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ACIDS IN CROSS-LINKING PROCESSES IN LOW-RANK COALS***

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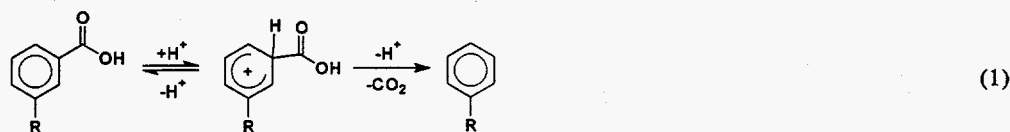
INVESTIGATION OF THE ROLE OF AROMATIC CARBOXYLIC ACIDS IN CROSS-LINKING PROCESSES IN LOW-RANK COALS.*

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INTRODUCTION

In recent years, oxygen functional groups in low-rank coals have clearly been shown to be the major actors in retrograde reactions that inhibit efficient thermochemical processing of low-rank coals. 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 CO₂ and H₂O [1,2]. Pretreatments such as methylation, demineralization, or ion-exchange of the inorganic cations reduce cross-linking and CO₂ evolution in pyrolysis [2a,3a]. In pyrolysis and liquefaction, the exchange of Na⁺, K⁺, Ca⁺⁺, or Ba⁺⁺ into demineralized coal increases cross-linking and CO₂ evolution [3,4]. Solomon et al. has modeled cross-linking in coals by including one cross-link for every CO₂ evolved [2a], while Niksa has modeled the evolution rates and yields of oxygen-containing species by including char links when non-condensable gases are expelled [5]. These results suggest that decarboxylation may occur by a pathway that initiates retrograde (cross-linking) reactions in the coal polymer. However, the mechanism by which decarboxylation occurs in low-rank coals is not known. Hence, it is not clearly understood how decarboxylation leads to cross-linking beyond the suggestion that decarboxylation could be a radical process that involves radical recombination or radical addition reactions. However, the role of decarboxylation in cross-linking processes has been brought into question by Manion et al. by their observation that the decarboxylation of benzoic acid derivatives in tetralin yielded only small amounts of aryl-aryl coupling products [6]. Further, we have recently conducted a study of the pyrolysis of 1,2-(3,3'-dicarboxyphenyl)ethane (1) and 1,2-(4,4'-dicarboxyphenyl)ethane (2) and found that decarboxylation occurs readily between 350-425 °C with no evidence of coupling products or products representative of cross-links [7]. We proposed that decarboxylation occurred primarily by an acid-promoted cationic pathway, and the source of acid was a second carboxylic acid (eq 1). The possible involvement of decarboxylation by a free-radical pathway was ruled out with our finding that no deuterium (<5 mol %) was incorporated into the aryl ring following decarboxylation of 1,1,2,2-tetradeuterio-1,2-(3,3'-



dicarboxyphenyl)ethane at 400 °C [7a,b]. The decarboxylation of 1 and 2 was also investigated in diphenyl ether and naphthalene as inert diluents. In each solvent, the rate of decarboxylation dropped by roughly a factor of 2 upon dilution from the neat liquid to *ca.* 0.4 mole fraction of acid, but further dilution had no effect on the rate, which is contrary to a bimolecular reaction mechanism. This could be a consequence of hydrogen bonding or an intramolecular protonation. Molecular mechanics calculations indicated that 1 and 2 can adopt an appropriate conformation for internal proton transfer from a carboxy group on one ring to the second aryl ring without a significant energy penalty. In addition, the dicarboxylic acid could internally hydrogen bond, which may further complicate the reaction mechanism. Therefore, we have conducted a study of the pyrolysis of a monocarboxybiphenyl, 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (3), to determine if decarboxylation occurs by an ionic pathway in the absence of intramolecular pathways.

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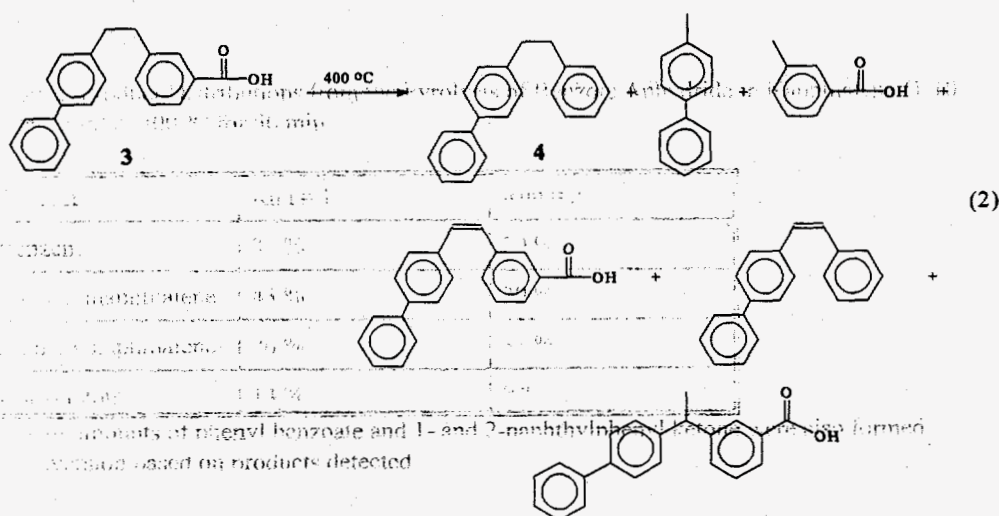
EXPERIMENTAL

1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (**3**) was synthesized as described previously [7d]. The anhydride of **3** was synthesized via dicyclohexylcarbodiimide (DCC) coupling of **3** in THF. 1-(3-carboxaldehydephenyl)-2-(4-biphenyl)ethane (**7**) was synthesized by reduction of **3** to the benzyl alcohol with LiAlH_4 , followed by oxidation to the aldehyde with pyridinium chlorochromate (PCC). 1-(3-(1-naphthyl)phenyl)-2-(4-biphenyl)ethane (**5**) was synthesized by $\text{Pd}(\text{PPh}_3)_4$ coupling of 1-naphthylboronic acid and 1-(3-bromophenyl)-2-(4-biphenyl)ethene followed by hydrogenation to the bibenzyl with Pd/C . Full details of these syntheses will be reported later. Naphthalene (Aldrich, 99.9 %) was used without further purification. 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. Reverse phase HPLC was obtained using a Water's 600E System equipped with a Nova-Pak C18 3.9 mm x 150 mm column (4 μm particle size), and a Water's 996 Diode Array detector using a solvent mixture of 50:50 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ for 10 min then a linear gradient to 90:10 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ at 25 min. Analysis of HPLC data was performed using Water's Millennium software.

Pyrolyses. Pyrolyses in naphthalene were performed by loading pyrex tubes with the appropriate amounts of carboxylic acid and naphthalene and conducting 3 freeze-pump-thaw cycles prior to sealing the tube at 10^{-5} Torr. Neat pyrolyses were performed in an analogous manner with the omission of naphthalene. The pyrolyses were performed in a Carbolite tube furnace, which maintained a temperature of $400 \pm 1^\circ\text{C}$. Following the pyrolysis, the samples were quickly removed from the furnace and cooled in liquid N_2 . The tubes were cracked open, and the solid products were removed with a 2:1 mixture of pyridine: N,O -bis(trimethylsilyl)trifluoroacetamide (BSTFA). Internal standards (2-phenylbenzoic acid and 3,5-dimethylbenzoic acid) were added and the reaction mixtures analyzed by GC and GC-MS. The identities of products from the thermolysis of **3** were determined by GC-MS analysis and were further confirmed by comparison with commercially available or synthesized authentic materials.

RESULTS AND DISCUSSION

Thermolyses of **3** were conducted in sealed, evacuated pyrex tubes at 400°C . The products identities were determined by GC-MS and comparison with authentic materials, either commercially available or independently synthesized, and the reaction products were quantitated by GC. The major products from the thermolysis of neat **3** are shown in equation 2, and a typical



product distribution for a 1 h pyrolysis is given in Table 1, entry 1. Product distributions were similar at higher conversions and mass balances were good (97 % at 40 % conversion). Several other products are formed in the pyrolysis that have not been identified, but based upon the GC

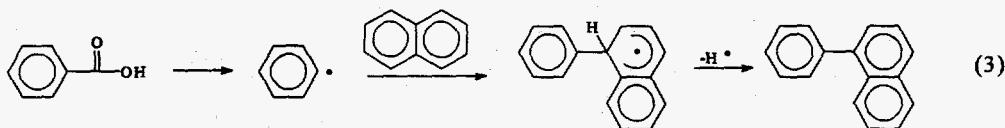
peak area and the good mass balance, the amount of these products are small (<2 mol %).

As observed with diacids **1** and **2** (see Introduction [7]), decarboxylation is the dominant process in the pyrolysis of **3**. The excellent mass balances establish that the decarboxylation pathway does not lead to any significant amounts of coupling or cross-linking products not detected by our analysis. The apparent first-order rate constant for decarboxylation of **3** to 1-(phenyl)-2-(4-biphenyl)ethane (**4**) at 400 °C was $2.8 \pm 0.7 \times 10^{-5} \text{ s}^{-1}$, which is similar to the rate constant for decarboxylation of **1** ($3.7 \pm 0.2 \times 10^{-5} \text{ s}^{-1}$). Based on the similar rate constants for decarboxylation and the similar products distributions of the monoacid and diacids, we propose that the decarboxylation of neat **3** is occurring primarily by the acid-promoted cationic mechanism as previously proposed for the decarboxylation of **1** and **2** (eq 1).

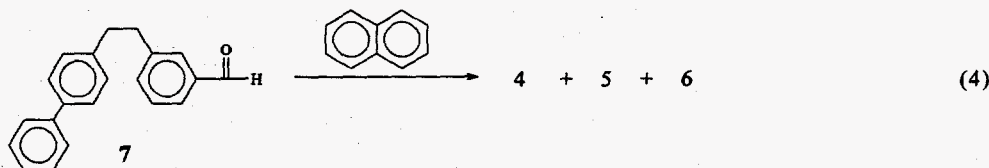
The study of the thermolysis of **3** was extended to dilution (10-fold) in a non-donor solvent, naphthalene, to better mimic the environment of carboxylic acids in coal. The major products from the thermolysis at 400 °C were the same as in the neat pyrolysis (see Table 1, entries 2 and 3), and the mass balances were excellent indicating that we are not missing any significant amount of unidentified products. In naphthalene, there is a small shift in the product distribution as a consequence of a decrease in the rate for the bimolecular decarboxylation reaction while the rate of C-C homolysis remained roughly constant. In addition, two new minor products (< 3 mol %), **5** and **6**, were identified in which naphthalene was grafted onto **4**. The identity of these new products was determined from MS, and the point of attachment to the



aromatic ring was confirmed by independent synthesis of **5**. Similar arylated products were also observed in the thermolysis of **1** diluted in naphthalene (10-fold). Specifically, the major product from the thermolysis of **1** at 400 °C for 45 min was monoacid (59 %), but a small amount of naphthylated products was found (2.7 %). The yield of **5** and **6** was reduced 2-fold by the thermolysis of **3** in a mixture of naphthalene:tetralin (1:1), when compared to a pyrolysis in naphthalene:biphenyl (1:1), indicating the pathway for arylation may involve the formation of an aryl radical as shown in equation 3. Stein has studied the free-radical reaction of aryl radicals, formed from the decomposition of aromatic aldehydes, with aromatic rings in the gas phase at

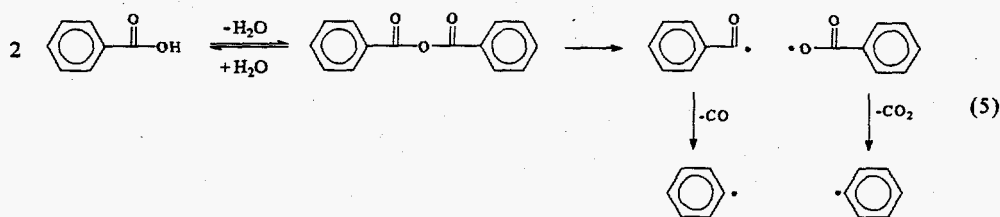


400 and 450 °C [8]. To investigate if **5** and **6** could arise from a free-radical pathway, we studied the pyrolysis of 1-(3-carboxaldehydephenyl)-2-(4-biphenyl)ethane, (**7**). The aryl radical can be produced by homolysis of the benzylic C-C bond of **7** to form benzyl radicals, hydrogen abstraction from the aldehydic hydrogen, followed by rapid decarbonylation. Pyrolysis of **7** under the same dilution conditions used for the acid (10:1, naphthalene:**7**) produced **4**:**5**:**6**, as the major products in a ratio of 1.0:1.1:1.0, respectively (eq 4), showing that **5** and **6** can arise via a



free-radical pathway. On the basis of the product distribution, the ratio of arylation to hydrogen abstraction by the aryl radical is 2:1. However, in the pyrolysis of **3** in naphthalene, >8 times more **4** is produced than arylated products (**5** and **6**) indicating that the majority of the decarboxylation (>80%) can not be produced by a radical pathway, which is consistent with our proposal that an ionic decarboxylation mechanism is dominant.

Formation of **5** and **6** from pyrolysis of **3** suggests that aryl radicals are formed during the pyrolysis. On the basis of bond strengths, it is unlikely that abstraction of hydrogen from the carboxylic acid (O-H 101 kcal/mol [9]) by benzylic radicals (from C-C homolysis of **3**) would be competitive with hydrogen abstraction from the benzylic hydrogens of **3** (86 kcal/mol [10]). At this point, it was unclear how aryl radicals could arise in the pyrolysis of **3**. However, it was later shown that water could affect the yields of **5** and **6**. The results of two runs in which 1.6 and 3.5 eq of H₂O:3 were added are shown in Table 1, entries 4 and 5. These results show that there is *ca.* 2-3-fold reduction in the rate of formation of these coupled products with H₂O present. Water did not have any influence on the ratio of 4:5:6 in the pyrolysis of 7:naphthalene:H₂O (1:10:1.5 molar ratio), indicating that the water does not inhibit the arylation reaction. Therefore, the reduction of products **5** and **6** with the addition of H₂O demands that their formation must come from a pathway that is inhibited by H₂O. One possible route to the formation of an aryl radical that would be sensitive to water is through the decomposition of an anhydride formed from the coupling of two carboxylic acids. Anhydrides are known to be formed if carboxylic acids (such as benzoic acid) are heated under conditions that remove H₂O [11]. As shown in equation 5, homolysis of the C-O bond of the anhydride would produce fragments that could decarboxylate and decarbonylate to form two aryl radicals. Although thermochemical estimates predict that



benzoic anhydride should not decompose by this pathway to any significant extent at 400 °C, we investigated the pyrolysis of benzoic anhydride diluted in naphthalene to determine if the reaction pathway outlined in equation 5 can occur at a reasonable rate at 400 °C (Table 2). Surprisingly, benzoic anhydride decomposed at an average rate of 12 %/h to benzene and 1-and 2-phenylnaphthalene, which is consistent with the formation of aryl radicals from the anhydride decomposition. Furthermore, the radical nature of the anhydride decomposition is supported by the formation of small amounts of binaphthyls in the pyrolysis: i.e. naphthyl radicals are formed by abstraction of hydrogen by an aryl radical or hydrogen atom, followed by coupling with a second naphthalene. Hence, if an anhydride could be formed in the pyrolysis of the acids, it appears it could produce phenyl radicals by its decomposition under these reaction conditions.

Because it is unlikely that the anhydride would be detectable by GC, we investigated whether the anhydride of **3** was formed during the pyrolysis of **3** in naphthalene by HPLC. In the pyrolysis of 3:naphthalene (1:4), at 400 °C for 1.5 h, a small amount of anhydride was found. The amount of anhydride is currently unquantified but most likely its formation is ~1% of the starting amount of **3** based on peak area. This is supported by the excellent mass balances obtained in these pyrolyses (Table 1), which do not include the anhydride. The identity of the anhydride was confirmed by comparison of the HPLC retention time of the product formed in the pyrolysis with an authentic sample of the anhydride prepared by independent synthesis. While the anhydride was detected without H₂O added, the addition of H₂O (1.5 eq to **3**), inhibited the formation of the anhydride. These results show that the anhydride can be formed in the pyrolysis of **3**, its formation is inhibited by H₂O, and benzoic anhydride decomposes at a reasonable rate to produce arylated products. More importantly, if we estimate that the conversion of the anhydride of **3** will be the same as benzoic anhydride, only ~1-3 % of the starting acid needs to be converted to the anhydride to produce the amount of coupling products observed in the pyrolysis as shown in Table 1. This calculation does not take into account any chain chemistry that may also be operating as a result of anhydride decomposition in the presence of carboxylic acids that could potentially lower the amount of anhydride needed to produce the coupling products.

SUMMARY AND CONCLUSION

The pyrolysis of **3** was studied both neat and diluted in naphthalene to determine the role of thermal decarboxylation in the thermal processing of low-rank coal. The mechanism of decarboxylation proceeds primarily by an acid-promoted ionic pathway that does not lead to cross-linking or coupling products. However, with a 10-fold dilution in naphthalene, 10-15 % of

the carboxylic acid lost can result in a cross-link by a pathway involving the formation of an aryl radical at the ring position of the carboxylic acid. The radical pathway can be reduced by a factor of 2 either by tetralin (in 1:1 mixtures with naphthalene) or H₂O. These preliminary results indicate that the radical pathway, in part, arises as a result of the formation and decomposition of the anhydride of 3. Further studies on the mechanism of the anhydride decomposition pathway and the influence of the anhydride decomposition in the presence of aromatic carboxylic acids are currently in progress. In addition, we are investigating further why the cross-linking is not evident in the pyrolysis of neat 3.

In reference to the behavior of low-rank coals, the results of this study suggest that carboxylic acids may lead to a small amount of cross-linking; however, it appears unlikely that the majority of acid decarboxylations produce a cross-link. If it is true that a cross-link is made in coal for every CO₂ evolved, there must be additional chemistry other than decarboxylation involved in cross-link formation. In addition, it is likely that the aromatic carboxylic acids in low-rank coals are contained on rings that contain electron donating groups, such as methoxy groups. The presence of these electron-donating substituents should increase the rate of decarboxylation by the ionic pathway, which could further minimize the amount of cross-linking observed from carboxy groups. However, while the results of this paper and our previous papers have established a framework for understanding the thermal chemistry of carboxylic acids, it should be realized that the results from our model compounds do not consider the restricted mass transport that would exist in coal. In addition, the carboxylic acids in low-rank coal may be present as carboxy salts and not as free carboxylic acids. These features need to be further explored before the role of decarboxylation and cross-linking can be fully evaluated.

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Table 1. Product Distributions from the Pyrolysis of 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (3) at 400 °C for One Hour Under Various Conditions.

Entry	1	2	3	4	5
Product (mole %) ^a	Neat	10 :1 Naph:3	10 :1 Naph:3	10 :1:1.6 Naph:3: H ₂ O	10 :1: 3.5 Naph:3: H ₂ O
PhCO ₂ H	0.3	0.2	0.2	0.2	nd
3-CH ₃ PhCO ₂ H	13.6	24.6	27.0	26.5	26.0
3-CH ₃ CH ₂ PhCO ₂ H	0.6	0.9	1.0	0.9	0.6
4-Ph-PhCH ₃	14.9	25.7	28.0	27.4	27.2
4-Ph-PhCH ₂ CH ₃	0.5	0.8	0.9	0.7	0.4
4-Ph-PhCH(CH ₃)Ph	0.2	0.2	nd	0.1	Nd
4-Ph-PhCH ₂ CH ₂ Ph (4)	44.9	27.0	20.2	21.9	25.2
4-Ph-PhCH=CHPh	1.1	0.5	0.5	0.4	0.7
4-Ph-PhCH ₂ PhCO ₂ H	0.8	0.4	0.4	0.5	nd
4-Ph-PhCH(CH ₃)PhCO ₂ H	7.8	4.7	5.0	5.0	3.6
4-Ph-PhCH=CHPhCO ₂ H	15.0	12.3	14.0	15.0	15.2
4-Ph-PhCH ₂ CH ₂ Ph-3-(1-naphthyl) (5)	nd	1.4	1.4	0.6	0.5
4-Ph-PhCH ₂ CH ₂ Ph-3-(2-naphthyl) (6)	nd	1.5	1.4	0.7	0.4
Conversion ^b	12.6	10.8	9.5	10.35	10.0
Mass Balance	98.1 %	100.1	99.7	99.8	100.0

a-Based on products detected and quantified.

b-Conversion based on products recovered.

Naph=naphthalene

nd-not detected

Table 2. Product Distributions from the Pyrolysis of Benzoic Anhydride in Naphthalene (1:10 molar ratio) at 400 °C for 50 min.

Product ^a	Run # 1	Run # 2
Benzene	31 %	30 %
1-Phenylnaphthalene	43 %	39 %
2-Phenylnaphthalene	26 %	31 %
Conversion ^b	14 %	9 %

a-Small amounts of phenyl benzoate and 1- and 2-naphthylphenyl ketone were also formed.

b-Conversion based on products detected.