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Pyrolysis of Simple Coal Model Compounds Containing Aromatic Carboxylic Acids: Does Decarboxylation Lead to Cross-Linking?*

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Introduction

In recent years, it has been proposed that oxygen functional groups, prevalent in low rank coals, are major actors in retrograde reactions which inhibit their efficient thermochemical processing. In the pyrolysis and liquefaction of low-rank coals, low temperature cross-linking reactions have been correlated with the loss of carboxyl groups and the evolution of CO_2 and H_2O [1,2]. Pretreatments such as methylation, demineralization, or ion-exchange of the inorganic cations reduce cross-linking and CO_2 evolution in pyrolysis, while the exchange of Na^+, K^+, Ca^{++}, and Ba^{++} into demineralized coal increases cross-linking and CO_2 evolution in pyrolysis and liquefaction [3,4]. These results suggest, in part, that decarboxylation pathways in coal may play an important role in the cross-linking of the coal polymer. However, the reaction pathways associated with the decarboxylation and cross-linking events in low rank coal are currently unknown. Furthermore, it is not known whether the reaction pathway that leads to decarboxylation also leads to cross-linking. Radical recombination or addition reactions have been suggested as being involved in retrograde reactions. However, the involvement of radical pathways in thermal decarboxylation reactions has recently been brought into question by the observation that decarboxylation of benzoic acid derivatives under coal liquefaction conditions yielded only small amounts of aryl-aryl coupling products [5]. Therefore, to gain a better understanding of the role decarboxylation plays in cross-linking reactions in low rank coals, we have studied the pyrolysis of several bibenzyls containing aromatic carboxylic acids. The structures currently under investigation are 1,2-(3,3'-dicarboxyphenyl)ethane (1) and 1,2-(4,4'-dicarboxyphenyl)ethane (2). These compounds are capable of forming reactive free-radical intermediates at *ca.* 400°C through homolysis of the weak bibenzylic bonds. This provides a constant source of free-radicals to potentially assist in the decarboxylation reaction.

Experimental

1,2-(3,3'-dicarboxyphenyl)ethane (1). Into a 1 L oven-dried flask, containing a magnetic stirbar, equipped with an oven-dried addition funnel and kept under positive argon pressure, was placed 3-bromobenzyl bromide (13.0 g, 5.22×10^{-2} moles) and dry THF (500 mL). The solution was cooled to -78°C, and the addition funnel was charged with 2.5 M *n*-butyllithium in hexane (54 mL, 1.35×10^{-1} moles). The *n*-butyllithium was added dropwise over a period of 20 min and the solution was stirred for 30 min at -78°C. Carbon dioxide, produced from warming dry ice and passing it through two separate drying tubes of $CaSO_4$ and $CaSO_4/CaCl_2$, was bubbled into the solution for 1.5 h. The reaction was warmed to room temperature and quenched with saturated aqueous $NaHCO_3$ (100 mL). The solution was transferred to a separatory funnel and diluted with H_2O (700 mL) and Et_2O (700 mL). The aqueous layer was collected and acidified with concentated H_2SO_4 to precipitate 1. The white precipitate was collected by vacuum filtration and air dried giving 6.884 g (98 %, GC purity 97 %). Further purification by 4 recrystallizations from isopropyl alcohol and drying over P_2O_5 in a vacuum desicator yielded the product in 99.9 % purity by GC analysis.

1,1,2,2-tetradeutero-1,2-(3,3'-dicarboxyphenyl)ethane (1-d_4) was synthesized by the procedure described above for the synthesis of 1 using 3-bromobenzyl bromide-d_2 which was synthesized as described below. The deuterium content of the product was 97 % d_4 by GC-MS analysis.

3-bromobenzyl bromide-d_2 Into a 1L oven-dried 2-neck flask, containing a magnetic stirbar, equipped with a reflux condenser and an addition funnel, was placed $LiAlD_4$ (Aldrich 98 % deuterium content, 5.00 g, 0.12 moles) and dry Et_2O (300 mL). The solution was stirred and

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3-bromobenzoic acid (20.0 g, 0.10 moles) in dry Et_2O (300 mL) was added from the addition funnel over a period of 30 min. The solution was refluxed for 1 h and was quenched with the cautious addition of H_2O (100 mL). The solution was poured into H_2O (200 mL) containing concentrated H_2SO_4 (16 mL) and stirred until all the solid dissolved. The Et_2O layer was collected and the aqueous layer was extracted with Et_2O (2 x 100 mL). The combined Et_2O extract was washed with dilute aqeous $NaHCO_3$, dried over Na_2SO_4, and the Et_2O was removed to yield 19.4 g of liquid, 3-bromobenzyl alcohol (100 %, crude yield). The deuterium content of the product was 99 % d_2 by GC-MS.

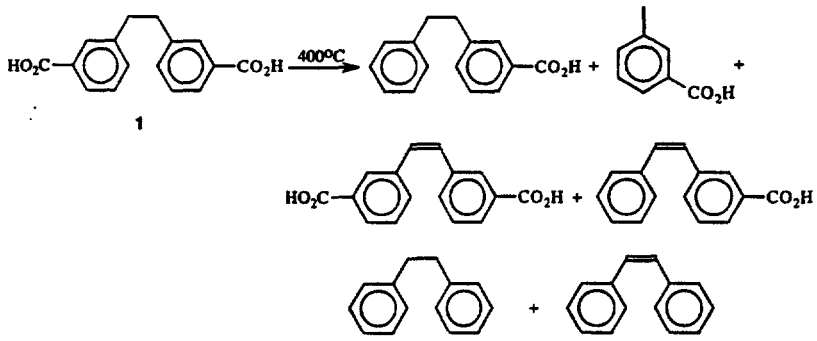
The crude 3-bromobenzyl alcohol (10.1 g, 53.7 mmol) was then placed into a 1-neck (100 mL) flask containing concentrated HBr (26 mL) and concentrated H_2SO_4 (4.0 mL). The solution was refluxed for 6 h, cooled to room temperature, and extracted with hexane (2 x 50 mL). The hexane was passed through a plug of Merck grade 60 silica gel in a (2.5 cm diameter x 2.5 cm long) column and the hexane was evaporated to produce a white solid (11.75 g, 89 % based on crude 3-bromobenzyl alcohol). By GC-MS analysis, the product was 99 % d_2.

1,2-(4,4'-dicarboxyphenyl)ethane (2) was synthesized as described previously [7].

Pyrolyses. Pyrolyses were performed in sealed pyrex tubes (sealed at ca. 10^{-5} Torr) in a Tecam fluidized sandbath at 400 $\pm$ 1.5 °C. Following pyrolysis, the samples were quickly removed from the sandbath and cooled in liquid N_2. The tubes were then cracked open and the solid products were removed with a 2:1 mixture of pyridine:N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). Internal standards (2,4,6-trimethylbenzoic acid and 2-phenylbenzoic acid) were added and the reaction mixtures analyzed by GC and GC-MS. Gas chromatography analysis was performed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a J&W Scientific 30 m x 0.25 mm id, 0.25 μm 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 to that used for GC analysis. The identities of products from the thermolysis of **1** and **2** were determined by GC-MS analysis and were further confirmed by comparison with commercially available or synthesized authentic materials.

Results and Discussion

Thermolysis of **1** and **2** was conducted at 400 °C in sealed pyrex tubes and analyzed by GC and GC-MS. The major products from the thermolysis of **1** are shown in equation 1 and account for ≥ 95 % of the mass balance at conversions of **1** up to 22 %. Several other



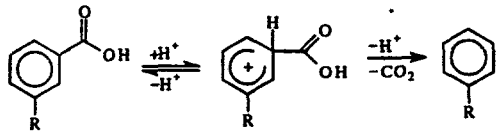
(1)

products are formed in the pyrolysis that have not been identified, but based upon the GC peak area and the good mass balance, the amount of these products are small (<2 %). The results obtained for the thermolysis of **1** at 400 °C at various time intervals are given in Table 1, entries 1-5. A similar product distribution and mass balance (>96 %) was obtained in the thermolysis of **2**.

The major product from the thermolysis of **1** and **2** is decarboxylation to 3-carboxybibenzyl and 4-carboxybibenzyl respectively. The good mass balances (≥95 %) suggest that the decarboxylation reaction does not lead to significant quantities of high molecular weight products that might not be observed by GC analysis. Analysis of the methylated (via diazomethane) reaction mixture from the thermolysis of **2** by reverse phase high performance liquid chromatography showed no new products. This result supports the premise that no non-volatile, high molecular weight products are formed. The rate constant for C-C homolysis of the bibenzylic bond was calculated to be 1.8 $\pm$ 0.1 x 10^{-6} s^{-1} for **1** and

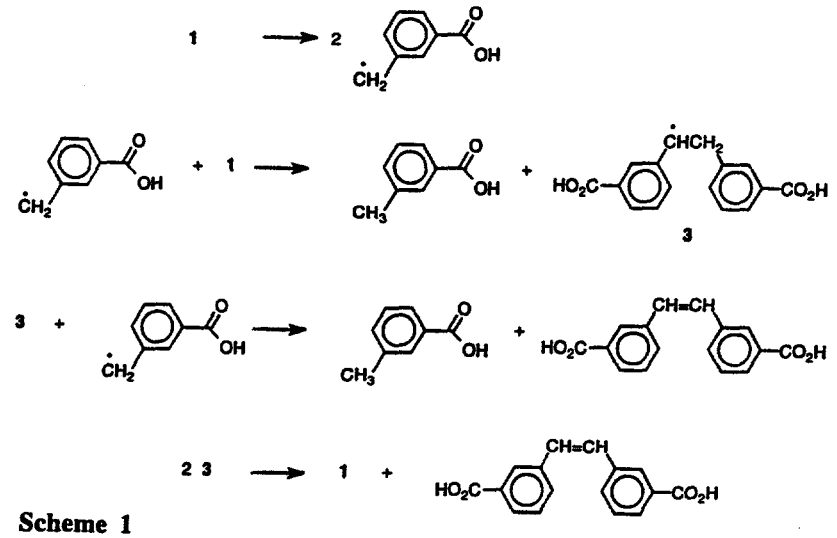
$3.8 \pm 0.6 \times 10^{-6}$ s^{-1} for **2** based on the amount of HO_2CPhCH_3 formed at conversions of less than 10 %. The rate constant is slightly lower than reported for homolysis of bibenzyl in tetralin (8.0×10^{-6} s^{-1}) [6]. The apparent first-order rate constant of decarboxylation of **1** and **2** has also been calculated to be $3.7 \pm 0.2 \times 10^{-5}$ s^{-1} and $6.6 \pm 0.2 \times 10^{-5}$ s^{-1}, respectively. The rate constant for decarboxylation of **1** is roughly a factor of 2 slower than that of **2**, suggesting that the decarboxylation mechanism is influenced by the position of the carboxy group on the aryl ring.

On the basis of the product distribution and rate of decarboxylation, the decarboxylation of **1** and **2** is proposed to proceed by an ionic pathway as shown in equation 2. Although the reaction order has not been determined, it is proposed that a second



(2)

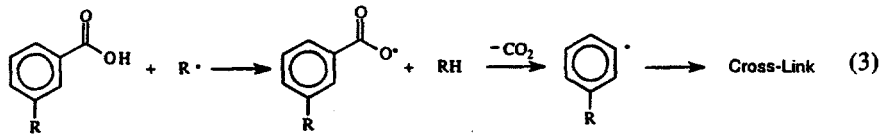
equivalent of starting material is the source of the acid. Catalysis by residual mineral acid, used to precipitate the diacid during its synthesis, is unlikely based on the similar thermolysis results obtained from the thermolysis of **2** prepared by simple precipitation from mineral acid, and **2** purified by dissolving in NH_4OH, titrating with HCO_2H, and washing with water, ether, and acetone. The difference in the decarboxylation rates of **1** and **2** also supports an ionic pathway. If the rate determining step is protonation of the aromatic ring, the *para*-substituent in **2** would stabilize the carbocation intermediate while the *meta*-substituent in **1** would not. The toluic acid and stilbene derivatives are formed by a free-radical reaction analogous to that reported for the thermolysis of bibenzyl [6,9]. Homolysis of **1** produces 2 (HO_2CPhCH_2•) followed by hydrogen abstraction from **1** to form HO_2CPhCH_2CH(•)$PhCO_2H$ (**3**) and toluic acid (Scheme 1). It is predicted that hydrogen abstraction by HO_2CPhCH_2• or



Scheme 1

3 would favor the benzylic C-H bond (86 kcal/mole) over the stronger O-H bond of the carboxylic acid (estimated as 101 kcal/mole). The stilbene derivatives are formed from the disproportionation of **3**, but no products from the coupling of **3** are observed, in contrast to the thermolysis of bibenzyl in which tetraphenylbutane is a major product [9], .

The decarboxylation and cross-linking of aromatic carboxylic acids has been assumed to arise from a free-radical pathway (eq 3), since free-radicals are known to be formed as the

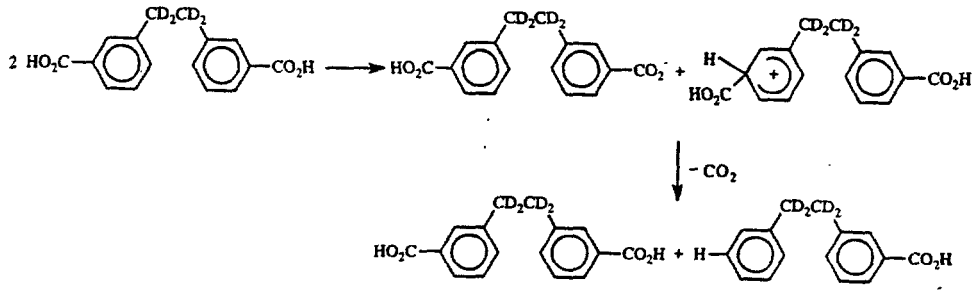


(3)

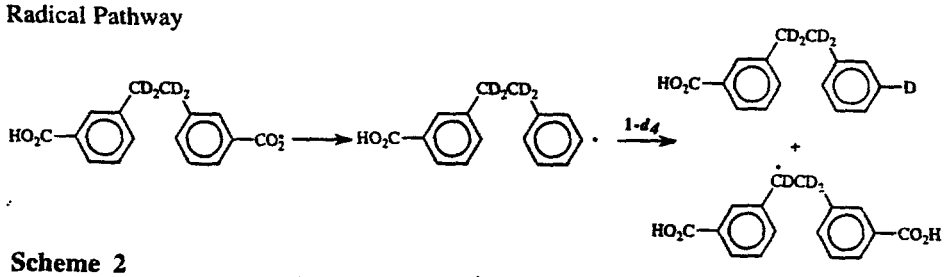
reactive intermediates in the thermolysis of coal. Aryl radicals are known to add to aromatic rings to form biaryls [6]. The data obtained from decarboxylation of **1** and **2** is inconsistent with a free-radical mechanism. Moreover, it is predicted that the hydrogen abstraction from the carboxylic acid in equation 3 should be the rate determining step in this decarboxylation, since it is known that aryl carboxy radicals undergo decarboxylation at rapid rates (*ca.* 10^6 s^{-1} at 23 °C [8]). Thus a free-radical mechanism should not show a difference in the rate of decarboxylation of **1** and **2**, because the carboxy radical is not in conjugation with the aromatic ring.

To further investigate the mechanism for the decarboxylation of **1**, the thermolysis of **1** containing deuterium in the ethylene bridge (**1-d_4**) was investigated. This molecule should allow us to distinguish if decarboxylation is occuring by an ionic pathway (eq 2) or free-radical pathway (eq 3). Decarboxylation by an ionic pathway would place a hydrogen at the 3-position while the free-radical pathway would place a deuterium at the 3-position of the aromatic ring from D abstraction of the aryl radical (Scheme 2). Preliminary data from a 30

Ionic Pathway



Radical Pathway



Scheme 2

min thermolysis of **1-d_4** are given in Table 1, entry 6. Analysis of the deuterium content of the major product, 3-carboxybibenzyl, by GC-MS showed that > 97 % of the product was d_4. No d_5 was detected, which strongly supports our assertion that decarboxylation of **1** is occuring by an ionic pathway. The deuterium content of the *m*-toluic acid is currently under investigation to determine if the benzylic radical can abstract hydrogen from the carboxylic acid to give *m*-toluic acid-d_2 as well as from the ethylene bridge to give *m*-toluic acid-d_3.

Summary and Conclusion

The thermolysis of two aromatic carboxylic acids **1** and **2** have been investigated at 400 °C as models of carboxylic acids in low rank coals. The major decomposition pathway observed is decarboxylation, which mainly occurs by an ionic pathway. This decarboxylation route does not lead to any significant amount of coupling or high molecular weight products that would be indicative of cross-linking products in coal. The pyrolysis of **1** and **2** will be investigated under a variety of conditions that better mimic the environment found in coal to further delineate the role that decarboxylation plays in coal cross-linking chemistry.

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Table 1 Product Distributions Observed from the Thermolysis of *m,m*-$HO_2CPhCH_2CH_2PhCO_2H$ at 400°C for Various Time Intervals.

Entry	1	2	3	4	5	6[c]
Products (mole %)	10 min	30 min	60 min	90 min	120 min	30 min
m-CH_3PhCO_2H	8.2	9.9	10.1	10.3	14.1	9.0
m-$CH_3CH_2PhCO_2H$	0.93	1.6	1.4	1.4	1.7	1.3
$PhCH_2CH_2Ph$	b	1.2	2.4	3.2	4.8	1.2
PhCH=CHPh	b	b	0.1	0.1	0.4	b
m-$HO_2CPhCH_2CH_2Ph$	83.7	80.3	76.4	73.3	82.3	84.6
m-HO_2CPhCH=CHPh	0.7	0.6	1.9	2.5	5.6	0.8
m,m-HO_2CPhCH=$CHPhCO_2H$	5.3	5.9	11.2	9.1	11.2	3.2
Conversion[a]	2.6	9.6	17.3	22.3	33.8	8.1
Mass Balance	97.8	96.0	93.0	94.7	90.0	98.4

a-Based on products identified. b-product not detected. c-1-d_4.

DISCLAIMER