CROSS-LINKING REACTIONS BETWEEN PHENOLS AND BENZOIC ACID: THE ROLE OF ARYL ESTERS

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Introduction

It has been proposed that oxygen functional groups (i.e., carboxylic acids and their salts, 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 and chemicals. In the pyrolysis and liquefaction of low-rank coals, cross-linking has been correlated with evolution of CO₂ and H₂O. To determine if decarboxylation leads to cross-linking, the thermal decomposition of aromatic carboxylic acids was investigated. It was determined that carboxylic acids predominately undergo decarboxylation by an acid promoted ionic pathway at 400 °C, but depending on the reaction conditions, small amounts (<5 mol%) of cross-linked products (i.e., arylated products) could be 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-xylene)-co-(5-carboxy-m-xylene)) at concentrations similar to those found in low rank coal (ca. 2.4 carboxyls per 100 carbons). Since these condensation reactions readily occur at temperatures found in the thermal processing of coal (350-425 °C), additional types of cross-linking reactions, such as the condensation of carboxylic acids and phenols to make aryl esters, might be possible. Since phenols are 2-5 times more concentrated than carboxylic acids in low rank coal, aryl esters 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 (s⁻¹) = 15.3 – 72.3 kcal mol⁻¹ / 2.303RT). Pyrolysis of phenyl benzoate at 700 °C produced 90% conversion, and produced phenol, biphenyl, benzene, and dibenzofuran as the major products, but the mass balance was poor (<60%). Thus, aryl esters could act as low temperature cross-links in low rank coal. However, there is little data on the formation and pyrolysis of aryl esters at temperatures relevant to those found in the thermal processing of coal (350-425 °C). In this study, we have investigated the pyrolysis benzoic acid in the presence of excess m-phenylphenol to study the formation and decomposition of aryl esters, and we have investigated the pyrolysis of phenyl benzoate at 400 °C to determine if aryl esters act as a thermally stable low-temperature cross-link.

Experimental

m-Phenylphenol, which contained 10% p-phenylphenol, was recrystallized from benzene/hexanes and dried in a vacuum desiccator over P₂O₅. Benzoic acid was purchased from Mallinckrodt, and no further purification was needed. Phenyl benzoate was purified by recrystallization from hexane/ethyl acetate (1:1) and dried in a vacuum desiccator over P₂O₅. Naphthalene was purified by sublimation. Cumene was fractionally distilled (2x). 2,5-Dimethylphenol was recrystallized in EtOH/ether. Acetone (OMNI-Solv) was used with no further purification. Benzyl phenyl ether was purchased from Aldrich and used as received.

Pyrolysis of the compounds was performed in heavy walled Pyrex tubes (8 mm o.d x 12.5 cm) that were thoroughly cleaned, oven dried and cooled under argon. The desired amount of substrate (typically 20-100 mg) was weighed into the tube, and 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 the temperature to ±1 °C. All samples were run in duplicate. After the pyrolysis, the samples were removed from the furnace and cooled in liquid N₂. The tubes were opened, and the solid products were dissolved in high purity acetone. Internal standards, 2,5-dimethylphenol, benzyl phenyl ether and cumene, were added. The products were analyzed by gas chromatography using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a J&W Scientific 30 m x 0.25mm id, 0.25 µm film thickness DB-5 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. The products were quantitated by injection onto the GC using a HP 7673 autosampler, and the data was averaged using the GC-FID output relative to the internal standards. Response factors were measured with authentic samples or estimated from measured response factors for structurally related compounds or 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 formation of aryl esters was investigated by the pyrolysis of mixtures of m-phenylphenol and benzoic acid. The phenyl substituted phenol was chosen instead of phenol to reduce the pressure inside the pyrolysis tubes, since pyrolysis of mixtures of phenol and benzoic acid tended to break the heavy walled glass tubes. The meta-isomer was chosen to reduce any substituent effect in the reaction, but the purified meta-isomer contained 10% of the para-isomer. Pyrolysis of a 3:1 mixture of m-phenylphenol and benzoic acid at 400 °C for 60 min produced a 69.7 ± 1.3 % yield of m-phenylphenol benzoate. When the ratio of m-phenylphenol to benzoic acid was reduced to 1:9:1, the yield of m-phenylphenol benzoate decreased to 53.6% showing that the concentration of phenol impacts the rate of condensation. The high efficiency of aryl ester formation in the sealed tube pyrolysis was surprising. It was initially thought that hydrolysis would be competitive with condensation and only a small quantity of aryl ester would be formed.

To determine the effect of temperature on aryl ester formation, a 3:1 mixture of m-phenylphenol and benzoic acid was heated for 60 min at 200, 250, and 300 °C. At 200 °C, only a small amount of ester (0.65%) was observed with no additional products. As the temperature was increased to 250 and 300 °C, the yield of m-phenylphenol benzoate increased to 6.3% and 32.3%, respectively, but no other products were observed. At 400 °C, m-phenylphenol benzoate was found in 69.7 % yield along with a small amount of other products (see Figure 1). As the reaction time increased from one to four hours, the yield of m-phenylphenol benzoate decreased while the yield of the other products increased. The majority of the products appear to arise from the decomposition of benzoic acid. For example, benzene could arise from the acid catalyzed decarboxylation of benzoic acid, while the arylated products, such as diphenylphenol, terphenyl, and diphenylphenyl benzoate, suggest that benzoic acid might be decomposing by a radical pathway to...
form aryl radicals. The phenol coupling products could also be formed by a radical pathway.

![Figure 1. Products from the 400 °C pyrolysis m-phenylphenol and benzoic acid.](image)

Pyrolysis of m-phenylphenol and benzoic acid in a 10-fold excess of naphthalene (relative to benzoic acid) at 400 °C produced the aryl ester as the dominant product. However, 1- and 2-phenylnaphthalene were the dominant arylated products rather than diphenylphenol, terphenyl, and diphenylphenyl benzoate. These results indicate that aryl radicals are possibly forming from the decomposition of benzoic acid and not from the decomposition of the phenol since no biphenylated naphthalene was observed. Aryl radicals could be formed from the formation and decomposition of benzoic anhydride as previously discussed. However, benzoic anhydride was not found as a product. Thus, the formation pathways for the arylated products are still under investigation.

![Figure 2. Products from the 400 °C pyrolysis m-phenylphenol and benzoic acid in naphthalene.](image)

The pyrolysis of phenyl benzoate was studied at 400 °C to determine the thermal stability of the aryl ester. The major products (shown in Figure 3) are similar to those found in the pyrolysis of benzoic acid and m-phenylphenol. Surprisingly, significant amounts of phenol and benzoic acid were observed at short reaction times. As the reaction time increased, the yield of benzoic acid decreased and the yield of benzene increased. This is most likely due to the ionic decarboxylation of the benzoic acid. 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 was thought to be unlikely since the reagents were stored over P₂O₅ before use, the reaction tubes were oven dried, and the samples were sealed under vacuum. However, since the reactions were typically run with 35 mg phenyl benzoate (177 µmol), one microliter of water (55 µmol) in the reaction tube could cause 31% conversion to phenol and benzoic acid. Thus, residual water could be responsible for most of the conversion followed by benzoic acid chemistry, but the mechanistic details of product formation are currently under investigation.

![Figure 3. Products from the pyrolysis of phenyl benzoate.](image)

**Conclusions**

The pyrolysis of mixtures of m-phenylphenol and benzoic acid were investigated at 400 °C to determine if condensation reactions could occur to form aryl esters, which could be low temperature cross-links. It was determined that aryl esters could slowly form at temperatures as low as 200 °C, but the efficiency of the reaction increased with temperature. Only m-phenylphenyl benzoate was found at temperatures up to 300 °C, but at 400 °C, other pyrolysis products were found which appear to arise from benzoic acid decomposition. The thermal stability of aryl esters was investigated through the pyrolysis of phenyl benzoate at 400 °C. As predicted, the aryl ester appeared to be thermally stable but hydrolytically unstable. In general, formation of aryl esters could be a low temperature pathway for the cross-linking of low rank coals. The reaction pathways for the formation of the arylated products found in the pyrolysis mixture at 400 °C are currently under investigation.

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**References**