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Pyrolysis of Coal Model Compounds Containing Aromatic Carboxylic Acids: The Role of Carboxylic Acids in Cross-Linking Reactions in Low-Rank Coal.

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ABSTRACT

The pyrolysis of 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (**1**) diluted in 10-fold excess of naphthalene has been studied at 400 °C to investigate whether decarboxylation of aromatic carboxylic acids can lead to cross-linked products. The dominant mechanism for decarboxylation was found to be an acid-promoted ionic pathway that does not lead to cross-linking. However, a small amount of cross-linked products (i.e. naphthalene grafted onto decarboxylated **1**) were formed. The yields of the cross-linked products were found to be decreased in the presence of a hydrogen donor solvent, tetralin, suggesting that these products were formed by a free-radical pathway. The mechanism for the formation of cross-linked products was proposed to occur from the formation and decomposition of anhydrides of **1** during the pyrolysis.

Keywords: carboxylic acid, decarboxylation, cross-linking, coal liquefaction

1. INTRODUCTION

In recent years, it has been proposed that decarboxylation reactions are major contributors in cross-linking processes observed during the thermal processing of low-rank coal [1]. However, this proposal has been brought into question by studies done by our group [2] and by McMillen and co-workers [3] on the pyrolysis of aromatic carboxylic acids, in which decarboxylation leads to only a limited amount of cross-linking. We proposed that thermal decarboxylation occurs primarily by an acid-promoted ionic mechanism for the neat liquid [2]. However, to further evaluate the decarboxylation of aromatic carboxylic acids in the presence of typical polyaromatic hydrocarbon structures present in coal, we now report some of our preliminary findings on the pyrolysis of 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (**1**) diluted in naphthalene.

2. EXPERIMENTAL

The synthesis of 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane has been previously described [2c]. The methods used for pyrolysis at 400 °C, analysis and quantitation of the products by GC.

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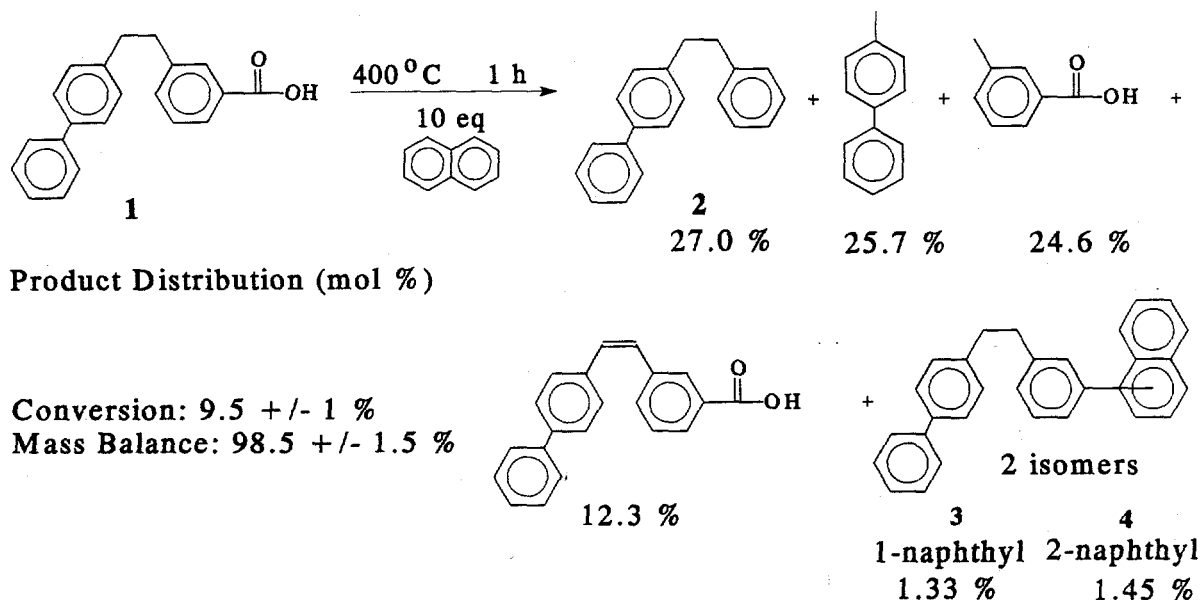
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GC/MS, and HPLC have all been detailed in previous publications [2].

3. RESULTS AND DISCUSSION

Thermolyses of **1** diluted in naphthalene (10-fold) were conducted in sealed, evacuated pyrex tubes at 400 °C. The major products and a typical product distribution for a 1 h pyrolysis are shown in Scheme 1. The dominant product from the decarboxylation of **1** is **2**. However, a small amount of products are formed in which naphthalene has replaced the carboxylic acid group (**3** and **4**). These products suggests that a small portion of the decarboxylation process leads to coupled products representative of a cross-link in coal (i.e. a linkage stable at $T < 400$ °C).

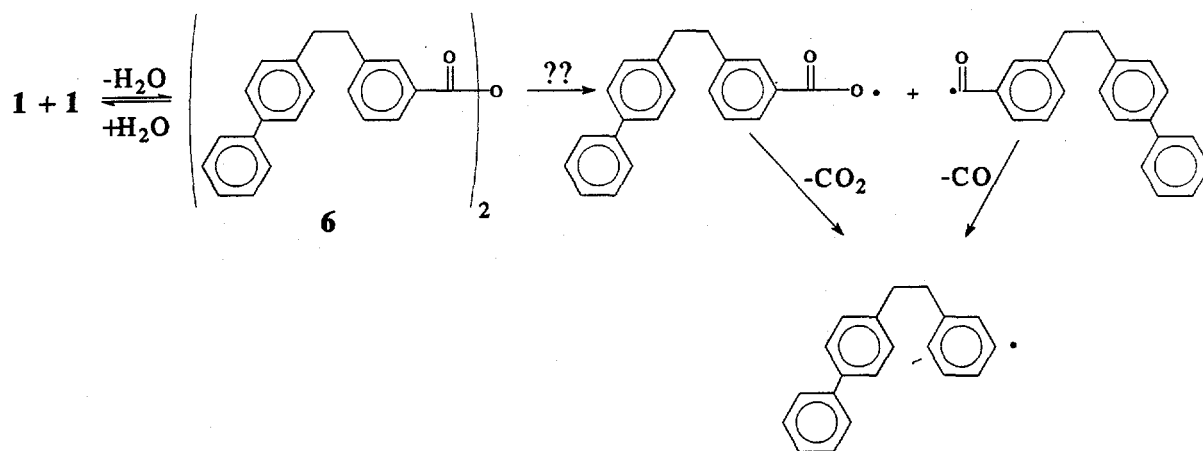


Scheme 1

On the basis of our previous work on the decarboxylation of 1,2-(3,3'-dicarboxyphenyl)ethane, the major pathway for decarboxylation of **1** to **2** (~ 3 %/h diluted 10-fold in naphthalene) is an acid-promoted ionic pathway [2]. Minor products **3** and **4** appear to arise by a free-radical pathway since their yield was reduced ~2-fold by the presence of a hydrogen donor solvent (comparing a mixture 1:1 of naphthalene:tetralin to a 1:1 mixture of naphthalene:biphenyl). Furthermore, to confirm that **3** and **4** can be formed by a radical pathway, the pyrolysis of 1-(3-carboxaldehydephenyl)-2-(4-biphenyl)ethane (**5**) was investigated [4]. Pyrolysis of **5** diluted in 10-fold of naphthalene at 400 °C produced **2**, **3**, and **4** in a 1:1.1:1 ratio. This result not only confirms that **3** and **4** can be formed by a radical pathway, but it also confirms that the bulk of the decarboxylation to form **2** cannot arise via a pathway involving the formation of an aryl radical. In the pyrolysis of **5** in naphthalene, the ratio of arylation to hydrogen abstraction (**3**+**4**:**2**) by the aryl radical is 2:1. However, in the pyrolysis of **1** under identical dilution conditions, >8 times more decarboxylated product is produced than arylated products (**3** and **4**) indicating that the majority of the decarboxylation producing **2** (>80%) *cannot* involve a radical pathway. This finding is consistent with our previous proposal that decarboxylation occurs predominantly by

an ionic mechanism in the pyrolysis of **1** [2].

Initially, it was not clear how an aryl radical was formed, since it is not thermodynamically favorable for a benzylic radical to abstract the carboxy hydrogen. However, it was discovered that the yield of **3** and **4** were reduced *ca.* 2-4-fold when H₂O (0.8-3.5 eq H₂O:1) was added to the pyrolysis medium, although the rate of decarboxylation remained roughly constant. It is unlikely that these products are inhibited by H₂O acting as a hydrogen donor [5]. Therefore, this result suggests that aryl radicals may come from a water sensitive intermediate. Further investigation of the reaction mixtures from the pyrolysis of **1** in naphthalene (1:3.5 eq, respectively) by reverse phase HPLC revealed that an additional product, **6**, an anhydride of **1**, was formed in the pyrolysis in a yield of ~ 1.5 %. However, **6** was not formed when H₂O was added to the pyrolysis medium (1.6 eq) and products **3** and **4** were reduced 3-fold. This result is consistent with the reversibility of anhydride formation in a sealed system (Scheme 2). This result suggests that the anhydride is a potential intermediate in the formation of aryl radicals that lead to **3** and **4**. As shown in Scheme 2, homolysis of the C-O bond of the anhydride would produce fragments that will decarboxylate and decarbonylate to form two aryl radicals that can add to naphthalene to form **3** and **4**. Although thermochemical estimates of the O-(C=O) bond strength predict that **6**



Scheme 2

should not decompose by this pathway to any significant extent at 400 °C, we investigated the pyrolysis of **6** diluted 10-fold in naphthalene. Surprisingly, the anhydride decomposed rapidly at 400 °C (84 %/h) to produce **2**, **3** and **4** as the major products in a ratio of (1:1.9:0.70). Decomposition of **6** appears to lead to the formation of aryl radicals. Additional evidence to support the formation of aryl radicals is that small amounts of binaphthyls were found in the pyrolysis, which can be formed by abstraction of hydrogen from naphthalene by an aryl radical, followed by coupling of the naphthyl radical with a second molecule of naphthalene. Since thermochemical estimates indicate that the homolytic decomposition of the anhydride at 400 °C is unlikely, a detailed investigation of the decomposition pathway of aromatic anhydrides is currently in progress. However, based on the conversion of **6** in naphthalene, <1 % of the starting acid needs to be converted to the anhydride to produce the amounts of **3** and **4** observed in the pyrolysis of **1**.

In summary, the results of this study show that thermal decarboxylation of **1** proceeds predominantly by an ionic pathway that does not lead to significant amounts of cross-linking products. However, a small amount of cross-linking chemistry can occur, by a free-radical pathway, and appears to arise from the formation and decomposition of an aromatic anhydride. Although this model compound study does not reflect the chemical complexity and limited mass transport that is found in coals, the findings do warrant a reevaluation of the functional groups that are present and involved in retrograde reactions in the pyrolysis and liquefaction of low-rank coals.

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4. The pyrolysis of **5** will result in the formation of an aryl radical at the position of the aldehyde, thus allowing for the evaluation of the products that would arise if an aryl radical was produced at the position of the carboxy group in our model carboxylic acid **1**. In the pyrolysis of **5** the aryl radical is produced by homolysis of the benzylic C-C bond to form benzyl radicals, abstraction of the aldehydic hydrogen of another molecule of **5** to produce a carbonyl radical that will rapidly decarbonylate to produce an aryl radical *see* (a) Fahr, A.; Stein, S.E. *J. Phys. Chem.* **1988**, *92*, 495. (b) Chen, R.H.; Kafafi, S.A.; Stein, S.E. *J. Am. Chem. Soc.* **1989**, *111*, 1418.
5. Water did not have any influence on the ratio of **2:3:4** in the pyrolysis of **5:naphthalene:H₂O** (1:10:1.5 molar ratio), indicating that the water does not inhibit the free-radical arylation reaction.

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