MECHANISTIC INVESTIGATIONS INTO THE DECARBOXYLATION OF AROMATIC CARBOXYLIC ACIDS

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MECHANISTIC INVESTIGATIONS INTO THE DECARBOXYLATION OF AROMATIC CAREOXYLIC ACIDS

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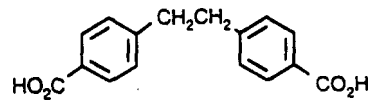
ABSTRACT

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



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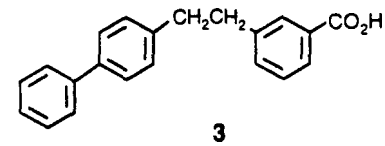

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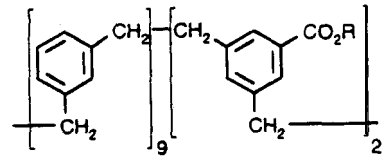
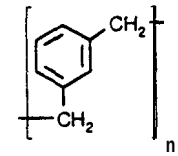


4 R = H
6 R = CH_3



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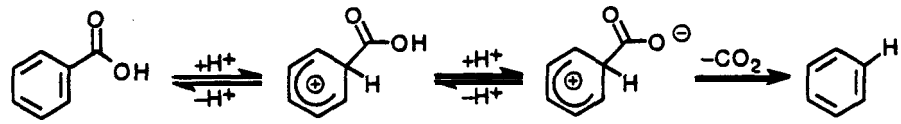
DECARBOXYLATION MECHANISMS

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),



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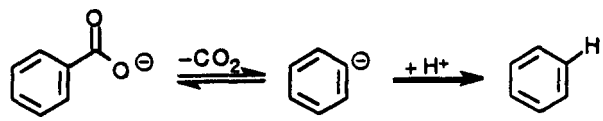

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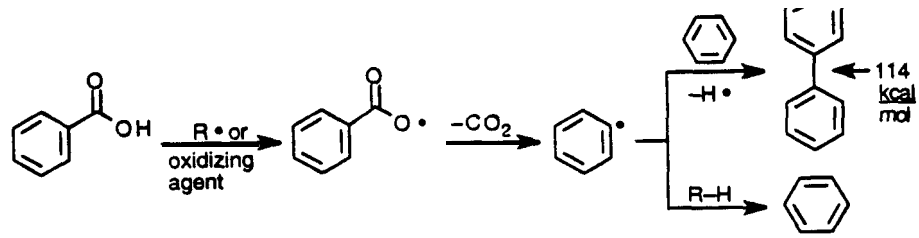
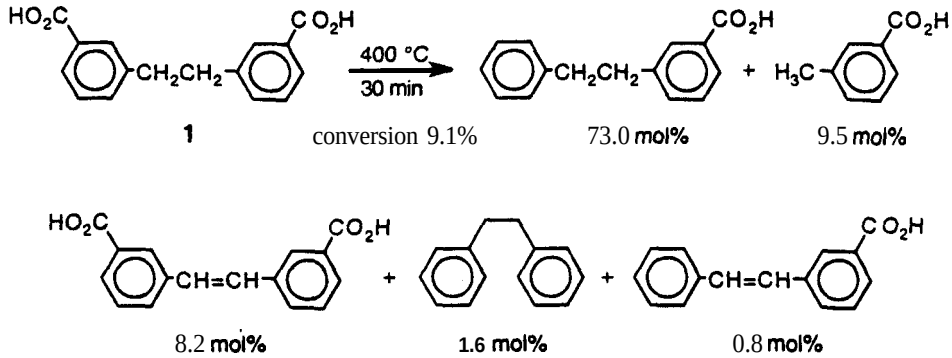
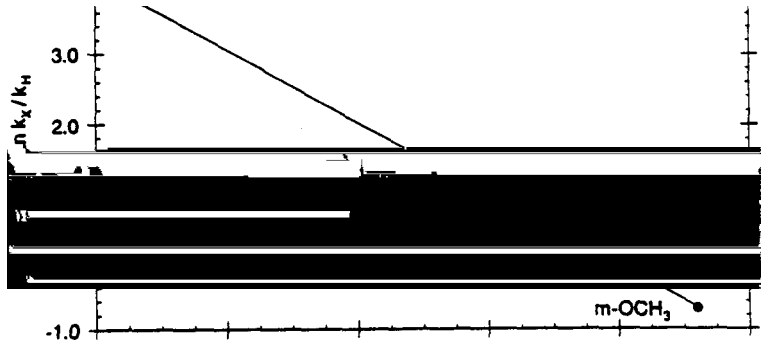


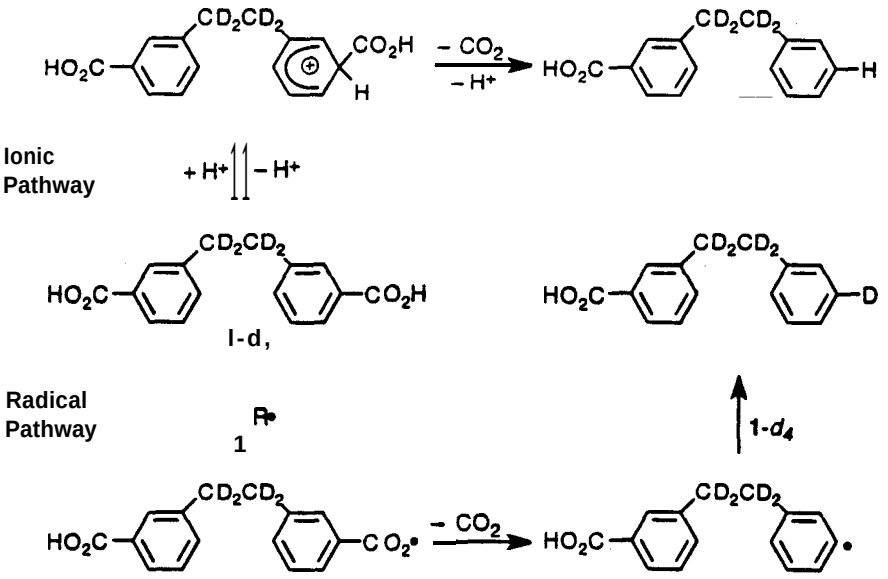
all the compounds studied, decarboxylation was the major product from the thermolyses. Excellent mass balances were obtained in these thermolyses even at high conversion (for 1, 97% mass balance at 67% conversion) indicating that no significant amounts of high molecular weight products were undetected 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



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.[13] 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.

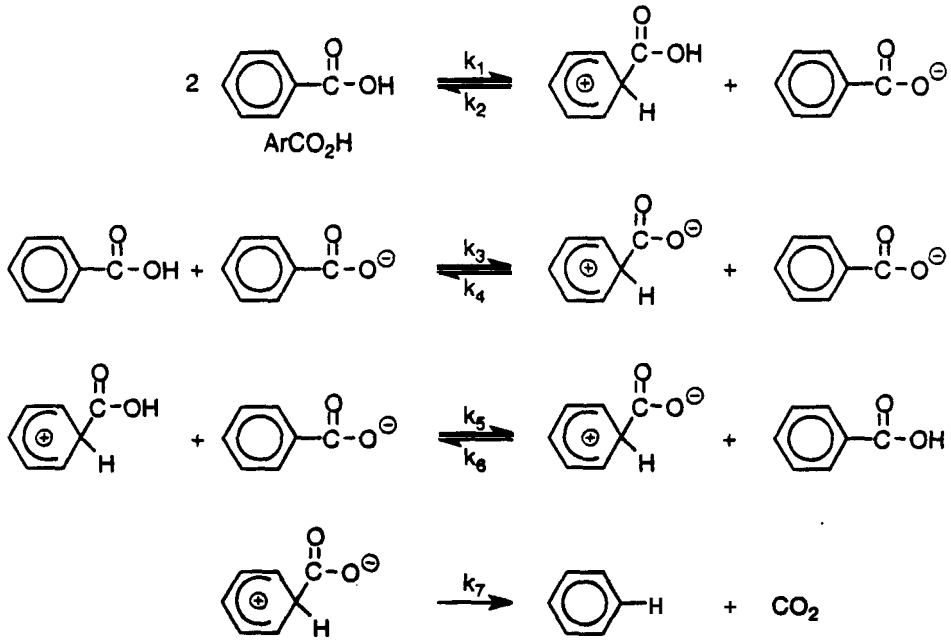


Scheme 1

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,

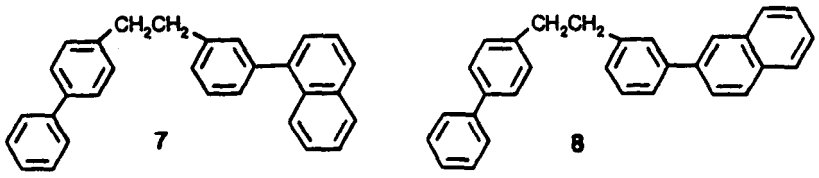
anilinium and pyridinium ions have been shown to catalyze the decarboxylation of salicylic acid." Thus, a new mechanism does not have to be proposed for the base or salt catalyzed decarboxyiation of aromatic carboxylic acids.



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.

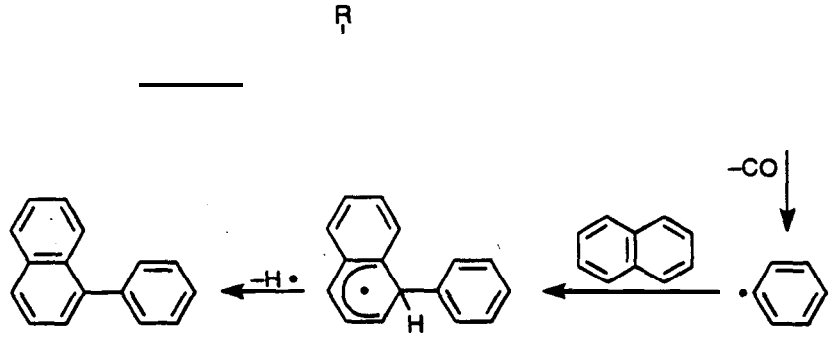


Arylated products were also found when biphenyl was used as the solvent, and 1- and 2-phenylnaphthalene were found in the thermolysis of benzoic acid in naphthalene. The formation of 7 and 8 were reduced by tetralin, a hydrogen donor solvent, indicating that the arylation reaction proceeded by a free 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.



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

ACKNOWLEDGMENT

This

[14] (a) Eskay, T. P.; Britt, P. F.; Buchanan, III, A. C. *Energy Fuels* 1997, II, 1278. (b) Eskay, T. P.; Britt, P. F.; Buchanan, III, A.