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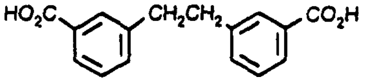
ABSTRACT

It has been proposed that carboxylic acids and carboxylates are major contributors to cross-linking reactions in low-rank coals and inhibit its thermochemical processing. Therefore, the thermolysis of aromatic carboxylic acids was investigated to determine the mechanisms of decarboxylation at temperatures relevant to coal processing, and to determine if decarboxylation leads to cross-linking (i.e., formation of more refractory products). From the thermolysis of simple and polymeric coal model compounds containing aromatic carboxylic acids at 250-425 °C, decarboxylation was found to occur primarily by an acid promoted ionic pathway. Carboxylate salts were found to enhance the decarboxylation rate, which is consistent with the proposed cationic mechanism. Thermolysis of the acid in an aromatic solvent, such as naphthalene, produced a small amount of arylated products (<5 mol%), which constitute a low-temperature cross-link These arylated products were formed by the rapid decomposition of aromatic anhydrides, which are in equilibrium with the acid. These anhydrides decompose by a free radical induced decomposition pathway to form aryl radicals that can add to aromatic rings to form cross-links or abstract hydrogen. Large amounts of CO were formed in the thermolysis of the anhydrides which is consistent with the induced decomposition pathway. CO was also formed in the thermolysis of the carboxylic acids in aromatic solvents which is consistent with the formation and decomposition of the anhydride. The formation of anhydride linkages and cross-links was found to be very sensitive to the reactions conditions. Hydrogen donor solvents, such as tetralin, and water were found to decrease the formation of arylated products. Similar reaction pathways were also found in the thermolysis of a polymeric model that contained aromatic carboxylic acids. In this case, anhydride formation and decomposition produced an insoluble polymer, while the *O*-methylated polymer and the non-carboxylated polymer produced a soluble thermolysis product

INTRODUCTION

It has been proposed that carboxylic acids and carboxylates, which are prevalent in low-rank coals, are major contributors to retrograde reactions that inhibit efficient thermochemical processing of low-rank coals. In the pyrolysis and liquefaction of low-rank coals, low-temperature (T <400 °C) cross-linking reactions have been correlated with the loss of carboxyl groups and the evolution of CO_2 and H_2O.[1,2] Solomon et al. has modeled the pyrolytic loss of solvent swelling in coal by including one additional cross-link for every CO_2 evolved,[2a,c] while Niksa has modeled the evolution rates and yields of oxygen bearing spies by including char links when noncondensable gases (CO_2, H_2O, and CO) are expelled. Pretreatments such as methylation or demineralization reduce cross-linking and CO_2 evolution in pyrolysis.[2a,3,4] Exchange of Na^+, K^+, Ca^{++}, or Ba^{++} into demineralized coals increase cross-linking and CO_2 evolution in pyrolysis and liquefaction.[2,5] These results suggest that the reaction pathways that lead to decarboxylation may play an important role in the cross-linking of the coal polymer. However, the chemical pathways for decarboxylation of aromatic carboxylic acids are not understood at temperatures relevant to coal processing (300-450 °C).[6] Therefore, to gain a better understanding of the role of decarboxylation in cross-linking reactions in low-rank coals, we have studied the liquid phase pyrolysis of simple (I-3) and polymeric (4-6) model compounds containing aromatic carboxylic acids from 250–425 °C (see below). These model compounds were chosen because aromatic carboxylic acids are known to exist in low-rank coals,’ their decarboxylation pathways can lead to cross-linking (see below), and homolysis of the weak bibenzylic bond provides a constant source of free-radicals that mimics some of the reactive intermediates found during the thermal processing of coal.’ Polymeric models were also investigated to study the impact of restricted mass transport on decarboxylation reaction pathways. A brief overview of the findings of these investigations will be presented as well as new data on pyrolysis of carboxylate salts.



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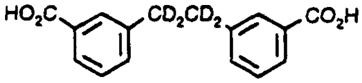

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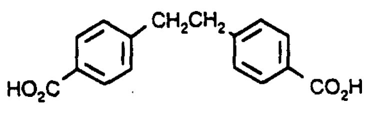

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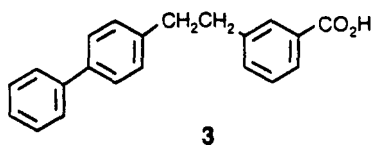

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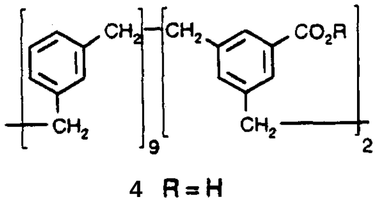
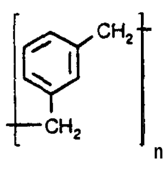


4 R = H

6 R = CH_3



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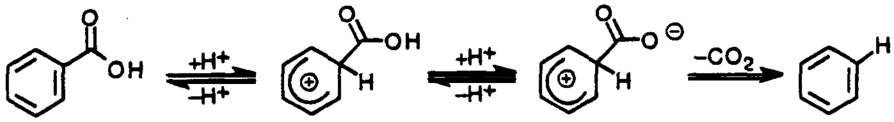
DECARBOXYLATION MECHANISMS

The reaction pathways for decarboxylation of aromatic carboxylic acids are surprisingly complex and **dependent** on the reaction **conditions.**[9] The two major pathways for aromatic decarboxylation reactions are ionic and free radical. In aqueous solution, ionic decarboxylations can be catalyzed by acid or base. Acid-catalyzed decarboxylation reactions are the most common, and the reaction pathways are dependent on acid concentration, ionic strength, and substituents on the aromatic **ring.**[9] **In** dilute acid, *ipso*-**protonation** of the aromatic ring is the rate-determining step (eq 1), while in highly acidic solutions, the rate **determining** step is decarboxylation of the aromatic cation. Electron donating substituents accelerate the **acid-catalyzed** decarboxylation reaction. In the absence of **an** acid-catalyst, decarboxylation of carboxylate salts or carboxylic acids with strongly electron withdrawing **substituents,** such as **2,4,6-trinitrobenzoic** acid, occur by **rate-determining unimolecular** elimination of carbon dioxide **from** the anion (q 2).



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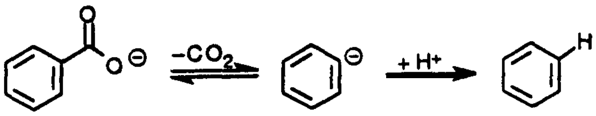
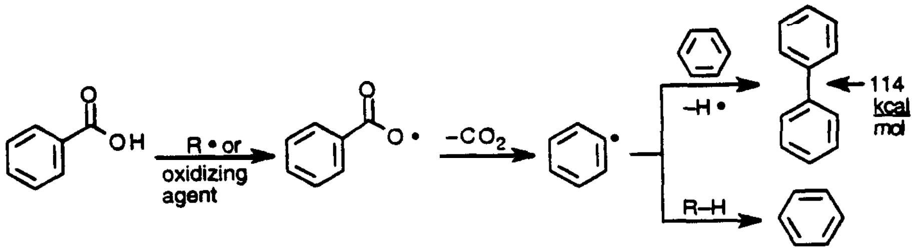


(2)

Decarboxylation of aromatic carboxylic acids can also occur by a free-radical pathway. Since free radicals are known to be formed as reactive intermediates in the **thermolysis** of coal, the free-radical decarboxylation pathway has been viewed as a possible route to cross-linking. Hydrogen abstraction or electron transfer to an **acceptor**[10] can form the **benzoyloxyl** radical **($PhCO_2$•)** which will rapidly decarboxylate (log k (s^{-1}) = 12.6 − 8.6 **kcal mol^{-1}/2.303RT)**[11] to form an aryl radical (eq 3). This highly reactive intermediate can abstract hydrogen or competitively add to an aromatic ring to form **biaryls.**[12] This **aryl-aryl** linkage is thermally **stable** at T **≤400 °C** and **would constitute a** low-temperature **cross-link.**



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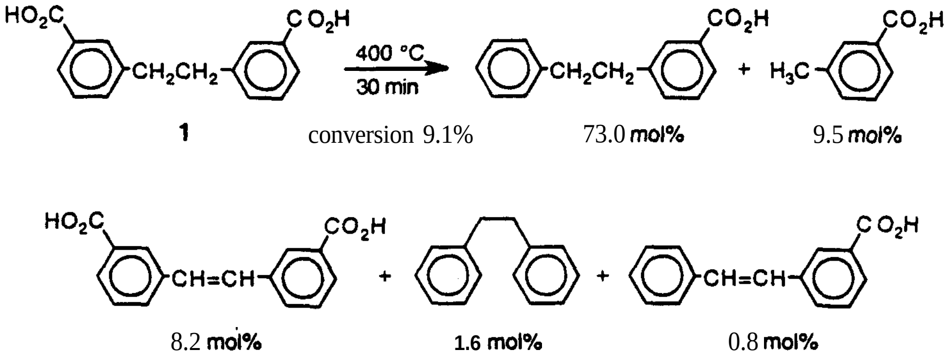
PYROLYSIS OF THE ACID

The liquid phase **thermolyses** of 1,[13] **2,**[13] **3,**[14] and substituted benzoic acids were conducted between **325-425 °C** in sealed, **degassed,** Pyrex tubes. The reaction mixtures were silylated with *N,O*-**bis(trimethylsilyl)trifluoroacetamide** (since 1 **and 2** were insoluble in most solvents) and **quantitated** by GC with FID. The products were identified by GC-MS and by **comparison** to authentic materials. Details of the experimental procedure can be found in references.[13,14] For all the compounds studied, decarboxylation was the major product from the thermolyses. Excellent mass balances were obtained in these thermolyses even at high conversion (for 1, 97% mass balance at 67% conversion) indicating that no significant amounts of high molecular weight products were undetected by the GC analysis. A typical product distribution from the thermolysis of 1 at 400 °C for 30 min (9.1% conversion) is shown below. Additional products



detected included 1,1-(3,3'-dicarboxyphenyl)ethane (4.6 mol%), 3-ethylbenzoic acid (1.3 mol%), 1-(3-carboxyphenyl)-1-phenylethane (0.3 mol%), and benzoic acid (0.1 mol%). The average conversion for a set of four 30 mm thermolyses at 400 °C was 9 ± 1%. and the average mass balance was 99 ± 2%. At 400 °C, the apparent first-order rate constants *for* decarboxylation of 1, 2, and 3 at low conversion was 3.7 ± 0.2 x 10^{-5}, 6.6 • 0.2 x 10^{-5}, and 2.8 ± 0.7 x 10^{-5} s^{-1}, respectively. The factor of two difference in the rate constant for decarboxylation of 2 relative to 1 and 3 indicates that the rate of decarboxylation is influenced by the position of the carboxyl group on the aryl ring (see below). The Arrhenius parameters for the apparent first-order rate constant for the decarboxylation of 1 to 1-(3-carboxyphenyl)-2-phenylethane was found to be log k (s^{-1}) = (9.4 ± 0.4) - (43 ± 1) kcal mol^{-1}/2.303RT. On the basis of the product distributions, mass balances, and decarboxylation rates, the decarboxylation of 1.2. and 3 was proposed to proceed by an acid promoted, ionic pathway as shown in q 1.

To provide additional evidence of the decarboxylation mechanism, the tbermolysis of *p*-toluic acid and p-toluic acid-d, (p-$CH_3C_6H_4CO_2D$) were compared at 400 °C.[15] The deuterium isotope effect k_H/k_D, determined from the average of four tbermolyses on each substrate, was 2.1±0.1 indicating tbat protonation of the aromatic ring is a rate-determining step (see below). The effect of electron donating substituents on the tbermolysis of benzoic acid was also investigated at 400 °C in the liquid phase. As previously found, decarboxylation to the substituted benzene was the major product. A Hammett plot[16] was constructed for the rate of decarboxylation (Figure 1), and a *better* linear correlation was obtained with σ^+ (R = 0.999) than with σ (R= 0.950). The slope (p) for the plot vs σ^+ was -5.2 indicating that a positive

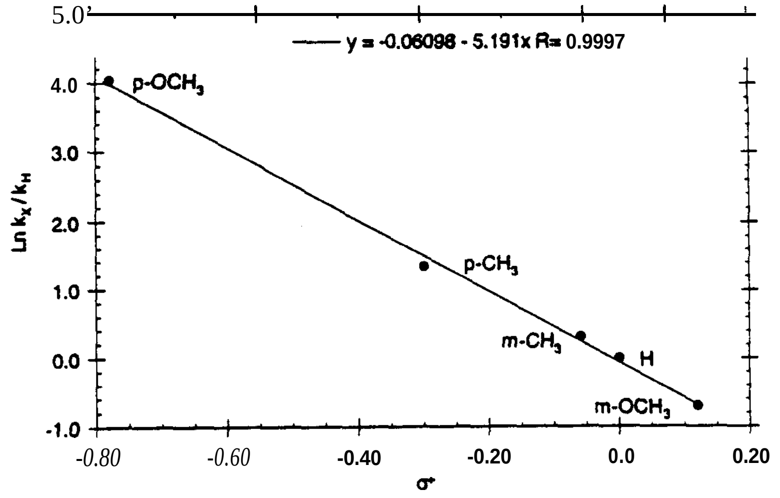
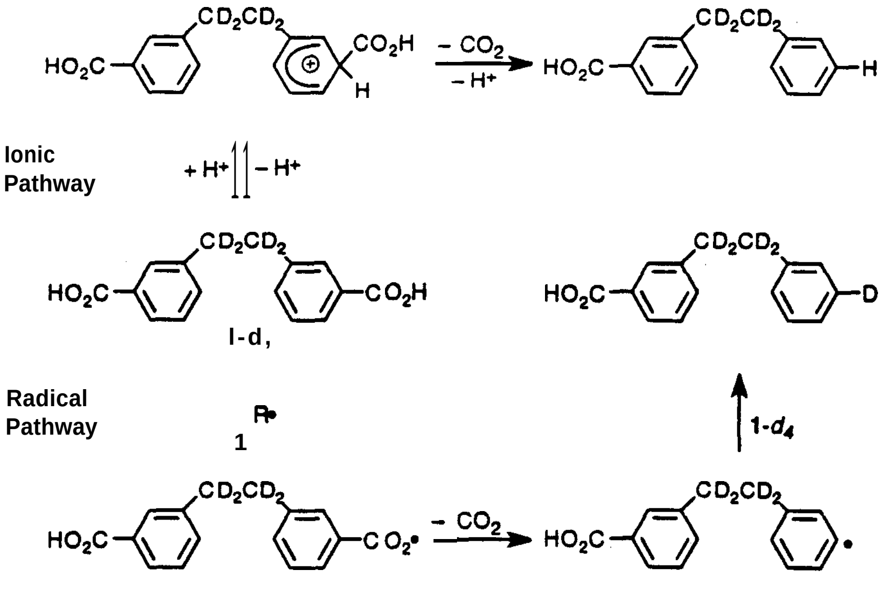


Figure 1. Hammett plot for the liquid phase tbermolysis of substituted benzoic acids at 400 °C.

charge develops in the transition state in the decarboxylation, which supports the proposed cationic mechanism for decarboxylation. Since in low-rank coals all the aromatic rings are substituted with electron donating substituents, such as alkyl and oxygen functional groups," it is predicted that acid promoted decarboxylation reactions will be very rapid at 400 °C ($t_{1/2}$ < 30 *min).*

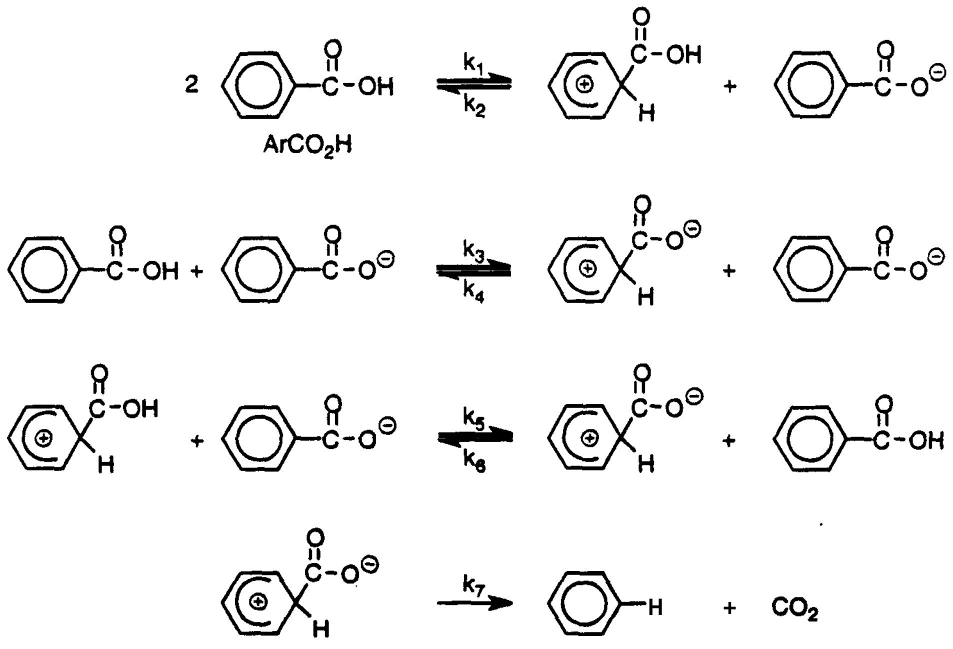
To investigate the possibility that the free-radical pathway may also contribute to the decarboxylation reaction, the thermolysis of 1 containing deuterium in the ethylene bridge (1-d_4) was investigated.’[3] If decarboxylation proceeds by the acid-promoted ionic pathway, a d_4-monoacid will be produced, while a free-radical pathway would place a deuterium at the 3-position of the aromatic ring (from D abstraction by the aryl radical) to form a d_5-monoacid (Scheme 1).[18] The thermolysis of 1-d_4 was performed at 325 °C and 400 °C, and the product distribution was similar to that reported for 1. At conversions ranging from 3-9%, GC-MS analysis of the 1-(3-carboxyphenyl)-2-phenylethane product showed no *evidence of a d_5 -species* (<5%), based upon the comparison of the observed and calculated M^+ and $(M+1)^+$ peaks for the trimethylsilylated derivative of the d_4-monoacid. These data provide convincing evidence that decarboxylation of 1 is occurring predominantly by an ionic pathway in the neat liquid.



Scheme 1

PYROLYSIS *OF* CARBOXYLATE SALTS

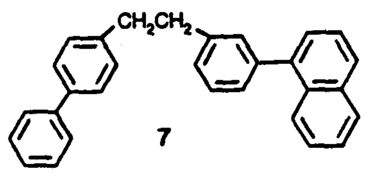
In coal, many of the carboxylic acids exist as carboxylate salts.[19] Exchange of inorganic cations, such as Na^+, K^+, Ca^{++}, or Ba^{++}, into demineralized low-rank coals can significantly decrease liquefaction yields and increase cross-linking.[2,5] For example, in the liquefaction of Zap lignite (400 °C, 30 min, tetralin, H_2), exchange of potassium cations into an acid demineralized coal decreased liquefaction yields 40% compared to the demineralized coal.[3,4] Thermolysis of the dipotassium salt of **1** was investigated at 400 °C for 30 min neat, in tetralin, and in naphthalene.[20] No thermolysis products were detected and **1** was recovered unreacted (>99 mol%). Calcium benzoate was also found to be relatively stable at 400 °C (0.05% conversion to benzene in lh). Addition of a small amount of water (l-3 equiv) to the reaction tubes did not significantly alter the conversions. However, if calcium benzoate was added to benzoic acid, the rate of decarboxylation increased. For example, the decarboxylation of benzoic acid increased by a factor of 7.7, 12.3 and 14.8 by me addition of 4.8, 11.1, and 15.1 mol% calcium benzoate, respectively. In the thermolysis of substituted benzoic acids, Manion et al. found that bases, such as pyridine. accelerated the decarboxylation of benzoic acid.” It was proposed that decarboxylation occurred by the anionic mechanism (eq 2). However, the cationic mechanism is still consistent with these results (eq 1), and a new mechanistic pathway does not have to be invoked to rationalize these experimental results. In the decarboxylation of 4-aminobenzoic acids in dilute aqueous acid, it was concluded either ipso-protonation of the aromatic ring (k’) or loss of the carboxyl proton (k_5) is wholly or partially rate controlling (Scheme 2).[21] If the anion decarboxylates, protonation of the aromatic ring is rate controlling (k_3). Thus, if both ipso-protonation and proton loss from the carboxylic acid are rate controlling, the rate of decarboxylation would be accelerated for the carboxylate salt. This prediction was confirmed by Kaeding’s study on the impact of benzoate salts on the decarboxylation of salicyclic acid in benzoic acid at 200-230 °C.[22] All the benzoate salts enhanced the decarboxylation rate, although the magnitude varied considerably with the metal. For example, the potassium, sodium, and calcium benzoate accelerated the decomposition of salicyclic acid at 212 °C by a factor of 16.1, 10.7 and 6.3, respectively, and the decarboxylation rate was directly proportional to the concentration of the salt. Thus, decarboxylation of carboxylic acids and their salts can be described by the cationic mechanism shown in Scheme 2. In the presence of a weak base, carboxylate salts are formed and a similar series of reactions can be proposed. Moreover, anilinium and pyridinium ions have been shown to catalyze the decarboxylation of salicylic acid.” Thus, a new mechanism does not have to be proposed for the base or salt catalyzed decarboxyiation of aromatic carboxylic acids.



Scheme 2

ANHYDRIDE FORMATION

The thermolysis of 3 was also studied in a non-hydrogen donor solvent, naphthalene, at 400 °C. In a IO-fold excess of naphthalene, the major products were the same as in the neat *thermolysis except* for the formation of two new minor products (<3 mol%) 7 and 8, which constitute cross-linked products. Thermolysis of 1 and 2 in naphthalene also produced naphthylated products, but the yield of these products was ca. three times smaller than that for 3.



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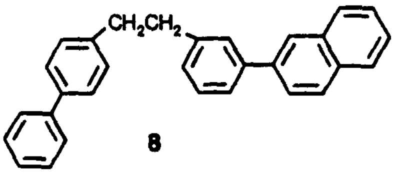

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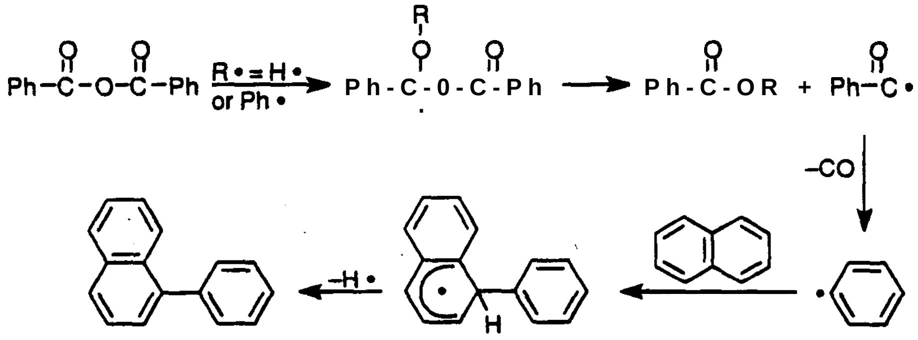
Arylated products were also found when biphenyl was used as the solvent, and 1- and 2-phenylnaphthalene were found in the thermolysis of benzoic acid in naphthalene. The formation of 7 and 8 were reduced by tetralin, a hydrogen donor solvent, indicating that the arylation reaction proceeded by a free radical pathway. The arylated products could also be reduced by small amounts of water (0.5-3 equiv).

The formation of small quantities of arylated products in the aromatic solvents was surprising on the basis of the liquid phase experiments. The yield of arylated products was found to be very sensitive to the reaction conditions and trace amounts of water, and at times, it was very difficult to obtain reproducible data. After the thermolysis of many model *compounds had* been investigated, it was concluded that the arylated products arise from formation and decomposition of aromatic anhydrides. In the thermolysis of benzoic acid in naphthalene (2.5 equiv) at 400 °C, a small amount of benzoic anhydride (ca 1.4%) was observed in addition to benzene (1.2%). 1-phenylnaphthalene (0.06%), and 2-phenylnaphthalene (0.06%). When water (0.5 equiv) was added to the mixture of benzoic acid and naphthalene, benzoic anhydride was not observed. In the thermolysis of 3 in naphthalene, a small amount of the anhydride of 3, (0.4%), was observed by HPLC and by LC-MS (by comparison with an authentic sample). These studies confirmed that anhydrides could be formed under the sealed tube reaction conditions used in this study and that small amounts of water minimize their formation.

Next, the thermolysis of the anhydrides were investigated since there was little literature information on the pyrolysis of aromatic anhydrides at moderate temperatures (<500 “C). It was discovered that the anhydrides decomposed very rapidly under the reaction conditions. The decomposition of benzoic anhydride (7.5% conversion) at 400 °C in naphthalene (10 equiv) was ca. 8 times faster than that for benzoic acid (0.97% conversion) under similar reaction conditions. The major products from the thermolysis of benzoic anhydride in naphthalene were benzene (29.5 mol%), 1-phenylnaphthalene (40.4 mol%), 2-phenylnaphthalene (26.4 mol%) and phenyl benzoate (6.2 mol%). The anhydride of 3 also decomposed more rapidly than 3 (ca. 22-times faster) at 400 °C in naphthalene. The yield of arylated products was also shown to be sensitive to the nature of the aromatic acceptor (i.e., ease and reversibility of addition) and concentration of hydrogen donors.

The high conversions for the aromatic anhydrides were surprising. The C(=O)–O bond dissociation energy for benzoic anhydride was estimated as 84 kcal mol^{-1}.[14] At 400 °C, C–O homolysis (to form the $PhCO\bullet$ and $PhCO_2\bullet$) would not occur to any significant extent (<<1%). Therefore, it was proposed that the decomposition of the aromatic anhydride occurred by an induced homolysis reaction (q 4), which has been observed in the decomposition of benzoyl



(4)

peroxide.[24] The induced decomposition is an addition-elimination reaction in which radicals add to the anhydride (most likely the C=O bond) and cleave to form a stable product, such as phenyl benzoate, and a new chain carrying radical, i.e., the benzoyl radical. The benzoyl radical will rapidly decarbonylate (log k (s^{-1}) = 14.6 – 29.4 kcal mol^{-1}/2.303RT)[25] to form the phenyl radical. The phenyl radical can add to an aromatic ring to form an arylated product" and produce a hydrogen atom, which can continue the chain reaction.[26] The induced decomposition pathway also requires that more CO be formed that CO_2. In the thermolysis of benzoic anhydride and the anhydride of 3, the ratio of $CO:CO_2$ was 3:1 and 25:1, respectively. The excess CO is consistent with the induced decomposition pathway and inconsistent with pure homolysis. In the thermolysis of acid 3 in naphthalene (10 equiv), the ratio of $CO:CO_2$ is 1:4. Thus, in the absence of water, small amounts of the aromatic anhydrides are in equilibrium with the parent carboxylic acid. Under free radical conditions, the anhydride undergoes a rapid free radical induced decomposition reaction, which produces aryl radicals that can lead to cross-linked products. Water and hydrogen donor solvents can reduce the yield of cross-linked products. However, can this sequence of reactions occur in the polymeric network structure of coal? To investigate this possibility, polymeric models of aromatic carboxylic in low-rank coals were prepared and their thermal chemistry investigated

THERMOLYSIS OF POLYMER MODEL

The polymer model compound 4 was prepared with 2.3 acids per 100 carbons,[27] which is similar to the concentration of carboxylic acids in Beulah-Zap coal, 2.2 acids per 100 carbons." Overall, the TGA behavior of 4 is analogous to that reported for low-rank coals in which CO_2 evolution occurs prior to tar evolution and *O*-methylation reduces char yield (i.e., cross-linking).[2,27] The carboxylated polymer 4, forms ca. 2.4 times more char upon heating to 800 °C than the non-carboxylated polymer 5. This indicates that the carboxylic acids are enhancing cross-linking in the polymer. Pyrolysis of 4 at 400 °C in a T-shaped tube, in which the volatile products are removed from the reaction, produced significant amounts of a THF insoluble residue (74 ± 2 wt%) independent of the thermolysis time (15-60 min). However, the thermolysis of 5 and 6 at 400 °C for 60 min produced a THF soluble residue. FTIR and solid-state ^{13}C NMR analysis of the THF insoluble residue confirmed the presence of the aromatic anhydride linkage. Thermolysis of 4 in a sealed tube, in which the volatile products were not allowed to escape, produced a THF soluble product and no anhydride was observed by FTIR. Thus, aromatic anhydrides can form low-temperature cross-links that hold the polymer structure together. However, if the anhydride linkages were completely hydrolyzed (confirmed by FTIR), the polymer remained insoluble. It is proposed that the anhydride linkages in the polymer decompose by an induced decomposition reaction to form aryl cross-links as was observed for the simple model compounds. In support of this mechanism, CO evolution is observed in the TG-MS experiments before significant depolymerization of the polymer backbone occurs. Thus, the small amount of cross-linking observed in the simple model compounds is enhanced in the polymer models. However, the extent of anhydride formation and cross-linking is very sensitive to the experimental conditions and the presence of water. Can similar chemistry occur in the thermal processing of low-rank coal? To answer this question, additional characterization studied are need on low-rank coals to determine if carboxylic acids form anhydrides during pyrolysis.

SUMMARY

The thermolysis of aromatic carboxylic acids was investigated to determine the mechanisms of decarboxylation at temperatures relevant to coal processing, and to determine if decarboxylation leads to cross-linking (i.e., formation of more refractory products). From ‘he thermolysis of simple and polymeric coal model compounds containing aromatic carboxylic acids at 250-425 °C, decarboxylation was found to occur primarily by an acid promoted ionic pathway. Carboxylate salts were found to enhance the decarboxylation rate, which is consistent with the proposed cationic mechanism. Thermolysis of the acid in an aromatic solvent, such as naphthalene, produced a small amount of arylated products (<5 mol%), which constitute a low-temperature cross-link. These arylated products were formed by the rapid decomposition of aromatic anhydrides, which are in equilibrium with the acid. These anhydrides decompose by a free radical induced decomposition pathway to form aryl radicals that can add to aromatic rings to form cross-links or abstract hydrogen. Large amounts of CO were formed in the thermolysis of the anhydrides which is consistent with the induced decomposition pathway. CO was also formed in the thermolysis of the carboxylic acids in aromatic solvents which is consistent with the formation and decomposition of the anhydride. The formation of anhydride linkages and cross-links was found to be very sensitive to the reactions conditions. Hydrogen donor solvents, such as tetralin, and water were found to decrease the formation of arylated products. Similar reaction pathways were also found in the thermolysis of a polymeric model that contained aromatic carboxylic acids. In this case, anhydride formation and decomposition produced an insoluble polymer, while the *O*-methylated polymer and the non-carboxylated polymer produced a soluble thermolysis product

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