

Decarboxylation and Coupling Reactions of Aromatic Acids under Coal-Liquefaction Conditions

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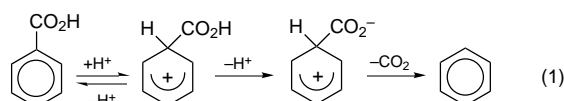
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Decarboxylation of a series of monomeric benzoic acid systems under liquefaction-relevant conditions was studied. The principal findings are the following: (1) decarboxylation rates of benzoic acids range from a few percent in 1 h at 400 °C for unactivated acids to >98% for species activated by OH in the ortho or para positions; (2) coupling of unactivated benzoic acids as a *direct* result of decarboxylation tends to be very minor (generally <10%); (3) decarboxylation of hydroxy-activated benzoic acids results in products that are susceptible to subsequent electrophilic coupling reactions; (4) under strongly oxidizing conditions, namely the absence of scavengers and the presence of one-electron oxidants, coupling of even unactivated acids can be as much as 50% of the decarboxylations; (5) amine bases tend to promote decarboxylation but either inhibit or do not affect coupling; (6) H-donors inhibit coupling but promote decarboxylation in the presence of the electron transfer agent Fe₃O₄; (7) small amounts of water do not affect the coupling/decarboxylation ratio; (8) rates of decarboxylation and coupling of calcium salts of aromatic acids are not significantly higher than those of the free acids. It is suggested that the increase in low-temperature coupling associated with the increased oxygen content of low-rank coals is not *directly* caused by the reaction of radical or ion fragments produced as decarboxylation intermediates of *unactivated aromatic acids*. However, coupling of phenolic products from activated benzoic acids may indeed be an important cross-linking route. An example of this secondary cross-linking is provided by the formation of xanthenes from the cresols generated in the decarboxylation of anisic acid. Furthermore, the decarboxylation and coupling behavior of *aliphatic acids* is substantially different, as is addressed in a separate publication.

Introduction

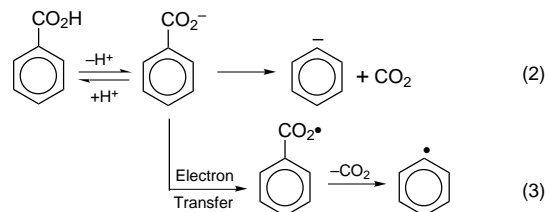
In recent years, it has become increasingly clear that retrograde reactions substantially hinder the liquefaction of low-rank coals and that oxygen functional groups in the coal structure are major actors in these retrograde reactions. Carboxyl functions have been implicated in the cross-linking of coals during heating at relatively low temperatures,^{1,2} and Serio et al.³ have been able to model the pyrolytic loss of solvent swelling by including one additional cross-link in the network for every CO₂ evolved. Moreover, pretreatments that have been found to be effective in promoting liquefaction have also shown a corresponding decrease in the early CO₂ evolution.⁴ However, from the limited mechanistic information available, it is not immediately obvious how decarboxylation would lead to cross-linking. For instance, organic chemistry textbooks such as that by March⁵ suggest two general mechanisms, involving either acid or base catalysis, for the decarboxylation of aromatic acids. Under acidic conditions, electrophilic attack of a proton results in displacement of the CO₂ group as exemplified

for benzoic acid in reaction 1.



Acids are, of course, activated toward such protolytic decarboxylation by the presence of electron-releasing substituents. With this mechanism, coupling does not seem likely unless an alternative agent (e.g., R⁺) were able to compete successfully with H⁺, a very good and sterically unhindered electrophile.

Under basic conditions, the carboxylate anion is thought to decompose directly to CO₂ and phenyl anion as exemplified in reaction 2.



While coupling of the phenyl anion is possible, in practice this strong base should be rapidly scavenged by any indigenous proton source. Alternatively, it may be possible to divert anionic decarboxylation by electron transfer from the carboxylate anion to some appropriate species (say in the coal mineral matter) to produce a

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carboxyl radical. This radical, which is not easily formed by direct abstraction of the strongly bonded carboxyl hydrogen from the acid, will decarboxylate extremely rapidly to give the aryl radical, which can indeed couple via radical addition reactions. Such a route (reaction 3), although plausible, should be readily interrupted by the addition of H-donor solvents.

As the above discussion makes clear, the circumstantial evidence suggesting a direct link between decarboxylation and retrograde reactions is not readily explained by our current understanding of the chemistry involved. A detailed assessment of this connection therefore requires a better understanding of the behavior of decarboxylation reactions under conditions relevant to coal liquefaction. A recent study by Siskin and co-workers⁶ showed that decarboxylation of naphthoic acid under hydrothermal conditions was attended by formation of some binaphthyl, but the coupling aspect was not elaborated in that paper.

We report here on a series of experiments with coal-related monomeric, aromatic carboxylic acids. We have examined rates of decarboxylation and coupling to see if cross-linking results directly from decarboxylation, as well as how cross-linking is affected by ion exchange, electron transfer reagents, the presence of a hydrothermal environment, and other conditions relevant to coal pretreatment and liquefaction. A preliminary account of some of these results has been previously presented.⁷ More recently, Britt and co-workers have addressed the question of whether incorporation of the carboxylic acids into polymeric or oligomeric networks makes cross-linking associated with decarboxylation more likely.^{8,9}

The choice of monomeric acids included in this study was based upon the limited information available on the nature and content of carboxylic acids in low-rank coals. Although low-rank coals are known to contain carboxylic acid functionalities,^{10,11} whose levels generally decrease with increasing rank,¹⁰⁻¹³ the precise nature of the acid groups has not yet been elucidated. Such coals are, however, known to contain lignin-like polymers and give products characteristic of lignin structural units upon oxidative breakdown.¹⁴ Thus, one expects the presence of hydroxy and methoxy substituted aromatic acids and/or rings with fatty acid side chains. In the present paper we discuss the behavior of compounds with the acid functionality attached directly to the aromatic ring; in a subsequent paper we examine how decarboxylation proceeds if the carboxyl group is at an aliphatic site.

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Experimental Section

Reaction Conditions and Analytical Procedures. Experiments on decarboxylation and coupling of monomeric carboxylic acids were carried out in fused silica ampules. The standard reaction time was 1 h at 400 °C, chosen to be roughly illustrative of the thermal severity of the early stages of coal liquefaction. Samples were sealed under vacuum, with each sample filling approximately one-half of the tube at room temperature. The sealed tube and an appropriate quantity of solvent for pressure equalization were placed in a stainless steel tube capped with compression fittings. This tube was then immersed in a temperature-controlled molten-salt bath for the desired time, after which the tube was removed and quenched in water. After cooling in liquid nitrogen to condense CO₂ and volatile organics, the ampule was opened and the sample removed by pipet and repeated washing of the tube with solvent. An internal standard was added and the sample analyzed by gas chromatographic analysis using a flame ionization and/or mass selective detector (Hewlett-Packard 5880 GC and 5970 mass selective detector fitted with J&W Scientific 30-m DB-5MS capillary columns of 0.25 mm i.d., 0.25 mm film thickness). Product quantitation was obtained using the FID analyses, with molar responses determined separately for those compounds for which we had authentic samples and estimated by comparison with similar species when no sample was available. For coupling products, the FID sensitivities were derived from a molecular weight based on the *apparent* molecular ion and on an assumed per carbon molar sensitivity increment. Generally, at least three split injections of each sample were performed using an autoinjector. For most species the reproducibility was within $\pm 2\%$ and we estimate the overall analytical accuracy to be within $\pm 5\%$. The highly polar carboxylic acids were an exception, exhibiting pronounced peak tailing in the gas chromatograms. These compounds showed much less reproducibility both in injection-to-injection and in the day-to-day variation in the molar response. For these species we estimate the overall analytical accuracy to be $\pm 12\%$.

Chemicals. Benzoic acid (99+% by GC analysis), *o*-anisic acid (2-methoxybenzoic acid, Aldrich, 99%), 3,4-dimethoxybenzoic acid (Aldrich, 99+%), vanillic acid (3-methoxy-4-hydroxybenzoic acid, Aldrich, 97%), *m*-hydroxybenzoic acid (Aldrich, 99%), naphthalene (Aldrich, 99+%), tetralin (Aldrich, 99%), pyridine (Mallinckrodt, AR grade, 99+% by GC analysis), cupric acetate monohydrate [Cu(CH₃CO₂)₂·H₂O, Fisher Scientific], Fe₃O₄ powder (supplier unknown, particle size $\approx 0.2 \mu\text{m}$), and FeS were used without further purification.

Preparation of Calcium Salts. To prepare the calcium salts of benzoic acid and *o*-anisic acid, the free acids were placed in a small amount of water and dissolved by the slow addition of an equimolar amount of NH₄OH solution. The calcium salts precipitated upon the slow dropwise addition of an equivalent amount of CaCl₂ solution. The cooled solutions were filtered and the salts recrystallized from ethanol and dried under vacuum. Purities of the salts were checked by adding a known amount of salt to an aqueous acid solution, extracting with organic solvent, and quantitatively analyzing via GC.

Results

Decarboxylation of Benzoic Acids under Reducing Conditions. In this section, we present the results obtained for a series of benzoic acids, both activated and unactivated, under typical "liquefaction" conditions (i.e., 400 °C for 1 h in tetralin), sometimes with small amounts of other additives such as base. Detailed discussion of the mechanistic aspects is deferred to the Discussion section. To give an idea of the rather limited coupling that occurs for a range of acids under a range

Table 1. Decarboxylation of Activated and Unactivated Benzoic Acids for 1 h at 400 °C

acid structure	solvent system ^a	concentration mol %	decarboxylation %	coupling/decarboxylation (%) ^b
PhCO ₂ H ^{c,d}	tet	5	3	<2
	tet/THQ/H ₂ O, 55/20/20	5	5	<20
	tet/PipPy, 75/20	5	77 ^e	<3
	tet/THQ/Zn(OAc) ₂ , 75/20	5	75	<5
	tet/1-naphthol, 80/10	10	3	<2 ^f
	naph	10	4	<3
Ca(PhCO ₂) ₂	naph/pyridine, 80/10	10	18	<3
	tet/1-naphthol, 80/10	10	3	<2
4-OH-PhCO ₂ H	tet	20	>98	<3
	naph	12	>99	<1
3-OH-PhCO ₂ H	tet	10	2	
	naph	14	(2)	
2-OMe-PhCO ₂ H	tet	10	88 ^g	<3 ^h
	tet	20	87 ^g	<3 ^h
	tet/pyrene	10	84 ^g	<3 ^h
	naph	14	92 ^g	6 ^h
3-OMe-4-OH-PhCO ₂ H	tet	10	>99	<2
3-OMe-4-OMe-PhCO ₂ H	tet	10	~75	<3

^a The characters tet represents tetralin, THQ is 1,2,3,4-tetrahydroquinoline, naph is naphthalene, and pipPy is the strong organic base/nucleophile 4-piperidinopyridine. ^b This figure should be considered an upper limit. It represents the sum of small unidentified high retention time peaks that are potential coupling products, given as a percent of decarboxylation. Thus, larger values listed for cases where there is more limited decarboxylation do not reflect larger absolute amounts of possible coupling products. ^c The second, third, and fourth sets of data for benzoic acid itself are taken from earlier, unpublished work, where coupling products were not the principal focus. Therefore, the upper limits set on coupling tend to be slightly higher. ^d For economy of space, the symbol Ph is used here to represent a single phenyl ring, regardless of whether there are three, four, or five unsubstituted positions on the ring. ^e Reaction time in this case was 0.5 h. ^f Does not include formation of naphthylbenzoate ester or rearranged product of this ester. ^g No unconverted acid remained; some undecarboxylated material was found as esters, mostly methyl anisate (see text). ^h Does not include esters of anisic acid.

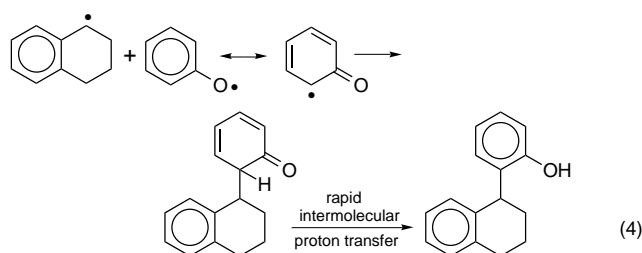
of conditions, the decarboxylation and coupling data for activated and unactivated benzoic acids in different reaction media are shown in Table 1. This table includes data obtained both in the presence of tetralin, as a rough approximation of liquefaction conditions, and in the absence of hydrogen donors, chosen to approximate the conditions that might apply in the interior of a coal particle during its passage through a liquefaction preheater. The data obtained for these acids in the presence of potential electron-transfer agents are given later.

For completeness, we report mass balances but consider that, by itself, a reported mass balance, say of 85%, is probably more a reflection of the $\pm 12\%$ precision limits of the GC analysis of tailing peaks than it is a valid implication of 15% coupling. Clearly, a mass balance less than 100% could imply the presence of products having molecular weights too high to be GC-observable. However, for such oligomers to be present in larger quantities than unobservable or marginally observable dimeric products would require the rate constant for, say, dimer to trimer to be substantially greater than the rate constant for dimer formation. In the present case, however, where the products consist mainly of aromatic rings linked together rather than of PAH of continually increasing size (and therefore progressively more susceptible to radical- or electrophilic substitution), we do not expect the rate constants for *n*-mer formation to be much greater than those for dimer formation.

Benzoic Acid. Data in Table 1 demonstrate that the decarboxylation of benzoic acid itself is slow at 400 °C in tetralin (3–5% in 1 h), unless a fairly strong base or other decarboxylation promoter is present. General products identified in all experiments include benzene and products from the solvent: naphthalene, solvent impurities, tetralin rearrangement products, and small amounts of tetralin-derived dimers. In some experiments, we specifically looked for coupling products but were unable to detect any products corresponding to reaction of benzoic acid (or phenyl radical) with itself,

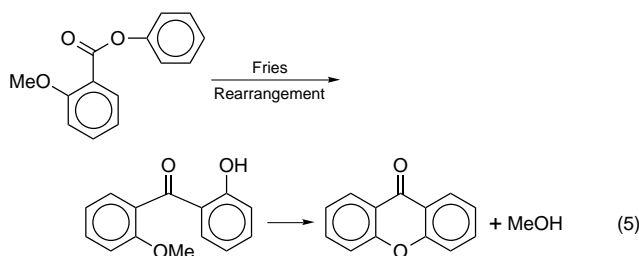
benzene, tetralin, or naphthalene. Detection limits on products that might have been expected (e.g., biphenyl, phenyltetralins, and phenylnaphthalene) are about 0.05 mol % of the starting benzoic acid. The only coupling products identified under these conditions were found when 1-naphthol was added to the reaction mixture; in this case naphthyl benzoate and an isomer, probably the Fries-rearranged product of this ester, were present in 7 and 1 mol % yields, respectively. Even prior formation of the calcium salt of benzoic acid, a step known to substantially increase cross-linking in low-rank coals, failed to result in any detectable coupling products when decarboxylation is conducted in a donor solvent.

4-Hydroxybenzoic Acid. In contrast to benzoic acid, this activated acid underwent near complete decarboxylation, giving phenol in almost 100% yield. GC–MS analysis showed the formation of several coupling products in trace quantities. Two lower level trace products, each accounting for roughly 0.3% of the starting acid, gave major peaks at 214 Da. The mass spectral data suggest that these two products are isomeric phenyl(hydroxy benzoates). The other trace products, with apparent molecular ions at 224 Da, were tentatively identified as two (hydroxyphenyl)tetralin isomers and tetralylphenyl ether. Each of these account for <0.05% of the starting acid; they most likely are ring-recombination products between 1-tetralyl and phenoxy radicals, as shown in eq 4 and do not arise as a direct result of decarboxylation.



3-Hydroxybenzoic Acid. This unactivated species gave phenol in 2% yield with no detectable coupling products.

***o*-Anisic Acid (2-Methoxybenzoic Acid).** In the three experiments with this substrate, decarboxylation was almost complete, ranging from 84 to 88%. No starting acid was recovered, and all undecarboxylated products consisted of esters; primarily methyl anisate formed (in the absence of methanol) presumably by a radical addition–elimination reaction between the methyl radical and anisic acid. The mass balance for anisic acid ranged from 93.5 to 98.6%. Major decarboxylation products included anisole and its known^{15,16} decomposition products, primarily phenol, *o*- and *p*-cresol, toluene, and benzyl alcohol, as well as traces of methylanisoles and dimethylphenols. Benzene, although previously reported as a product, was not determined, because of interference with the THF solvent that was used in these experiments. Inability to determine benzene may in part explain the slight mass imbalance. The only discrepancy with previous results on anisole decomposition was the apparent lack of formation of diphenyl ether, which was previously reported¹⁵ as a minor coupling product of anisole (2.3 wt %) under similar conditions. Although no diphenyl ether was detected, small quantities of other coupling products were found, in total accounting for <2% of the starting material. These included a small peak with its molecular ion at $m/z = 182$, identified as xanthene by GC–MS comparison with an authentic sample, a peak with molecular ion at $m/z = 184$, assigned as *o*-benzylphenol (the ring-opened xanthene), and a peak with molecular ion at $m/z = 196$, identified as xanthone (9H-xanthene-9-one) on the basis of its mass spectrum. Two peaks were also found with ions at $m/z = 228$ and, on the basis of their mass spectra, identified as phenyl anisate and an isomer (*o*- or *p*-hydroxyphenyl)*o*-methoxyphenyl ketone. The latter is probably a product of the Fries rearrangement, as shown in eq 5 and considered further in the discussion section.



Vanillic Acid (4-Hydroxy-3-methoxybenzoic Acid). As with 4-hydroxybenzoic acid, decarboxylation was nearly complete in 1 h at 400 °C. Major products were guaiacol (2-methoxyphenol) and products expected from guaiacol decomposition: catechol and methylcatechols. Some small unidentified peaks were found in the coupling region of the chromatogram, but together these could account for no more than 2% of the starting material.

Veratric Acid (3,4-Dimethoxybenzoic Acid). In contrast with vanillic acid, about 25% of the starting material was recovered as the free acid. Major products included dimethoxybenzene, guaiacol, and various prod-

ucts expected from the breakdown of these species. Trace chromatographic peaks having retention times characteristic of coupling products were not identified, but together these accounted for <3% of the starting acid.

Decarboxylation of Benzoic Acids in the Absence of H-Donors. Having seen very little coupling resulting from decarboxylation under reducing conditions, we broadened the range of reaction conditions in an attempt to bring about more coupling and perhaps approximate more closely conditions encountered early in the thermal processing of low-rank coals. Essentially, this means reaction in more oxidizing systems, that is, systems with potential oxidants for carboxylate ions and with little or no hydro- or alkylaromatics. Under these conditions, literature data for the reactions of phenyl- and other aryl radicals^{17–19} lead us to expect that any phenyl radicals formed will add very readily to essentially any aromatic system, displacing hydrogen to form biaryl linkages.

Benzoic Acid. The rate of decarboxylation in naphthalene was not significantly different from that in tetralin, increasing slightly from 3 to 4% (Table 1). Under these conditions, however, we were able to identify the coupling products 1- and 2-phenylnaphthalene at the level of 0.11% of the starting acid, higher than that observed with tetralin as solvent but still quite minor. Given the very large naphthalene/benzene ratio (>200), the absence of significant binaphthyl in this system is strong evidence that the species responsible for coupling is formed during decarboxylation and not simply from the benzene and naphthalene that are present in the product mixture. The phenylnaphthalenes, which were not present at all when tetralin was the solvent, still represent only 2.7% of the decarboxylated material. No other coupling products were found.

Although the coupling we observe when benzoic acid decarboxylates in the presence of arenes such as naphthalene (either with or without the presence of tetralin) is very limited, it is appropriate to ask whether in a polymeric network even a small amount of coupling might be sufficient to have sufficient effect on the polymeric network. With this question in mind, Britt and co-workers have incorporated benzoic acid groups into polymeric networks⁸ and into intermediate molecular weight oligomers⁹ and have observed their behavior upon pyrolysis. Although their work is limited thus far to linear polymers subject either to unzipping or to dominant weak-bond homolysis (i.e., polystyrene- and bibenzyl-type polymers), their results with respect to coupling basically mirror those presented in this paper, namely that very little cross-linking results from decarboxylation of *unactivated aromatic* carboxylic acids. However, the decarboxylation rates they observe are 3–6 times faster than those reported here for benzoic acid. These and other differences bear on the mechanism of decarboxylation for these unactivated acids and are discussed below under "Effect of Base".

4-Hydroxybenzoic Acid. As with tetralin solvent, this

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Table 2. Effects of Different Electron-Transfer Agents and Donor Solvent on Coupling and Decarboxylation of Benzoic Acid^a

BA (mol %) ^b	solvent system (mol %) ^b	results				
		% unc acid	% coupling ^c	% decarbox ^d	% (coup/dec)	% product balance ^e
9.6	naph, 90.4	102.2	0.11	4.4	2.7	106.7
11.3	naph/pyridine/Fe ₃ O ₄ , 68.8/9.8/10.1	19.5	7.7	57.6	13.4	77.4
10.1	naph/Fe ₃ O ₄ , 79.5/10.4	99.7	4.9	9.9	48.5	106.3
10.0	naph/Fe/S, 79.9/10.1	53.0	2.6	45.5	5.7	101.1
10.4	naph/pyridine/CuAc, 70.4/8.9/10.3	<0.1	3.0	83.4	3.6	86.4
9.8	tet/MN/naphthol/pyridine/CuAc, 29.9/29.9/12.2/9.6/9.7	45.9	0.51 ^f	46.5	1.1	92.9

^a Reaction time 1 h at 400 °C. ^b BA = benzoic acid; naph = naphthalene; tet = tetralin; MN = 1-methylnaphthalene; naphthol = 1-naphthol; CuAc = cupric acetate monohydrate [Cu(CH₃CO₂)₂·H₂O]. ^c As mol % of benzoic acid; refers to all peaks in the coupling region of the chromatogram (all peaks after naphthalene except for identified impurities or solvent coupling products). ^d Based on identified decarboxylated products including benzene and phenyl-containing coupling products. ^e Σ(% unc acid + % coupling + % decarbox). Note that tailing of benzoic acid limits precision of this component to ±12%. ^f This figure, does not include 1% formation of naphthyl benzoate from benzoic acid and naphthol.

species was essentially fully decarboxylated in naphthalene (Table 1). Coupling products were still very minor, consisting mainly of the same two peaks having apparent molecular ions at $m/z = 214$ (presumed to be isomeric phenyl(hydroxybenzoates)) that were found when tetralin was the solvent. These were present at the levels of 0.24 and 0.25%, respectively. Several other unidentified trace peaks in the coupling region of the chromatogram were found at levels <0.05%. Total coupling accounted for only 0.8% of the starting acid.

o-Anisic Acid (2-Methoxybenzoic Acid). At 92%, decarboxylation in naphthalene was slightly higher than the 84–88% that was found with tetralin as the solvent (Table 1). Again, no starting acid remained, and the undecarboxylated material was converted to esters, mostly methyl anisate. Anisole and its decomposition products were found in proportions similar to those observed in the experiments with tetralin. The primary coupling products were again xanthene (1.5%), *o*-benzylphenol (0.26%), xanthone (1.1%), and the two peaks with molecular ions at $m/z = 228$ (0.4 and 0.3%, identified as before as phenyl anisate and hydroxyphenyl-*o*-methoxyphenyl ketone). Small quantities of unidentified products, accounting for about a third of the coupling products, were also found, with total coupling accounting for 5% of the starting material.

As shown by the above data, in the absence of additives, rates of decarboxylation were largely unaffected by the change to a nondonor solvent. Slightly larger quantities of coupling products were found under the nonreducing conditions, but coupling still remained a minor fraction of decarboxylation.

Effect of Base. The addition of 10 mol % of pyridine to the naphthalene/benzoic acid mixture increased decarboxylation 4-fold, from 4.3 to 18.1% (Table 1). This result is in accord with the second mechanism that was suggested in the Introduction, namely that this unactivated species undergoes decarboxylation (in the absence of strong acid) primarily via the carboxylate anion. The only coupling products were again phenylnaphthalenes. The fact that base did not substantially affect the coupling-to-decarboxylation ratio (see Table 3) indicates that rate acceleration does not involve a change in the mechanism.

The results of Britt and co-workers on polymeric acids^{8,9} are also interesting from the point of view of the decarboxylation mechanism. They conclude that, even for the nominally unactivated aromatic acids they studied (1,2-di(carboxyphenyl)ethanes), decarboxylation

is primarily a result of protolytic attack. The basis for this conclusion is the observation that the para isomer decarboxylated twice as fast as the meta isomer and that decarboxylation in the presence of deuterated hydrogen donors resulted in no measurable incorporation of deuterium at the aryl position that had borne the carboxylic acid group. Their results would indeed appear to rule out dominant decarboxylation of the arylcarboxyl radical. That conclusion, as far as it goes, is quite consistent with our results with benzoic acid: there is very little coupling that would lead one to invoke dominant production of aryl radicals in the coupling process. However, the absence of deuterium incorporation is also consistent with dominant decarboxylation via the carboxylate anion; the aryl anion thus generated would clearly be protonated by the remaining carboxylic acid before it could react with the much more weakly acidic benzylic protons (that had been deuterated).

The accelerating effect of the pyridine base observed in the present work seems much more consistent with an anionic decarboxylation process. On the other hand, the faster reaction Britt and co-workers⁹ observe for the para isomer of the dicarboxylated bibenzyl and the fact that decarboxylation of that material (neat) is 3–6 times faster than what we observe for 10% benzoic acid in tetralin do indeed suggest a protolytic pathway. In fact, these results, taken all together, may simply support the suggestion (see below under decarboxylation of calcium benzoate) that both anionic and cationic decarboxylation pathways are accessible.

Effect of Electron-Transfer Agents on the Decarboxylation of Benzoic Acid. Electron-transfer agents may be present in coal in the form of inorganic material, as well as in certain organic structures, such as hydroquinones/quinones. To probe their possible effects, we selected several additives that were found from our previous studies to affect decarboxylation, including Fe₃O₄, FeS, and mixtures of pyridine/Cu(OAc)₂. The results are summarized in Table 2.

Pyridine/Cu(OAc)₂/Naphthalene. As literature recipes for copper/amine promoted decarboxylation would lead one to expect,^{20–23} decarboxylation of benzoic acid

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Table 3. Effect of Fe₃O₄ and Pyridine on Decarboxylation and Coupling of Benzoic Acid in Naphthalene^a

	1 mol %	2 mol %	3 mol %	4 mol %	5 mol %	6 mol %
reactants						
benzoic acid	9.57	10.00	10.13	9.74	10.16	11.26
naphthalene	90.43	80.23	79.49	71.64	69.56	68.80
pyridine		9.77				9.82
tetralin					9.52	
H ₂ O				9.26		
Fe ₃ O ₄			10.38	9.35	10.76	10.11
products						
benzoic acid	102.2	92.6	99.7	92.9	67.0	19.5
naphthalene ^c	99.8	99.9	98.4	102.7	101.6	96.1
pyridine		78.9				87.5
benzene	4.26	18.1	6.47	6.86	26.5	54.1
biphenyl ^b	<0.004	<0.004	<0.004	<0.004	<0.004	0.14
1-phenylnaphthalene ^b	0.058	0.23	2.36	2.65	1.90	2.20
2-phenylnaphthalene ^b	0.055	0.20	1.02	1.12	0.78	0.99
1-pyridinylnaphthalene ^b		<0.004				2.14
2-pyridinylnaphthalene ^b		<0.004				0.79
1,1'-binaphthyl ^b	<0.004	0.015	0.45	0.60	0.14	0.39
1,2'-binaphthyl ^b	<0.004	0.027	0.72	0.93	0.22	0.72
2,2'-binaphthyl ^b	<0.004	0.007	0.22	0.26	0.06	0.22
Ph-naph/binaph ^d	>9.4	8.8	2.4	2.1	6.4	2.4
% decarboxylation ^e	4.4	18.5	9.9	10.6	29.2	57.6
% (coupling/decarbox) ^{e,f}	2.7	2.6	48.5	52.4	10.6	13.4

^a Reaction time 1 h at 400 °C. ^b Mole percentages are based on starting benzoic acid. ^c Based on starting naphthalene. ^d Ratio of phenylnaphthalenes (Ph-naph) to binaphthyls (binaph). ^e Based on identified decarboxylation products. ^f Coupling product yield, as a percent of decarboxylation. For the purposes of this table it is assumed that pyridinylnaphthalenes and binaphthyls are coupling products that stem from decarboxylation after a shift of the radical center from the initial phenyl radical to either pyridine or naphthalene (see text).

increased from ~4% in naphthalene-only mixtures to ≥83% for a mixture containing 10 mol % each of pyridine and Cu(OAc)₂. This is well beyond the 18% decarboxylation that resulted from the addition of pyridine alone (Table 1) and beyond the 58% level reached with naphthalene, pyridine, and Fe₃O₄. It should be noted that the benzoic acid peak was completely missing in the product chromatogram and that 83% is a minimum figure based on the production of benzene and phenylnaphthalenes, the only two monomeric products identified as containing a phenyl unit from benzoic acid. We are uncertain of the fate of the remainder but did not make a detailed search, since our primary interest was in the most readily analyzable coupling products. All peaks representing dimeric coupling products were identified. They resulted from small amounts of phenylnaphthalenes, binaphthyls, and pyridinylnaphthalenes that together account for less than 4% of the decarboxylated acid. We believe that all three of these are coupling products that stem directly or indirectly from decarboxylation, as will be discussed shortly. Despite the large increase in decarboxylation observed in this system, the ratio of all coupling to decarboxylation was only 0.036, essentially unchanged from the values near 0.027 that were found in the absence of the an electron-transfer agent.

Pyridine/Cu(OAc)₂/H-Donors. When the naphthalene was replaced by a mixture of the hydrogen donors, tetralin/1-methylnaphthalene/naphthol, decarboxylation induced by pyridine/Cu(OAc)₂ was reduced substantially with 46% (vs none) of the benzoic acid recovered intact (see Table 2). The yields of phenylnaphthalenes, binaphthyls, and pyridinylnaphthalenes were cut by about 70%. Thus, the ratio of total coupling to decarboxylation was reduced to 0.011, below even the value of 0.036 obtained in mixtures of pyridine/Cu(OAc)₂/naphthalene. The mechanistic implications of this result are discussed later.

FeS. Decarboxylation increased from 4% with naphthalene alone to 46% when FeS was present, while 53% of the benzoic acid was unconverted. The identified coupling products were phenylnaphthalenes (2.4%) and binaphthyls (0.27%). Several other unidentified peaks were also present at the trace level (<0.1%). In total, the ratio of coupling-to-decarboxylation was 0.057. This value is twice the 0.027 found in the absence of an electron-transfer agent but still means that only a very small minority of the decarboxylation intermediates are involved in coupling reactions.

Fe₃O₄. In striking contrast with the behavior of the additives described above, Fe₃O₄ increased decarboxylation only slightly, to 6.5%, but increased the coupling/decarboxylation ratio by a factor of almost 20, to 0.49. The predominant coupling products were again phenylnaphthalenes and binaphthyls.

Effect of H-Donors, Base, and Water on Fe₃O₄-Induced Coupling. Among the decarboxylation environments we have studied, only those containing Fe₃O₄ were found to lead to coupling as a major process, accounting in the case of benzoic acid for nearly one-half of the decarboxylated material. The distribution among coupling products for benzoic acid remained similar in all systems, which suggests that the chemistry responsible for coupling is also similar in these systems. Given this similarity in the distribution of coupling products, it seemed most profitable to focus on the decarboxylation environment that produced the most coupling. Table 3 provides a more detailed breakdown of products of the Fe₃O₄/benzoic acid/naphthalene system under various conditions, showing the effects of the addition of 10 mol % of an H-donor (tetralin), base (pyridine), and water.

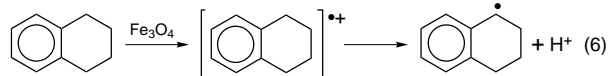
Fe₃O₄ Tetralin. In comparison to the Fe₃O₄-only system, tetralin had two primary effects, increasing decarboxylation by a factor of 2.9 but decreasing the coupling/decarboxylation ratio by a factor of nearly 5

Table 4. Effect of Fe₃O₄ on the Decarboxylation and Coupling of *o*-Anisic Acid and its Products^a

	1 % ^b	2 % ^b	3 % ^b	4 % ^b	5 % ^b
reactants					
<i>o</i> -anisic acid	14.25	9.83	10.00		
<i>o</i> -cresol				9.74	8.04
phenol					8.21
naphthalene	85.75		80.23	80.31	75.47
tetralin		90.17			
Fe ₃ O ₄			9.77	9.95	8.28
products					
<i>o</i> -anisic acid	<0.1	<0.1	<0.1		
naphthalene	99.3	1.99	97.9	96.6	96.8
tetralin		97.1			
anisole	58.6	33.6	19.8		
phenol	18.9	42.7	46.3	6.25	91.0
cresols	1.04	1.04	14.4	68.7	76.8
methyl anisate	7.95	11.9	<0.1		
xanthene	1.52	<0.1	6.89	0.36	2.12 ^c
methyl xanthenes	<0.1	<0.1	1.76	4.22	0.99 ^c
xanthone	1.10	0.51	<0.1	<0.1	<0.1
BP ^d	0.26	<0.1	0.20	<0.1	<0.1
MPN ^d	0.10	<0.1	0.66		
HPN ^d	<0.1	<0.1	0.36	<0.1	<0.1
HBN ^d	0.026	<0.1	0.99	1.50	1.31
reactant mass balance ^h	93.8	93.5	98.6	92.6	90.4
% decarboxylation ^h	91.5 ^e	88.1 ^e	≥98.6 ^f		
% (coupling/decarbox)	5.5 ^g	1.75 ^{e,g}	12.8 ^{e,g}		

^a Reaction time, 1 h at 400 °C. ^b Reactants are given as mole percentages. Products of anisic acid, cresol, and phenol are given as a percentage of the phenyl units of the starting material which they contain. Thus, percentages for products derived from two units of starting material are *twice* the mol %. ^c As a percent of the total phenolic feed (i.e., cresol + phenol). ^d BP = *o*-benzylphenol; MPN = (*o*-methoxy)phenylnaphthalene; HPN = (*o*-hydroxy)phenylnaphthalene; BN = (*o*-hydroxybenzyl)naphthalene. ^e Based on identified anisic-acid-derived compounds. ^f No carboxyl containing compounds were identified. This figure is limited by the mass balance. ^g Percent coupling refers to the total percentage of anisic acid phenyl units present in retrograde products. The figure is based on the sum of all peaks in the coupling region of the chromatogram. Unidentified products were assumed to contain two phenyl units of anisic acid, and molar responses were estimated by comparison with those of known compounds. ^h These figures include not only the listed products but also the sum of all trace and/or unidentified products inferred from their retention times to be either simple decarboxylation or coupling products.

(the net result being a slight decrease in the absolute amount of coupling product generated). Interestingly, in the absence of iron oxide, tetralin had little effect on the rate of decarboxylation (Table 1). The very different result found in the presence of iron oxide obviously indicates a strong interaction between Fe₃O₄ and tetralin or a tetralin-derived species. We believe that the most likely explanation for this is that the π -system of the tetralin is oxidized by Fe₃O₄ to give the tetralyl radical cation. Such radical cations are known to be very strong acids²⁴ and will readily lose a proton, thus increasing the rate of acid-catalyzed decarboxylation:



Fe₃O₄ Pyridine. Pyridine had a larger accelerating effect on decarboxylation than did tetralin, increasing decarboxylation 6-fold in comparison to the Fe₃O₄-only system. However, its inhibiting effect on coupling was similar to that of tetralin, decreasing the ratio of coupling to decarboxylation by a factor of 4. The spectrum of coupling products remained qualitatively unchanged, consisting of small amounts of phenylnaphthalenes, binaphthyls, and pyridinylnaphthalenes.

Fe₃O₄ Water. In contrast to tetralin or pyridine, the addition of 10 mol % water had essentially no effect on the course of the reaction when compared to the Fe₃O₄-only system.

Decarboxylation of *o*-Anisic Acid in the Presence of Fe₃O₄. As shown by the data described earlier, significant coupling of unactivated benzoic acids can be promoted by Fe₃O₄ under some nonreducing conditions. However, the slow-to-moderate decarboxylation rates observed for benzoic acid even at 400 °C suggest that it must be primarily the activated carboxylic acids that decarboxylate in the region of low-temperature cross-linking of low-rank coals (eg., 300–350 °C). Therefore, we probed the effect of an electron transfer agent on an activated acid by performing experiments with a mixture of *o*-anisic acid, naphthalene, and Fe₃O₄.

Our results, summarized in Table 4, show that iron oxide promoted decarboxylation. No undecarboxylated material was identified in the product mixture, in contrast with about 10% remaining as methyl anisate in the absence of Fe₃O₄. Although promotion of coupling was less dramatic than with benzoic acid, the yield of coupling products was roughly doubled so that the percentage of the decarboxylated anisic acid units appearing in coupling products was increased from 5.5 to 12.8 (vs 48.5 for benzoic acid). The coupling product distribution was different from that found in the absence of iron oxide and included a substantial amount of xanthene (6.9%, as a percent of total anisic acid units), two methylxanthene isomers (1.7%), two chromatographic peaks having their apparent molecular ions at *m/z* = 234 identified as 1- and 2-(*o*-hydroxybenzyl)-naphthalene (1- and 2-HBN, 1.0%), two more peaks with ions at *m/z* = 234 assigned to 1- and 2-(*o*-methoxyphenyl)naphthalene (1- and 2-MPN) on the basis of their mass spectra (0.66%), and two peaks with ions at *m/z*

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Table 5. Decarboxylation and Coupling of the Calcium Salts of Benzoic and Anisic Acid^a

reactants (mol %) ^b	results		
	% unr acid	% coupling ^c	% decarbox
calcium benzoate/tet/1-naphthol, 10/80/10	83.4	<2 ^d	2.1 ^e
calcium anisate, 100	<0.3	5.0	99.7 ^f
calcium anisate/naph, 9.3/90.7	<0.3	7.0	90.7 ^f
calcium anisate/tetralin, 9.1/90.9	<0.3	4.9	92.3 ^f

^a Reaction time 400 °C for 1 h. ^b The characters naph = naphthalene; tet = tetralin. ^c Percentage of decarboxylated substrate that appears as coupling products. It refers to all peaks in the coupling region of the chromatogram. ^d No peaks were found in the coupling region of the chromatogram. ^e Based on formation of benzene. No other products were identified. ^f This figure is limited by the mass balance, and no undecarboxylated products were identified.

= 220 identified as the demethylated derivatives of the above compounds, i.e., 1- and 2-(*o*-hydroxyphenyl)-naphthalene [(1-and 2-HPN), 0.36%]. Although there were numerous chromatographic peaks at the trace level, the above nine compounds were responsible for nearly 90% of the coupled acid. Notable for their absence were three compounds observed when iron oxide was *not* present: xanthone, phenyl anisate, and hydroxyphenyl-*o*-methoxyphenyl ketone (*o/p*-HPMPK). Monomeric products were qualitatively similar to the those found in the absence of Fe₃O₄, although iron oxide led to increased production of cresols and cleavage of the O–Me ether linkage in anisole. The Lewis acid catalysts FeCl₃ and NiCl₂ were previously observed to have a similar effect on anisole conversion.¹⁶

Decarboxylation of the Calcium Salts of Benzoic Acids. The calcium or magnesium forms of low-rank coals produce more CO₂ and show more evidence of cross-linking on heating.^{3,10,25,26} It has been suggested, therefore, that the salts of the carboxylic acid structure in these coals may be prone to cross-linking reactions.^{3,10} To examine this question, we performed several experiments with the calcium salts of benzoic and anisic acid, prototypical unactivated and activated species. The results are discussed below and summarized in Table 5.

Calcium Benzoate/Tetralin. Decarboxylation of the salt in tetralin was only 2.1%, slightly slower than that of the free acid under similar conditions (3–5%; see Table 1). Qualitatively, a slower rate of decarboxylation might seem consistent with a contribution from acid-catalyzed decarboxylation (eq 1), but the observed moderate decrease does not seem commensurate with the orders of magnitude increase in pH that accompanies stoichiometric salt formation. (It is, however, difficult to say how much the higher basicity of the carboxylate anion compensates for the lower H⁺ activity.) A decrease in rate with the salt is also in apparent contrast to the 4-fold acceleration observed when the reaction medium contains 10% pyridine. We were unable to identify any coupling products under these conditions.

Calcium Anisate. No undecarboxylated material was found in the reaction of the neat salt of anisic acid. This result is perhaps surprising, given the traditional notion that decarboxylation of activated acids proceeds via an acid-catalyzed route,⁵ and there is nominally no acid (although the salt is predominately a dihydrate) in this system. Evidently, either the increased basicity of the carboxylate anion compensates for the lower acidity, or other decarboxylation routes not involving H⁺ are

equally facile at 400 °C. The distribution of monomeric products was qualitatively similar to that found in experiments with the free acid, with anisole, phenol, and cresols accounting for 45, 30, and 10 mol % of the anisate. The coupling product mixture was more complex than in experiments with the free acid, although the major products were still xanthene (1.3%), *o*-benzylphenol (BP, 1.0%), and methylxanthenes (0.6%). No xanthone or esters of anisic acid were found. Total coupling accounted for 5.0% of the anisate phenyl units.

Calcium Anisate/Naphthalene. The addition of naphthalene to the salt did not greatly change the monomeric product distribution, with anisole, phenol, and cresols accounting for 44, 21, and 11 mol % of the anisate. Xanthene, BP, and methylxanthenes remained the primary coupling products and were formed in yields similar to those found in the reaction of neat salt. Total coupling was 7.0%, not substantially different from the value of 5.5% noted in the analogous experiment with the free acid (see Table 4). Undecarboxylated material such as was present in reacted mixtures of the free acid, e.g., methyl anisate and other esters, was not found.

Calcium Anisate/Tetralin. Replacement of naphthalene with tetralin had little effect on the monomeric product distribution; anisole, phenol, and cresols accounted for 43, 29, and 9 mol % of the starting anisate. Again, no undecarboxylated material was identified. The major coupling products observed in the previous experiments, xanthene, BP, and methylxanthenes, were still present but in yields of only 0.26, 0.28, and 0.10%, respectively. Total coupling was 4.9%, slightly lower than found under less reducing conditions.

The primary result of these experiments with calcium anisate is that they show that rates of decarboxylation and coupling of the calcium salts are not very different from those of the free acids. Coupling is generally somewhat greater than with the free acids but not tremendously so. Distributions of the major products are also similar except for the absence of esters and xanthone, products which were found in some experiments with the free acid. This result is consistent with the suggestion, discussed below, that xanthone is formed from the reaction of one of these esters. Finally, as with the free acids, the naturally low levels of coupling can be further suppressed by the presence of H-donors.

Discussion

General Implications of Low Levels of Coupling.

The near-absence of coupling, together with the slow decarboxylation of benzoic acid and 3-hydroxybenzoic acid at 400 °C, would make it appear that *unactivated aromatic* carboxylic acids do not represent the species that undergo facile decarboxylation between 250 and

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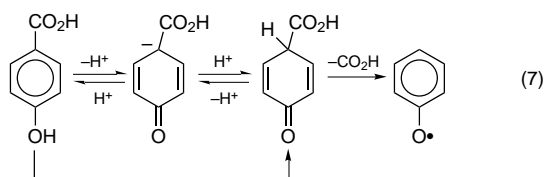
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400 °C during the heating of low-rank coals and reportedly give rise to cross-linking. The only substantial identified coupling products from an unactivated acid in the presence of tetralin resulted from the esterification of benzoic acid by naphthol. We have previously observed that esters do not survive liquefaction conditions when even small amounts of water are present,²⁷ as it typically is in coal liquefaction, so we currently do not consider these "nonpermanent" linkages to be of clear importance with regard to retrograde reactions. It should be noted, however, that under some conditions esters could be intermediates along a path to a more permanent linkage, either through direct rearrangement of the ester (e.g., the Fries rearrangement discussed below) or by holding coal fragments together until other reactions lead to stronger linkages.

The other benzoic acid derivatives that we examined are known⁵ to be activated toward decarboxylation via electrophilic attack. For all of these, except veratric acid (3,4-dimethoxybenzoic acid, last row in Table 1), conversion of the free acid in tetralin was almost complete in 1 h at 400 °C. Rapid decarboxylation appears to be interrupted only by esterification of the free acid. Excluding the formation of esters observed in some instances, there were no substantial level of coupling products formed from any of these activated acids in the presence of tetralin alone.

Activation by -OH or -OMe. All species with an -OH group attached ortho or para to the carboxyl group underwent complete decarboxylation, while those with an -OMe substituent were slightly less reactive, showing only about 90% decarboxylation due to either esterification or incomplete reaction of the starting acid. Since no meaningful rate constants can be derived from reactions that are essentially 100% complete, it is difficult to say whether these observed differences merely reflect the modestly more negative value of σ_p^+ for -OH^{5,28,29} or if a contributing mode of CO₂ loss somehow involves the hydroxyl hydrogen. The importance of the hydroxyl hydrogen would suggest that either the phenoxy anion or the keto form accessible through it is an intermediate in the decarboxylation.

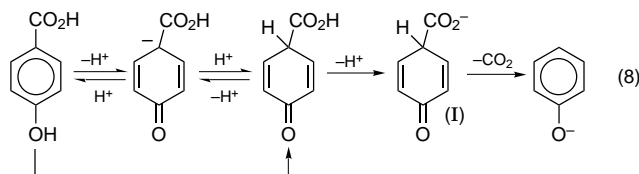
One possibility involving loss of the hydroxyl proton is that the keto form of the acid, generated via intermolecular proton transfer (or possibly unimolecular tautomerization), undergoes thermal unimolecular bond cleavage (homolysis) as shown in reaction 7 to yield a stabilized phenoxy radical and the radical $\bullet\text{CO}_2\text{H}$, in exact analogy to the thermal cleavage of benzyl and phenoxy phenols that has been previously elucidated.³⁰



However, this particular possibility is ruled out by the estimated enthalpy change for reaction 7. Because

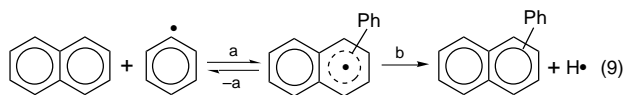
$\bullet\text{CO}_2\text{H}$ is not a very stable radical, reaction 7 is endothermic (for the overall reaction from enol form to phenoxy radical) by about 80 kcal/mol,^{31,32} which dictates that the decarboxylation would have a half-life substantially greater than 1000 h at 400 °C.

An alternative route involving the keto intermediate has proton loss occurring from the carboxylic acid functionality, followed by decomposition of the carboxylate directly to CO₂ and the phenoxy anion:



The sequence of proton transfers leading to the keto form of the carboxylate anion could also begin with initial proton loss from the carboxylic acid group. The point is that since formation of a small pre-equilibrium concentration of the keto form of related compounds is facile under similar conditions,³⁰ such a pre-equilibrium is also likely to be established in the present case. Intermediate **I**, once formed, should decarboxylate extremely rapidly.

Product Distributions and Mechanisms of Coupling of Benzoic Acid. The decrease in coupling observed when tetralin is present suggests that the primary mode of coupling involves aryl radicals, which are readily scavenged by the H-donor. The most likely mode of aryl radical production is from $\text{C}_6\text{H}_5\text{CO}_2\bullet$, which should rapidly decompose to $\text{C}_6\text{H}_5\bullet$ and CO₂. The carboxyl radical presumably arises, in the presence of an electron-transfer agent, from the oxidation of the anion as suggested by reaction 3 in the Introduction. In naphthalene alone, where there is nominally no electron-transfer agent present, we are not certain what the electron acceptor is. It could be naphthalene itself or possibly some surface reaction. We suggest that these alternatives are more likely than radical abstraction of the strongly bonded carboxylic acid hydrogen atom, because the higher radical steady state concentration present in tetralin solution should have enhanced such an abstraction. In any case, once formed, aryl radicals are expected to add readily to the aromatic system of naphthalene,¹⁷ as exemplified in reaction 9.



Our observed product distributions, wherein 1-phenylnaphthalene is typically 2–3 times more abundant than 2-phenylnaphthalene, are different from that reported in the phenylation of naphthalene in the gas phase at 450 °C, where the 2-isomer was favored by a factor of about 1.3–1.4.^{17,19} As discussed by Fahr and Stein,¹⁷ the 1-position is the preferred site of addition, but formation of the 2-isomer apparently dominates in the gas phase because of the reversibility of step 9a. Our product distributions imply much less reversibility in

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(28) Swain, G. C.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

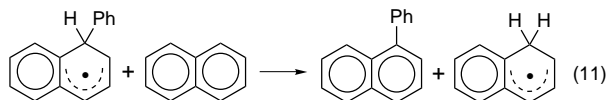
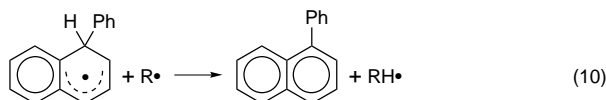
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the condensed phase, suggesting that loss of hydrogen from the coupling intermediate is aided, as expected, by bimolecular processes, either radical disproportionation (reaction 10) and/or radical hydrogen transfer (RHT, reaction 11):³³



The formation of binaphthyls and pyridinylnaphthalenes can be explained by the addition of pyridinyl and naphthyl radicals to naphthalene in a manner analogous to that described above for phenyl. One way such radicals could arise is by abstraction of hydrogen by the phenyl radical prior to its successful addition to naphthalene.

In the case of the binaphthyls, the distribution of 1,2'-, 1,1'-, and 2,2'-binaphthyl is typically 3:2:1 and shows no dependence on the additives. This product distribution is slightly different than that reported by Stein³⁴ but is consistent with a statistical preference for the 1,2'-isomer, a rather small (1–2 kcal/mol) preference for abstraction of the naphthalene 1-hydrogens,³⁴ and a slight kinetic preference for the highly exothermic addition of an aryl radical to the favored^{35,36} 1-position of another naphthalene.

With the pyridinylnaphthalenes, the point of connection of the pyridine to the naphthalene ring is inferred from the elution order of substituted naphthalenes on our column (1-isomers typically eluting first), but the connections to the pyridine ring are unknown. Both the pyridinyl naphthalene and binaphthyl isomer distributions are generally consistent with the expected position of preferential aryl radical addition to the naphthalene. However, as discussed below, the total amount of these secondary coupling products (those formed when the initial phenyl radical does not itself add, but abstracts, a hydrogen from a solvent molecule to form a new radical, which then adds to an aromatic ring system) formed in the presence of Fe₃O₄ is surprisingly high.

To establish a perspective on the relative levels of primary and secondary coupling products, it is necessary to consider the abstraction/addition ratios for the various radical and acceptor species. Thus, reaction of phenyl radical with toluene in the gas phase at 450 °C gives a ratio of abstraction/arylation, k_{ab}/k_{ar} , of 4/1 to 5/1.¹⁹ Toluene has weakly bound benzylic hydrogens, and a ratio of k_{ab}/k_{ar} substantially higher than 1 was to be expected. In contrast, H-abstraction from naphthalene, the main component in many of the present experiments, is much more difficult. From the ratio of binaphthyl/phenylnaphthalene in experiment 2 of Table 3 (benzoic acid, naphthalene, pyridine, without added iron oxide), we calculate $k_{ab}/k_{ar} = 0.11$, a value that is much lower than that for toluene and seems reasonable.

Curiously however, when Fe₃O₄ was added without scavenger, we found larger ratios of secondary to primary coupling products (0.42 and 1.3), even though this presumably requires abstraction of very strongly bound aryl hydrogens from naphthalene. Taken at face value, these ratios indicate that in the presence of Fe₃O₄, hydrogen abstraction from naphthalene now occurs 30–60% of the time, suggesting that iron oxide somehow aids in the transfer of the aryl hydrogens.

Also surprising is the fact that pyridinylnaphthalenes are formed in amounts similar to those of the binaphthyls in experiment 6 of Table 3, despite the fact that the reaction mixture contains 7 times as much naphthalene as pyridine. One might expect a more statistical distribution if these radicals were arising via abstraction of similarly strong aryl hydrogens by the original phenyl radical produced in the decarboxylation. Since the additional products are pyridinylnaphthalenes and not phenylpyridines, the facilitated reaction evidently is unusually facile formation of pyridinyl radicals and not facile radical addition to the pyridine ring. This conclusion is consistent with similarly minimal rates of dealkylation observed for both long-chain alkylbenzenes and alkylpyridines.³⁷ One explanation is that, to the extent that phenyl radicals are formed by the interaction of iron oxide with the complex C₆H₅CO₂[−](C₅H₅NH⁺), the pyridine may be more subject to attack because of its proximity to the nascent phenyl radical.

To check our assumption that the secondary products result from decarboxylation in the first place, we performed control experiments with mixtures of benzene, pyridine, and naphthalene in the presence of Fe₃O₄ but in the absence of any carboxylic acid. Although no significant quantity of phenylnaphthalenes were formed, we surprisingly did find some pyridinylnaphthalenes and binaphthyls. Assuming no other changes in the chemistry, their amounts indicate that as much as 30–40% of the *secondary* coupling products in the Fe₃O₄/naphthalene experiments could arise from mechanisms not involving decarboxylation as the original radical source. However, the bulk of the secondary coupling products and *all* of the primary coupling products (i.e., those between phenyl and naphthalene) do result from the decarboxylation.

Mechanism of Decarboxylation of Benzoic Acid in the Presence of Pyridine/Cu(OAc)₂. It is interesting that a mechanism for the widely used copper/quinoline-promoted decarboxylation of aromatic acids was not published until 1970^{20,21} and is still not entirely clear. It is thought to involve the formation of cuprous benzoates as key intermediates, which then decompose to an organocopper compound or organocopper/base complex. In the presence of H⁺ from the starting free acid, the organocopper intermediate is apparently converted to the arene. At least at the lower temperatures of the literature studies (≤200 °C), the reaction is thought to proceed without the formation of a free aryl radical. However, we observed (Table 2) that the pyridine/Cu(OAc)₂-promoted reaction at 400 °C resulted in a very small (0.03) ratio of coupling to decarboxylation similar to that observed with the naphthalene-only and naphthalene–pyridine solvent systems. Both the pyridine-promoted and the pyridine/Cu(OAc)₂-promoted decarboxylation could proceed entirely through the same

(33) Malhotra, R.; McMillen, D. F. *Energy Fuels* **1990**, *4*, 184.

(34) Stein, S. E.; Griffith, L. L.; Billmers, R.; Chen, R. H. *J. Org. Chem.* **1987**, *52*, 1582.

(35) Herndon, W. C. *J. Org. Chem.* **1981**, *46*, 2119.

(36) McMillen, D. F.; Malhotra, R.; Chang, S.-J.; Fleming, R. H.; Ogier, W. C.; Nigenda, S. E. *Fuel* **1987**, *66*, 1611.

(37) Mushrush, G. W.; Hazlett, R. N. *I&EC Fundam.* **1984**, *23*, 288.

intermediate, which does not seem likely, since the only plausible common intermediate is the carboxylate anion and there is no obvious way in which $\text{Cu}(\text{OAc})_2/\text{pyridine}$ would be more effective than pyridine alone in generating the carboxylate anion. Alternatively, we seem to be faced with the fortuitous consequence that in both the copper-promoted and unpromoted decarboxylations, a similar fraction of the material on its way to decarboxylation via different noncoupling routes branches to carboxyl radicals, which then decarboxylate and couple. In any case, both the base line decarboxylation system (in naphthalene) and the copper-catalyzed system are very different from the Fe_3O_4 -catalyzed reaction, which seems to proceed primarily through a free radical route. Evidently, more than one mechanism is operative for transition-metal-catalyzed decarboxylations.

Curiously, both decarboxylation and coupling were substantially slowed when H-donors were used as solvent in the pyridine/ $\text{Cu}(\text{OAc})_2$ -promoted reaction. Decarboxylation decreased from $\geq 83\%$ in naphthalene solvent to 47% in a mixture of tetralin/1-methylnaphthalene/naphthol, while the coupling/decarboxylation ratio decreased from 0.030 to 0.011. The effect of added scavenger would suggest that at least the coupling that does occur in this system proceeds via the same free radical routes outlined in the previous section on Fe_3O_4 . However, since the mechanism of the Cu-promoted decarboxylation is not known at this time, any statement about the inhibition of decarboxylation by tetralin is unavoidably speculative. It is possible, for instance, that the reduced decarboxylation in the presence of H-donors is a result of parasitic reduction of a cupric salt by the H-donor. However, this explanation would not appear consistent with the suggestion that the nitrogen base helps promote decarboxylation because it reduces Cu^{2+} to Cu^+ .²⁰

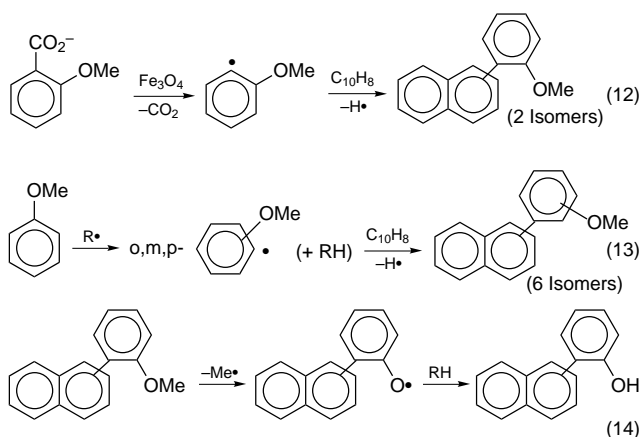
All uncertainties about Cu-promoted decarboxylation aside, the very low ratio of coupling to decarboxylation observed would seem to rule out the possibility that during coal pretreatment/liquefaction, an indigenous agent acting in the manner of pyridine/ $\text{Cu}(\text{OAc})_2$ could be responsible for retrograde reaction associated with decarboxylation. On the other hand, this result would by itself suggest that if decarboxylation-promoted coupling (such as that induced by iron oxides) were limiting liquefaction yields, the addition of an agent like the copper salt would increase the liquefaction yields. Unfortunately, electron-transfer agents can have countervailing effects, such as solvent adduction³⁸ associated with the use of pyridine or other nitrogen-containing materials in the liquefaction media.

Mechanisms of Coupling of Anisic Acid. One question is whether the coupling products observed for anisic acid are entirely the direct result of decarboxylation or whether they also stem from secondary reactions of already decarboxylated species. We suspected that phenol and cresol, which are descendants of the initial anisic acid decarboxylation product anisole, might be reactive toward electrophilic substitution under these conditions and responsible for some of the coupling products, so we carried out experiments with mixtures of cresol/naphthalene/ Fe_3O_4 and cresol/phenol/naphtha-

lene/ Fe_3O_4 . In these experiments we found several of the same coupling products identified in the anisic acid mixtures, including xanthene, methylxanthenes, and 1- and 2-HBN. Total coupling of phenolic units was 7.8% with both sets of mixtures. However, we did not find the peaks previously identified as (methoxyphenyl)- and (hydroxyphenyl)naphthalenes. The absence of the first of these compounds is not surprising, since no anisole was present in the mixture. The absence of the second compound indicates that Fe_3O_4 does not promote coupling of phenol and naphthalene to the same extent that it is able to promote pyridine/naphthalene coupling.

The formation of (methoxyphenyl)naphthalene (MPN) in the anisic acid experiments can best be explained by the net addition of methoxyphenyl radical to naphthalene. The *o*-methoxyphenyl radical could arise by one-electron oxidation of the anisate anion by Fe_3O_4 to give the appropriate carboxyl radical, which would rapidly decompose to give the aryl radical. Net addition of this species to the 1- and 2-positions of naphthalene would lead to two isomers of MPN (reaction 12) as observed. If the methoxyphenyl radical were generated by hydrogen abstraction from anisole after decarboxylation (reaction 13), we would expect ortho, meta, and para radicals to be formed and a total of six isomers of MPN would have been expected rather than the two that were observed.

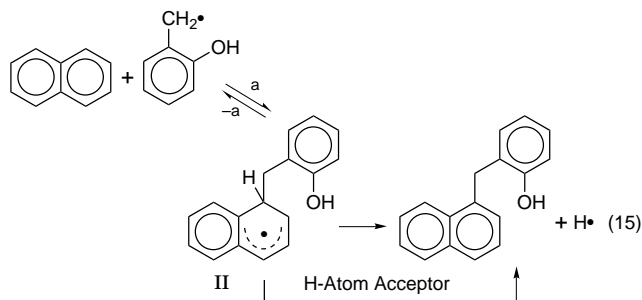
The two isomers of (hydroxyphenyl)naphthalene (HPN) apparently result from breakage of the methyl ether linkage in MPN (reaction 14) in a manner analogous to that observed for anisole itself. This explains why we also found only two isomers of this product. Although these products account for only about 1% of the anisic acid, the number of isomers detected is strong evidence that they are formed as a direct result of decarboxylation.



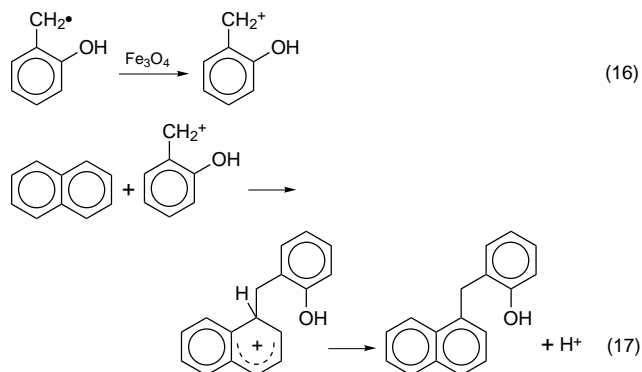
In contrast, because 1- and 2-HBN are prominent coupling products of cresol and naphthalene alone (Table 4, experiments 4 and 5), it seems likely that these species do not arise as a direct result of decarboxylation of anisic acid. Most likely, these products arise directly or indirectly from *o*-hydroxybenzyl radical. Direct displacement of hydrogen by ipso addition of stabilized radicals, such as in reaction 15, is difficult because of the large endothermicity of unimolecular H-atom loss, estimated to be 22 kcal/mol. This endothermicity makes

(38) (a) Derbyshire, F. W.; Odoerfer, G. A.; Whitehurst, D. D. *Fuel* **1984**, 63, 56. (b) Hellgeth, J. W.; Taylor, L. T. *Fuel* **1984**, 63, 961.

addition of benzylic radicals (reaction 15) much more reversible than the analogous addition with phenyl radicals (reactions 9 and 12).



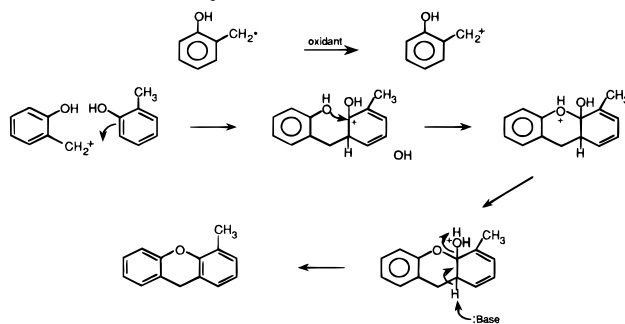
Thermochemical estimates suggest that bimolecular H-transfer processes will not in this instance be easily able to compete with unimolecular re-elimination of the hydroxybenzyl radical (reaction 15(-a)). Although radical addition to naphthalene is rapid, with an estimated rate constant of $10^{5.9} \text{ M}^{-1} \text{ s}^{-1}$ at 400°C , decomposition of the adduct radical through reaction 15(-a) is estimated to be $\sim 10^5$ times as fast as unimolecular loss of the hydrogen atom. To account for the observed quantities of HBN through radical addition and unimolecular H-atom loss, the average concentration of *o*-hydroxybenzyl radical would have to be $\sim 10^{-7} \text{ M}$, which is higher than thermochemical estimates lead one to expect. The alternative H-loss processes most likely involve either bimolecular H-atom transfer from intermediate II in reaction 15 or a Friedel-Crafts-type alkylation after oxidation of the radical by Fe_3O_4 (reactions 16 and 17).



Based on the elution order observed for other substituted naphthalenes on our column (phenyl-, benzyl-, and naphthyl-naphthalenes), we were able to tentatively assign the ratio of 1- to 2-HBN as ~ 1.6 . Such a ratio is consistent with either a radical- or an ionic coupling mechanism⁵ and cannot be used to distinguish them. Finally, although these products do not appear to be a *direct* result of decarboxylation, it should be noted that to the extent that decarboxylation reactions are a source of radicals, they may serve to increase the general radical pool and thereby lead indirectly to such coupling products. In general such radical sources will be more important for reactions in the absence of hydrogen donors, since donors such as tetralin can themselves be a major source of radicals through the reverse of radical-disproportionation reactions.³⁹

(39) Billmers, R.; Griffith, L. L.; Stein, S. E. *J. Phys. Chem.* **1986**, *90*, 517.

Scheme 1. Probable Mechanism for the Formation of Methylxanthene from Cresol



The mechanism of formation of xanthene and methylxanthene is less clear, although it is undoubtedly associated with the increased formation of cresols that occurs in the presence of Fe_3O_4 (Table 4). One reasonable possibility is put forth in Scheme 1, in which an *o*-hydroxybenzyl radical is oxidized to the corresponding cation, which then alkylates another cresol molecule. When the position of this electrophilic attack is the ortho position, the adduct is set up for ring closure and water elimination to form methylxanthene. This mechanism, which suggests that two cresols will react to give methylxanthene while cresol plus phenol will give xanthene, is consistent with the product ratios observed in the experiments with cresol and cresol/phenol mixtures (Table 4). In experiment 5, for instance, where an equimolar amount of cresol and phenol was used (in the presence of Fe_3O_4 but in the absence of anisic acid), the ratio of xanthene/methylxanthene was 2.1/1, very close to the statistical value of 2 predicted on the basis of the number of available addition sites ortho to the hydroxy group. Interestingly, although the amount of cresol in the experiments with anisic acid and Fe_3O_4 (experiment 3) was a factor of 7–100 less than in those where cresol and phenol were the starting materials, more xanthene was formed in the experiment with anisic acid. It is not clear if this indicates that additional routes to this product exist in the anisic acid system or if it merely indicates that the concentration of the *o*-hydroxybenzyl radical intermediate is much higher when anisic acid is the starting material. Note that the benzylic C–H bond of *o*-cresol is very weak and will be readily attacked by most radicals. Thus, to the extent that more radicals are generated in the anisic acid system, one might not expect a simple correlation between the amounts of cresol and the amounts of xanthene.

The last of the major coupling products to be explained is xanthone, which was present only in the experiments *without* added iron oxide. This compound could possibly result from the oxidation of xanthene after reaction. However, when product mixtures containing xanthene were reanalyzed after several months of storage, no xanthone was found. We had earlier noted that in the same experiments where xanthone was found, there were two peaks at $m/e = 228$, which were identified as phenyl anisate and *o*- or *p*-hydroxyphenyl-*o*-methoxyphenyl ketone (*o/p*-HPMPK). The latter is a product of the Fries rearrangement of phenyl anisate.⁴⁰ Formation of xanthone from *o*-HPMPK is

(40) Kwart, H.; King, K. In *The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Wiley and Sons: London, 1969; p 347.

straightforward as shown in reaction 5 above. The ring closure to xanthone is exactly analogous to that shown in Scheme 1 for xanthene. Notwithstanding the fact that the formation of diphenyl ethers is generally slow, ring closures by the formation of ether linkages are much faster, having precedents such as the very rapid ring closure at 400 °C of 2, 2'-dihydroxybiphenyl to dibenzofuran.⁴¹

This route to xanthone is consistent with the fact that when iron oxide is present and xanthone is absent, esters of anisic acid are also completely absent. However, at present we are unable to answer the question as to whether or not Fe₃O₄ inhibits the formation of esters, accelerates their decomposition through other routes, or merely accelerates decarboxylation so that ester formation is kinetically uncompetitive.

Conclusions

The rates of decarboxylation of benzoic acids range from a few percent in 1 h at 400 °C for unactivated acids to >98% for species activated by OH in the ortho and para positions. No single decarboxylation mechanism suffices for all benzoic acids, and even a given substrate apparently can react by a combination of pathways. Rates of decarboxylation of unactivated aromatic acids can be increased by the addition of amine base and/or one-electron oxidants, but our experiments demonstrate that coupling reactions of activated and unactivated monomeric carboxylic acids are generally *not* major processes under coal liquefaction conditions *in the absence of* electron-transfer agents such as Fe₃O₄. In general, in the absence of one-electron oxidants, fewer than 1 in 10 decarboxylations leads to a cross-linking reaction. Furthermore, the rates of decarboxylation and coupling of the calcium salts of the activated and unactivated *aromatic* acids studied here are *not* significantly higher than those of the free acids. This is in apparent contrast to the fact that the calcium or magnesium forms of low-rank coals produce more CO₂ and show more evidence of cross-linking on heating.^{3,10-14,25} Decarboxylation and coupling reactions of benzoic acid are induced by the potential electron-transfer agents FeS, Cu(OAc)₂, and Fe₃O₄, and under some conditions (i.e., with Fe₃O₄), one coupling reaction can occur for every two decarboxylations. However, the rate of coupling in the presence of Fe₃O₄ is greatly reduced by both base and H-donors such as tetralin. Fe₃O₄, the most effective of the agents at promoting cross-linking of unactivated aromatic acids, was less able to enhance the coupling of the activated species anisic acid.

Anisic acid, by itself, is slightly more prone to coupling than unactivated acids like benzoic acid. However, this coupling is not a *direct* result of recombination or addition of intermediates having the radical or ionic site at the carbon that originally bore the carboxylic acid group. Instead, coupling appears to reflect the fact that the secondary decarboxylation products, such as phenol or cresol in the case of anisic acid, are much more susceptible to electrophilic attack than was the original hydroxy acid.

In the case of the product mixture from anisic acid decarboxylation, attack of an *o*-hydroxybenzylic fragment on another phenol leads to ring coupling and ring closure to form rather refractory fused-ring xanthene structures.

When water was added to the reaction system in which decarboxylation produced the most coupling, namely benzoic acid–naphthalene–Fe₃O₄, there was no discernible effect on either decarboxylation or coupling. On the other hand, water can be expected to have an effect where coupling proceeds through an intermediate ester, such as in the generation of xanthone via Fries rearrangement of an ester. Also, in related studies,⁴² we have found that the addition of water can substantially affect products generated from *aliphatic* acids, where coupling appears to proceed via acid anhydride and/or ketene intermediates that can be destroyed by water.

The overall conclusion is that, to the extent that *aromatic* carboxylic acid species are representative of coal structures, rather selective (i.e., nonreductive) conditions are necessary for the decarboxylation reaction itself to result in substantial coupling during coal liquefaction. This suggests that other structures, either alone or in concert with carboxylic acids, are largely responsible for the retrograde reactions associated with CO₂ evolution. On the other hand these results suggest that, if decarboxylation is involved, it ought to be possible to interrupt these reactions by appropriate control of the conditions. The limited coupling and the ease with which it is suppressed by H-donors suggest that the increased low-temperature coupling associated with the increased oxygen content of low-rank coals is probably not *directly* caused by the reaction of radical or ion fragments produced as decarboxylation intermediates of aromatic acids. However, since the decarboxylation of –OH-activated aromatic acids produces structures (cresols, catechols, etc.) that are much more susceptible to electrophilic attack than the original acids, coupling of these phenolic products may indeed be an important cross-linking route. An example of this secondary cross-linking is provided by the formation of xanthenes from the phenols generated in the decarboxylation of anisic acid.

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(42) Manion, J. A.; McMillen, D. F.; Malhotra, R. Decarboxylation and Coupling Reactions of Phenylacetic Acid under Coal-Liquefaction Conditions. *Energy Fuels*, to be submitted.