72.3 \text{ kcal mol}^{-1} / 2.303RT$ ).<sup>iv</sup> Thus, it is predicted that aryl esters could act as low temperature cross-links in low rank coal. However, there is little data on the low temperature pyrolysis of aryl esters. The only reported on aryl ester pyrolysis study to date is that of phenyl benzoate at 700 °C.<sup>v</sup> The study concluded that the major products formed from the pyrolysis were phenol, naphthalene, biphenyl, benzene, dibenzofuran, and trace amounts of benzaldehyde.

Preliminary studies have shown that sealed tube pyrolysis of mixtures of phenol and benzoic acid (3:1) at 350 and 400 °C form phenyl benzoate in moderate yields (ca. 35%).<sup>vi</sup> In this study, we have investigated the thermolysis of phenyl benzoate at 400 °C, a temperature relevant to coal processing, to determine if this aryl ester acts as a thermally stable low-temperature cross-link, or whether it is thermally labile. The goal of this study is to gain more insight into the fundamental reaction chemistry that leads cross-linking in low rank coals.

#### Experimental

All reagents were 99.9% pure, through GC analysis. Phenol was purified by recrystallization in petroleum ether/benzene and dried over P<sub>2</sub>O<sub>5</sub> in a vacuum desiccator. Benzoic acid was purchased from Mallinckrodt, and no further purification was needed. Phenyl benzoate was purified by recrystallization in hexane/ethyl acetate (1:1) and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. Naphthalene was purified by sublimation. Cumene was fractionally distilled repeatedly. 2,5-Dimethylphenol was recrystallized in EtOH/ether. Acetone (Omni-

Solv) was purchased from EM Scientific, and used with no further purification. Benzyl phenyl ether was purchased from Aldrich and used as received.

Gas chromatography was performed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a J&W Scientific 30 m x 0.25mm id, 0.25  $\mu\text{m}$  film thickness DB-1 column and a flame ionization detector. Mass spectra were obtained at 70 eV on a Hewlett-Packard 5972 GC-MS equipped with a capillary column identical with that used for GC analysis.

## Pyrolysis

Pyrolysis of the compounds was performed by loading Pyrex tubes (8mm o.d x 12.5 cm, thoroughly cleaned, oven dried and cooled under argon) with the appropriate amount of phenyl benzoate, typically 30 mg. Three freeze-pump-thaw cycles were performed prior to sealing the tube at ca  $10^{-5}$  Torr. Tube volumes were kept to a minimum with the solid filling roughly one-half of the sealed pyrolysis tube. The pyrolyses were performed in a Carbolite tube furnace, which maintained a temperature of  $400 \pm 1^\circ\text{C}$ . After the pyrolysis, the samples were removed from the furnace and cooled in liquid  $\text{N}_2$ . The tubes were opened, and the solid products were dissolved in high purity acetone (with exception to the experiments with  $\text{H}_2\text{O}$ , where  $\text{CH}_2\text{Cl}_2$  was used as the solvent). Internal standards, 2,5-dimethylphenol, benzyl phenyl ether and cumene, were added and the reaction mixtures were analyzed by GC and GC-MS. The identities of products from the thermolysis were determined by GC-MS analysis and further confirmed by comparison with commercially available compounds. Samples were injected four times onto the GC using a HP 7673 autosampler. The products were quantitated, and the data was averaged using the GC-FID output relative to the internal standards. Typical shot to shot reproducibility was  $\pm 2\%$ . Response factors were measured with authentic samples or estimated from measured response factors for structurally related compounds and based on carbon number relative to the internal standards. Mass balances were calculated by comparing the recovered starting material and product equivalents to the initial charge of starting material.

## Results and Discussion

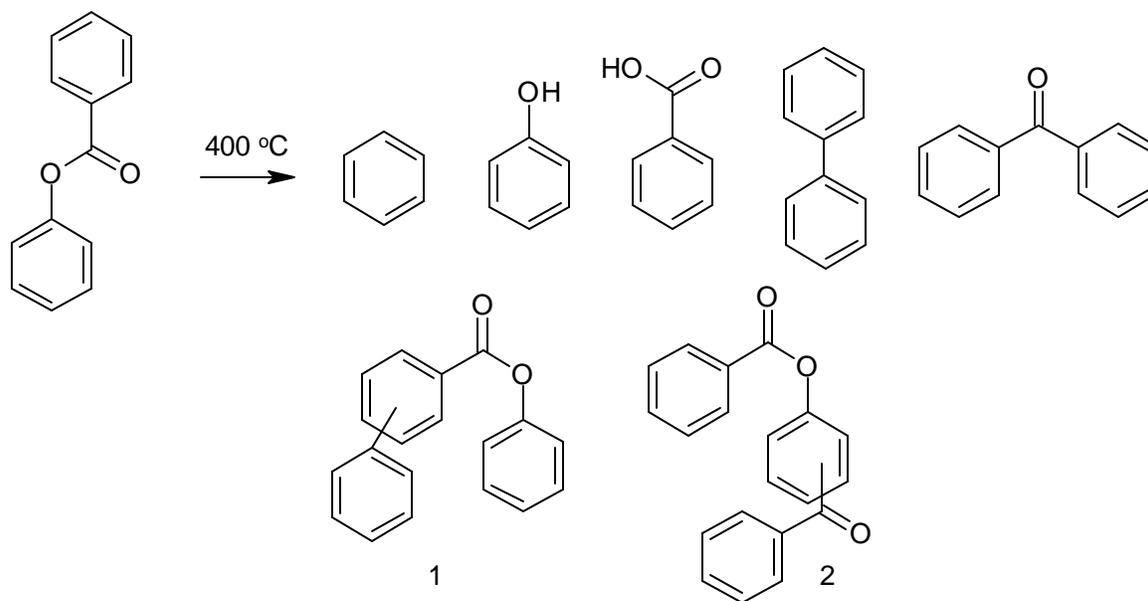
The products from the thermolysis of phenyl benzoate at  $400^\circ\text{C}$  are presented as a function of reaction time (1-4 h), Table 1. The major products produced from the pyrolysis of neat phenyl benzoate are benzene, phenol, and benzoic acid, while the minor amounts of are biphenyl, benzophenone, phenyl biphenylcarboxylate, **1** and phenyl benzoylbenzoate, **2**, were formed (see Figure 1). Multiple isomers of **1** and **2** were also observed. The mass balances are good with a conversion  $<10\%$  indicating that we are accounting for most of the products at low conversion. As conversion increases, the mass balance decreases, which is due to formation of secondary products, which are currently not identified.

The formation of phenol and benzoic acid could arise from the simple hydrolysis of the phenyl benzoate by residual water in the reagents or reaction vessel (although this unlikely because the reagents were stored over  $\text{P}_2\text{O}_5$  before use, the tubes were oven dried and the samples were sealed under vacuum). Benzene yields were found to increase with conversion at the expense of benzoic acid. This is most likely a result of ionic decarboxylation of benzoic acid as previously observed.<sup>2</sup> The yields of **1** and **2** were found to increase with reaction time. Yields of biphenyl, phenol, and benzophenone appear to remain constant over time. These products could arise from ionic or radical pathways.

**Table 1.** Products from the thermolysis of phenyl benzoate at 400 °C.

Products <sup>a</sup> (% mol)	1 h	2 h	3 h	4 h
% Conversion	4.5	4.5	6.8	7.5
Mass Balance	98.6	100.1	98.1	96.2
Rate (%/h)	4.8	2.3	2.3	1.9
Benzene	7.7	22.6	19.6	21.1
Phenol	54.2	38.5	39.0	48.5
Biphenyl	2.2	1.6	1.6	1.4
Benzoic Acid	27.7	0.0	1.81	4.2
Benzophenone	0.0	4.0	4.6	5.5
<b>1</b>	3.6	12.8	12.9	7.5
<b>2</b>	4.2	4.5	7.2	3.6

<sup>a</sup>Results are from an average of a minimum of 2 runs (typically  $\pm 5\%$ ).

**Figure 1.** Decomposition products of phenyl benzoate at 400 °C.

The influence of concentration on the pyrolysis of phenyl benzoate was investigated by dilution in an inert solvent, i.e., naphthalene. At a 10:1 dilution in naphthalene, similar products were found as reported in the neat solution, see Table 2 and Figure 2. However, 1- and 2-phenylnaphthalene and isomers of binaphthyl were found. This indicates that aryl radicals are present in the reactions. Surprisingly, dilution did not decrease the reaction rate, but increased it by ca. 14 %.

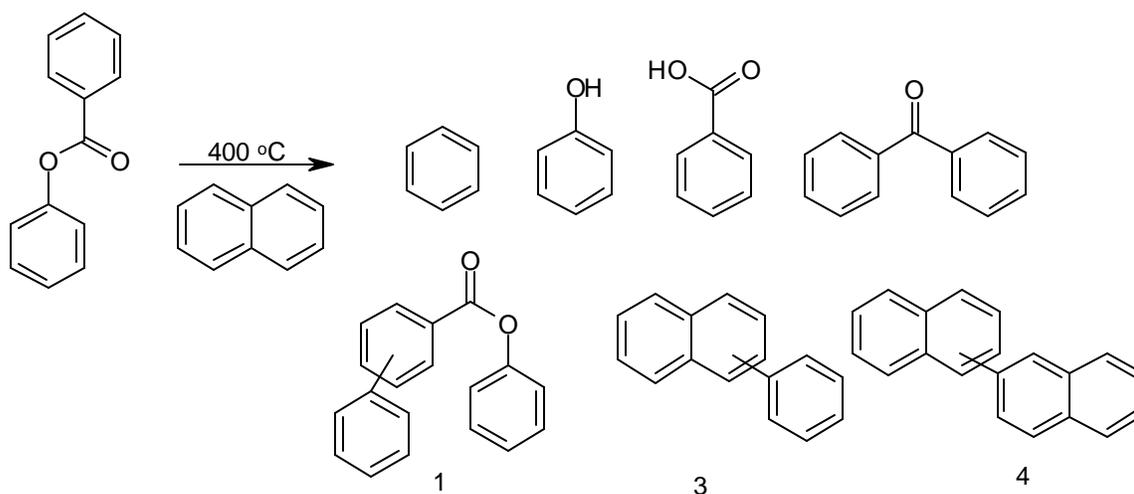
In our previous study on the pyrolysis of benzoic acid in naphthalene, phenylnaphthalenes were observed.<sup>2</sup> These products were formed from the formation and decomposition of benzoic anhydride. Since benzoic acid is a product in the pyrolysis of phenyl benzoate, a similar pathway could explain the formation of the phenylnaphthalenes. However,

benzoic anhydride was not found in the reaction mixture. Conversely, the possibility exists that the benzoic anhydride could rapidly decompose as it is formed, so that its concentration does not build up. Currently, the impact of added anhydrides, i.e. toluic anhydride, on the decomposition of phenyl benzoate is under investigation to determine if anhydrides are responsible for the arylated products.

**Table 2.** Products from the thermolysis of phenyl benzoate in naphthalene 1:10 and in water at 400 °C.

Products <sup>a</sup> (% mol)	Napthalene 2 h	Napthalene 4 h	10 mol% H <sub>2</sub> O 4 h	20 mol% H <sub>2</sub> O 4 h
Mass Balance	99.9	96.5	98.0	95.4
Conversion	6.5	7.5	35.9	34.6
Rate (%/h)	3.3	1.9	9.1	8.8
Benzene	28.2	30.0	19.0	17.1
Phenol	48.7	46.9	48.0	48.2
Biphenyl	0.0	0.0	1.3	1.2
Benzoic Acid	<0.1	<0.1	13.7	17.8
Benzophenone	0.71	0.88	3.2	2.4
<b>1</b>	0.0	0.33	6.7	4.8
<b>2</b>	0.0	0.0	0.82	0.74
<b>3</b>	13.0	2.7	0.0	0.0
<b>4</b>	12.8	2.5	0.0	0.0

<sup>a</sup>Results are from an average of a minimum of 2 runs (typically  $\pm 10\%$ )



**Figure 2.** Decomposition products of phenyl benzoate diluted in naphthalene 1:10 at 400 °C

The formation of phenol and benzoic acid could arise from the simple hydrolysis of the phenyl benzoate by residual water in the reagents or reaction vessel. To determine if similar products are found when small amounts of water are added to the reaction mixture, the pyrolysis of phenyl benzoate was investigated with 10 and 20 mol% water. Addition of water to phenyl

benzoate dramatically increased the production of benzoic acid and reduced the production of the **1** (ca. 40 and 58% for 10 and 20 mol% addition, respectively) and **2** (ca. 81%). The water also appears to slow the decarboxylation of the benzoic acid. Currently, experiments are underway with O<sup>18</sup>-water to determine if the benzoic acid contains O<sup>18</sup> from hydrolysis or if there are other pathways for benzoic acid formation

## Conclusions

The pyrolysis of phenyl benzoate at 400 °C both neat and diluted in naphthalene has provided additional information for the possible formation of low temperature cross-links in low rank coal from the thermal degradations of aryl esters. Dilution with naphthalene produces arylated naphthalenes at the expense of the phenylated-benzoic acid, indicating a radical pathway is involved. Water decreases the yields of the cross-linked phenyl biphenylcarboxylate, **1**, and phenyl benzoylbenzoate, **2**. However, the mechanistic origins of all the products are still not known. Are benzoic acid and phenol formed by simple hydrolysis or is there a radical induced decomposition? Are phenyl radicals formed from formation and decomposition of benzoic anhydride? These mechanistic questions are currently under investigation. New results into the thermal decomposition of phenyl benzoate will be presented and discussed.

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<sup>ii</sup> Eskay, T. P.; Britt, P. F.; Buchanan, A. C. III *Energy Fuels* **1997**, *11*, 1279.

<sup>iii</sup> Britt, P. F.; Mungall, W. S.; Buchanan, A. C. III *Energy Fuels* **1998**, *12*, 660.

<sup>iv</sup> Ghibaudi, E.; Colussi, A. J. *J. Chem. Soc., Chem. Comm.* **1984**, 433.

<sup>v</sup> Patterson, J. M.; Shiue, C. Y.; Smith, W. T., Jr. *J. Org. Chem.* **1973**, *38*, 387.

<sup>vi</sup> Kidder, M. K.; Britt, P. F.; Buchanan, A. C. III Unpublished results.