

DECARBOXYLATION AND COUPLING REACTIONS OF PHENYLACETIC ACID UNDER COAL-LIQUEFACTION CONDITIONS

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INTRODUCTION

The conversion of low-rank coals to liquids or volatile hydrocarbons is known to be substantially hindered by retrograde reaction, and oxygen functional groups in the coal structure are strongly correlated with these retrograde reactions. Carboxyl functions have been implicated in the crosslinking of coals during heating at relatively low temperatures,^{1,2} and Solomon et al.³ have been able to model the pyrolytic loss of solvent swelling by including one additional crosslink in the network for every CO₂ evolved. However, carboxyl groups are not the dominant oxygen-containing moieties, even in low-rank coals, and we suspected hydroxyl functions may play just as large a role, particularly since phenolic -OH in polyhydroxy systems are known to lead to furanic systems under coal liquefaction conditions.⁴ Therefore we have examined the rates of decarboxylation some prototypical carboxylic acids to see if crosslinking results directly from decarboxylation, as well as how crosslinking is affected by H-donors, electron transfer reagents, the addition of water, and other conditions relevant to pretreatment and liquefaction of coals.

We have previously reported the decarboxylation and coupling reactions of aromatic carboxylic acids and their calcium salts,⁵ and found that little coupling generally followed from these decarboxylations. Generally, fewer than one in ten decarboxylations led to a crosslinking reaction, except in the presence of 1-electron oxidants where, under some non-reducing conditions, one coupling reaction occurred for every two decarboxylations of benzoic acid. Recently Eskay, et al. prepared and studied polymers containing unactivated aromatic carboxylic acids to test whether the presence of a polymeric structure would significantly enhance crosslinking reactions, but they also observed little coupling resulted from decarboxylation of unactivated benzoic acid structures.⁶

For activated aromatic acids, we found that coupling by direct reactions of radical fragments is very low, but coupling as an indirect result of decarboxylation can be very substantial. Loss of the electron-withdrawing carboxyl group from, for example, 2-hydroxybenzoic acid, allows the hydroxy group to exert its full activating effect toward any subsequent substitution by electrophiles. Thus we showed that by this route, decarboxylation of activated aromatic acids can lead to ring coupling and even to subsequent ring-closure, though not by the radical-coupling routes that are often cited.

Because it is likely that some carboxyl groups in low-rank coals are not attached directly to an aromatic ring, we have extended our examination to the thermal behavior of phenylacetic acid, a prototypical structure with an aliphatic acid side chain. In addition to a very early report on the thermolysis of the neat liquid,⁷ there are more recent gas phase studies at high temperature.⁸ A recent study of PAA decomposition at 250°C reported that a major pathway for phenylacetic acid decomposition at 250°C involves net elimination of H₂O and CO₂ to form the coupling product dibenzyl ketone (DBK) and proposed a four-membered ring rearrangement of the anhydride to the unstable β-keto acid, which then easily decarboxylates.⁹ The presence of water completely inhibits the ketone formation.

EXPERIMENTAL

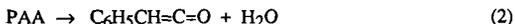
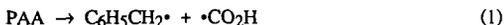
Reactions were performed in fused silica ampoules, heated inside a stainless steel pressure jacket, as described previously.⁵ Products were analyzed by GC (FID) and GC-MS. The estimated overall accuracy was ±2% in most cases, ±5% for some polar products, and ±12% for phenylacetic acid itself. Phenylacetic acid (99+% by GC analysis), naphthalene (Aldrich 99+%), tetralin (Aldrich, 99%), pyridine (Mallinckrodt, AR grade, 99+% by GC analysis), and Fe₃O₄ powder (particle size ~0.2 μm) were used without further purification.

RESULTS AND DISCUSSION

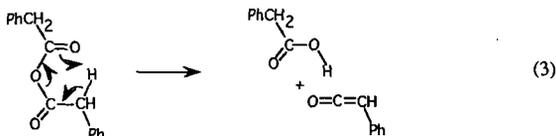
Decarboxylation Rates and Major Products. Table 1 shows the major thermal decomposition products of PAA in naphthalene/tetralin mixtures. In 1 hour at 400°C, 28 to 43% decarboxylation is observed. The primary products were toluene and dibenzyl ketone (DBK), as described in the literature,⁷⁻⁹ along with one isomer of tetralylbenzyl ketone (TBK), bibenzyl, and trans-stilbene. Also found were small quantities of benzylnaphthalenes, dihydrobenzylnaphthalenes, phenylnaphthalenes, and an isomer of benzyltetralin. Benzene accounted for less than 0.5% of the PAA that was consumed. We also found coupling products formed entirely from solvent: binaphthyls, bi-tetralyls, their cross products, and partially hydrogenated versions of these compounds. Together, these solvent coupling products accounted for less than 0.5% of the starting acid. Mass balances were generally >97%, except in the two experiments with naphthalene-only solvent, where only 91% of the PAA was accounted for.

Figure 1 shows the changes in the distribution of the main products as the solvent was shifted from naphthalene to tetralin. Decarboxylation of PAA, as measured by toluene formation, decreased by about 25%, but the proportions of toluene and total ketones were not changed significantly.

Mechanism of Decarboxylation. Although the mechanism of the condensed phase thermal decarboxylation of phenylacetic or other aliphatic acids has not, to our knowledge, been fully elucidated, the thermal reaction in the gas phase has been reported to proceed via reactions (1) and (2) at temperatures between 587 and 722°C.⁸ Reaction 1 would give toluene in two steps, but its parameters, as selected in a critical review of the work,¹⁰ would dictate a half-life for PAA of about 10,000 h at 400°C.

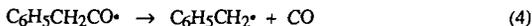


This projected half-life is orders of magnitude longer than that actually observed here, and therefore the liquid phase reaction must proceed via another mechanism. Similarly, four-center elimination of water from the phenylacetic acid, as implied by Reaction 2 as written, is unlikely under our conditions because the analogous elimination from acetic acid, for instance, has a very high activation energy (68 kcal/mol¹¹). It is more likely that reaction proceeds through an anhydride intermediate, which can eliminate PAA and generate phenyl ketene in a favorable 6-center transition-state (Reaction 3). Radical addition to ketene could then give the observed ketone products. The parameters reported¹² for acetic acid anhydride decomposition, $k/s^{-1} = 10^{12.0} \cdot 7540/T$, would lead to a half-life of only about a tenth of a second at 400°C, easily fast enough to give the required ketene, provided that the formation of the anhydride is itself facile.



The anhydride could be formed via either a concerted or an acid- or base-catalyzed elimination of water. While the formation of toluene is consistent with reaction via $\text{PhCH}_2\cdot$, as previously suggested,⁹ the observation of small amounts of 1,2-diphenylethane (1,2-DPE), trans-stilbene, benzylnaphthalenes, and dibenzyl ketone (see below) appear more consistent with the presence of benzyl radicals. Similarly, decomposition of the anhydride to ketene is not limited to a concerted reaction. Since H-atom chain reactions are often, at high temperatures, close competitors to electrocyclic eliminations, the ketene could also be formed from the anhydride by an H-abstraction, β -scission process to yield phenylacetate radical as the companion product. This radical would decarboxylate extremely rapidly, possibly leading to some reaction of its product benzyl radical with ketene before they left the solvent cage. If benzyl radical and ketene are formed exclusively by an H-abstraction, β -scission process chain process, then the presence of substantial cross products indicates escape from the cage is competitive with cage addition of benzyl radical.

Effect of Donor Solvent on Ketone Formation. As the reaction medium was shifted from naphthalene to tetralin, a gradual four-fold drop in formation of dibenzyl ketone was observed, while a new species, tetralylbenzyl ketone, became a prominent product. This result, shown graphically in Figure 2, suggests that benzyl radicals are increasingly scavenged by tetralin. The formation of cross-products certainly means that DBK does not form exclusively by the sequence of concerted rearrangement to a β -keto acid, followed by facile decarboxylation, as has been suggested previously.⁹ Cross products also mean that radical reaction is not limited to recombination within a cage. Therefore, we suggest instead that dibenzyl ketone is formed in reactions (5) and (6). No rate parameters for (5) have been reported, but the reaction would be expected to be rapid.



As tetralin is added to the system, benzyl radicals will be partly scavenged by tetralin, and tetralyl radicals will replace benzyl radicals in Reaction 5 to give tetralyl benzyl ketone, as reflected in the data in Figure 2. Because the 1-tetralyl radical is ~12 kcal/mol more stable than the 2-isomer,¹³ the TBK product should be almost entirely 1-tetralyl benzyl ketone, as observed. However, even in pure tetralin, only about 2/3 of the dibenzyl ketone was replaced with tetralylbenzyl ketone. The inability of tetralyl radicals to intercept a greater proportion of the presumed intermediate phenyl ketene needs to be considered carefully because it bears on the hypothesis that this radical addition is the route to benzylnaphthyl ketene.

Because the equilibrium constant¹⁴ for Reaction 7 is ≥ 10 , and because the tetralin was in substantial excess over toluene, it is apparent from the ratio of DBK/TBK (Table 1), that either Equilibrium 7 has not been established, or k_5/k_7 is very large. Estimation of the rates of reactions 5 and 7, based on measured rates of analogous reactions and thermochemical data, suggests that indeed, scavenging of benzyl radical is simply not fast enough to completely outpace its addition to ketene.

The Effect of Added Water. A rationale involving reaction through the anhydride and the corresponding ketene suggests that the addition of water to the reaction mixture should slow the formation of ketenes, both through hydrolysis of the proposed anhydride intermediate and by the rapid reaction of phenylketene with water¹⁵ to re-form phenylacetic acid (Reaction -2, above). In partial accord with this expectation, and as Katritzky et al. have reported⁹ for lower temperatures, we found that the addition of 34 mol% of water to a mixture of naphthalene and PAA led to more than a seven-fold drop in dibenzyl ketone formation (Table 1). Curiously, however, there is *no* decrease in the rate of decarboxylation: the decrease in ketone formation corresponds almost exactly to the increase in toluene formation. Added water does *not* simply send anhydride or ketene back to acid. Since water with its very strong HO-H bond is a terrible radical scavenger but a good acid, the diversion of ketone to toluene suggests an anhydride-like intermediate whose benzyl fragment can act as a carbanionic species. This reaction would be similar to hydrolysis of the anhydride, except that the CO-CH₂ bond would act as the electrophile, rather than the C=O double bond, as occurs in a normal hydrolysis.

Water also caused a three-fold decrease in benzylnaphthalenes and a six-fold decrease in the sum of dibenzyl and stilbene. The system containing water had the lowest coupling/(total reaction) ratio at 0.024. Because dibenzyl and stilbene can plausibly result only from benzyl radical recombination, and because water is a poor radical scavenger, this observation provides additional evidence that water shifts decomposition of PAA more towards ionic pathways, so that fewer radicals are generated in the first place. This explanation would require an intermediate X that decomposes either via radical production or via an ionic pathway: by increasing the rate of the ionic pathway, the steady state concentration of X (and the consequent generation of radicals) is reduced, though the overall decarboxylation rate remains unchanged. Water, acting as an acid, captures an anionic benzyl fragment from the intermediate, increasing the toluene yield and decreasing those products that result from radical reactions.

Non-Ketone Coupling Products. In pure naphthalene solvent, traces of benzylnaphthalenes were observed. When tetralin was added to the naphthalene, we observed increased levels of benzylnaphthalenes, as well as dihydrobenzylnaphthalenes and a single isomer of benzyltetralin [identified by mass spectrometry as α -benzyltetralin (1,2,3,4-tetrahydro-1-benzylnaphthalene)]. The absence of significant amounts of benzylnaphthalenes in pure naphthalene presumably reflects the fact that addition of benzylic radicals to aromatic systems forms an initial cyclohexadienyl adduct radical having a very weak C-C bond, and is therefore a highly reversible process. The initial adduct cannot be stabilized unless the ipso-hydrogen is rapidly removed, in a bimolecular fashion, by some H-acceptor species. However, when tetralin is present, α -tetralyl radicals will constitute a significant part of the radical population and can provide additional routes to benzylnaphthalenes.

The marked increase in benzylnaphthalene formation with added tetralin is accompanied by a similar increase in the ratio of 1-benzylnaphthalene/2-benzylnaphthalene. As the reaction medium is shifted from naphthalene to pure tetralin, the yield of benzylnaphthalenes increases by 20X, and the ratio of the 1-isomer to the 2-isomer increases from near 1 to almost 40 (Figure 3). This predominance of 1-benzylnaphthalene, together with the observation that only the α -isomer of benzyltetralin was observed, suggests that in tetralin, 1-benzylnaphthalene is formed predominantly by recombination of benzyl radical with the dominant α -tetralyl radical, followed by dehydrogenation of the α -benzyltetralin. In pure naphthalene, on the other hand, the benzylnaphthalenes are evidently formed only by radical addition to naphthalene, which should show more limited selectivity, though still favoring the 1- position of naphthalene.

The Effect of an Amine Base. The addition of 10 mol% of pyridine to the naphthalene/PAA mixture (Table 1) did *not* increase decarboxylation, but did increase toluene yield by about 20%. The effect is thus different than that observed with benzoic acid, where 10% pyridine increased decarboxylation fourfold.⁵ The effect of base on ketone formation was minor, decreasing formation of dibenzylketone by about 10%. More surprising was its effect on the other coupling products. The sum of 12DPE and trans-stilbene was increased a factor of 2.5, and new products appeared, including diphenylmethane (DPM, 0.47%), an isomer of phenylpyridinylethane (0.17%), phenylnaphthalenes (0.12%), pyridinylnaphthalenes (0.13%), and various unidentified coupling products of higher molecular weight. The precise sources of these products are unclear: DPM has been identified by Miller and Stein¹⁶ as a significant product in the *later* stages of neat 1,2-DPE pyrolysis, but they were unable to identify the route to this product. It is not likely to arise from addition of benzyl radicals to benzene, since the formation of the initial adduct would be even more readily reversed than in the benzylnaphthalene case discussed above. Similarly, the formation of phenylnaphthalenes and pyridinylnaphthalenes suggests that the generation of aryl radicals from the solvent components is somehow being promoted by pyridine. Although we

observed similar coupling products in the case of decarboxylation of aromatic acids,⁵ in that case the addition of pyridine actually resulted in a *lower* total yield of products most easily attributable to radicals.

The Effect of Fe₃O₄. In the previous study of aromatic acids, we had found that under some conditions the addition of electron transfer agents, which may be present in coals as inorganic components, increased the rates of decarboxylation and coupling. Fe₃O₄ was the most effective of these agents at promoting coupling, and therefore we examined its effect on the decarboxylation and coupling of PAA. The effects of iron oxide on the course of the reaction were somewhat different, depending on whether the solvent was pure naphthalene, or contained a donor component. When the solvent was naphthalene only, addition of 10 mol% Fe₃O₄ doubled the total conversion of PAA, but resulted in little or no increase in the "major" products: dibenzyl ketone was unchanged, and toluene increased only 25%. Most of the additional conversion resulted in various "minor" coupling products, which were increased to the point where they constituted, in total, about half of the coupling products. The sum of bibenzyl and t-stilbene was increased by a factor of nearly 25 when compared to the case without added Fe₃O₄. Benzylnaphthalenes were increased by a factor of 45, with both isomers now found in similar quantities. Perhaps most surprising was the presence of phenylnaphthalenes, not formed at all without added Fe₃O₄, but now found at about 75% of the level of the benzylnaphthalenes. A new ketone, benzylphenyl ketone, was found at about 10% of the level of dibenzyl ketone.

When the solvent contained tetralin, Fe₃O₄ roughly doubled the fractional conversion of PAA, as it had in pure naphthalene solvent, but with the donor present, dibenzyl ketone was increased by 300%! Toluene and most of the minor coupling products, such as benzylnaphthalene and phenylnaphthalene, decreased significantly. This effect can also be stated in terms of tetralin addition: in the absence of Fe₃O₄, tetralin addition suppresses dibenzyl ketone by ~70% (essentially replacing it with tetralylbenzyl ketone), but when Fe₃O₄ is present, tetralin addition increases dibenzyl ketone by 300%.

Evidently, Fe₃O₄ increases the number of decomposition intermediates, or complexes, regardless of whether tetralin is present. If tetralin isn't present, then most of these decomposition intermediates go on to generate radicals that are distributed in the bulk of the solvent, and therefore primarily give coupling products that involve one or two solvent molecules. However, when tetralin is present, it evidently can prevent escape of benzyl radicals from the "cage" of decomposition intermediates, and send most of the intermediates to dibenzylketone. If the last step in ketone formation from PAA is indeed radical addition to phenyl ketene, then stabilization of the adduct requires transfer of a hydrogen *to* that adduct; tetralin would clearly help to provide this hydrogen. This case is in curious contrast to the "normal" case of retrograde reaction, where addition to an aromatic ring system requires H-removal *from* the initial adduct in order to achieve a stable, aromatic coupling product. In that case, formation of a stable adduct is most facilitated by a hydrogen *acceptor*, rather than a hydrogen *donor*.

Implications for Coal Liquefaction and Gasification. Because of its ca. 1-h half life at 400°C, phenylacetic acid, and by extension, other short chain fatty acids, are probably not related to the coal species that undergo rapid decarboxylation below ca. 400°C. Thus, barring substantial promotion of decarboxylation rates by indigenous coal substances, these aliphatic acids appear unlikely to account for the crosslinking at mild conditions that has been observed for low-rank coals. Such decarboxylation would appear to be limited to aromatic acids activated by hydroxy substitution. On the other hand, the primary coupling reactions of PAA, which lead to ketones, and the secondary coupling reactions, which lead to alkyl-aryl and aryl-aryl coupling products through addition of substrate- and solvent-derived radicals, could well contribute to retrograde reactions that occur between 400 and 450°C. Such ketone formation is expected to be quite general for other fatty acids possessing α -hydrogens. In coal structures, these reactions that require two acid groups may be restricted by limited availability of other acid functionalities in the nearby coal matrix. In fact, the opportunity to form retrograde products via anhydride intermediates could help to explain how such products are enhanced when divalent metal cations are ion-exchanged into low-rank coals, forming di-acid salts. The observed diversion by water of dibenzyl-ketone-forming intermediates to toluene could also help to explain some of the reported benefits^{17,18} of added water on coal liquefaction.

Decarboxylation to generate radical species which then undergo simple recombination reactions or addition to aromatic rings appears to be directly responsible for only a limited amount of coupling, with generally less than one crosslink for every ten decarboxylations of PAA. These radical-recombination or addition routes can be partially controlled through the use of H-donors. As the solvent composition is shifted from pure aromatic to hydroaromatic, the dominant route to alkyl-aryl coupling products can be seen to shift from radical addition to radical recombination, where the bulk of initial recombination products survive at 400°C only because aromatization enormously increases adduct bond strength.

The electron transfer agent Fe₃O₄ caused a two-fold enhancement of decarboxylation, but because it seems to primarily enhance radical pathways, resulted in a four-fold enhancement of coupling products. In the presence of Fe₃O₄, added tetralin caused a dramatic enhancement of dibenzyl

ketone formation rates. This unexpected effect, presumably a result of enhanced trapping of a cage addition product, provides yet another illustration of fact that "hydrogen transfer" is not always good for liquefaction, in that it is equally necessary for both the formation and the scission of strong bonds.

SUMMARY AND CONCLUSIONS

Phenylacetic acid in naphthalene at 400°C undergoes about 25% decarboxylation in one hour, intermediate to the rates of the activated and unactivated aromatic acids. The rate decreases about 25% as the solvent medium is switched to tetralin, but is essentially unchanged by the addition of amine base or water. The major coupling products of PAA are dibenzylketone (DBK) and, when tetralin was present, tetralylbenzyl ketone (TBK), probably formed from reaction of phenylketene with benzyl and tetralyl radicals, respectively. Smaller amounts of 1,2-diphenylethane, trans-stilbene, benzyl-naphthalenes, and benzyltetralins are also formed. Total coupling is between 14-23% of reaction except in the presence of added water, where the coupling was reduced to about 2%. The ketones account for 40-90% of the coupling products, with the percentage decreasing as tetralin is added. Only ~2 to 15% of the total retrograde products result from actual recombination of the parent benzyl radicals, the commonly invoked retrograde reaction.

Water inhibits the formation of the ketones without decreasing the extent of decarboxylation, presumably by diverting intermediates that could have led to anhydride or ketene formation. Other coupling products evidently result from radical recombination or addition/elimination reactions. The one-electron oxidant Fe_3O_4 caused a two-fold increase in decarboxylation and a more substantial increase in products expected from radical reactions. Fe_3O_4 added to naphthalene had little effect on DBK formation, but Fe_3O_4 added in the presence of tetralin markedly increased the formation of DBK and increased the ratio of coupling/(total reaction) to about 0.5, independent of the amount of tetralin present (at tetralin > 10%). In the presence of tetralin and Fe_3O_4 , about 80% of the total coupling was due to formation of DBK.

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Table 1
MAJOR REACTION PRODUCTS OF PHENYLACETIC ACID IN
NAPHTHALENE/TETRALIN MIXTURES^a

REACTANTS ^b	J40	J75	J39	J67	J71	J70	J72	J25
% Tetralin	0.0	0.0	0.0	12.38	47.90	66.38	77.23	100.00
Ph-Acetic Acid	9.83	6.59	10.92m	11.07	10.04	9.97	9.90	10.29m
Naphthalene	79.01	59.12	89.08m	77.92	46.87	30.27	20.52	-
Tetralin	-	-	-	11.01	43.09	59.76	69.58	89.71
Pyridine	11.16	-	-	-	-	-	-	-
H ₂ O	-	34.17	-	-	-	-	-	-
PRODUCTS ^b								
Pyridine	77.4	-	-	-	-	-	-	-
Ph-Acetic Acid	61.3	57.5	57.1	64.8	65.9	70.4	71.9	67.2
Naphthalene	99.2	102.8	99.2	87.7	52.6	34.7	24.2	2.7
Tetralin	-	-	-	11.9	46.3	64.6	75.1	94.1
Benzene ^c								
Toluene	31.6	32.9	27.2	27.4	25.4	22.2	22.4	19.7
Bibenzyl	0.36	0.028	0.24	0.071	0.056	0.067	0.069	0.026
t-Stilbene	0.46	0.026	0.071	0.11	0.086	0.060	0.061	0.037
Benzylphenyl ketone	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dibenzyl ketone	5.10	0.75	5.57	5.75	3.87	2.71	2.92	1.40
Benzyltetralyl ketone	< 0.01	< 0.01	< 0.01	0.68	1.76	1.33	1.60	1.32
Bz-Naph(H) ₂ ^d	< 0.01	< 0.01	< 0.01	0.11	0.13	0.15	0.16	0.14
1234H-5-BzNaph ^e	< 0.01	< 0.01	< 0.01	0.049	0.098	0.23	0.21	0.26
Unk. 20,20	< 0.01	< 0.01	< 0.01	< 0.01	0.21	-	0.053	0.0
Bz-Naph(H) ₂ ^d	< 0.01	< 0.01	< 0.01	0.043	0.078	0.14	0.17	0.23
Bz-Naph(H) ₂ ^d	< 0.01	< 0.01	< 0.01	0.011	0.024	0.047	0.053	0.081
1-Ph-Naphthalene	0.053	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
2-Ph-Naphthalene	0.067	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
1-Bz-Naphthalene	0.025	0.0084	0.023	0.21	0.37	0.42	0.49	0.48
2-Bz-Naphthalene	0.028	0.0054	0.024	0.016	0.020	0.014	0.015	0.012
Sum Bz-Naph(H) _x ^f	0.053	0.014	0.047	0.43	0.72	1.01	1.10	1.19
Sum coupling	7.93	0.82	6.09	7.04	6.73	5.24	5.86	4.53
coupling/Rxn ^g	0.21	0.024	0.14	0.200	0.23	0.18	0.20	0.14
Sum PAA products ^h	98.9	91.2	90.8	99.3	97.8	97.9	100.0	93.6
Sum Bz-Naph(H) ₂	< 0.01	< 0.01	< 0.01	0.15	0.22	0.34	0.38	0.45
1/2 Bz-Naph ⁱ	0.90	1.56	0.95	13.0	18.5	29.4	32.6	38.3
Sum Ketones	5.10	0.75	5.57	6.43	5.63	4.05	4.52	2.72

- Reaction time 1 hr @ 400°C.
- Reactants are shown in mole % of reaction mixture; products of phenylacetic acid are shown as a mole % of the starting acid, naphthalene and tetralin are shown as mole % of the sum of starting naphthalene and tetralin, and coupling products are shown as a mole % of the starting acid that they contain.
- Benzene not determined because of interference by GC solvent.
- An unspecified dihydro-benzynaphthalene isomer.
- 1,2,3,4-tetrahydro-5-benzynaphthalene.
- The sum of various partially hydrogenated benzynaphthalenes.
- The ratio of phenylacetic acid incorporated in coupling products to the sum of that which has undergone reaction of any kind.
- The sum of phenylacetic acid and all identified phenylacetic acid products, as a mole % of the starting acid.
- The ratio of 1-benzynaphthalene to 2-benzynaphthalene.

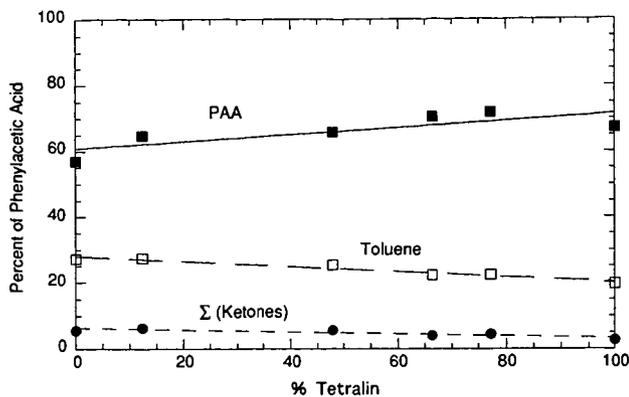


Figure 1. Formation of major products as a function of the H-donor content of the solvent.

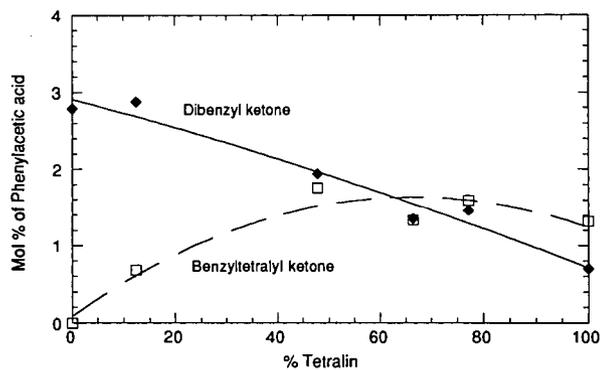


Figure 2. Ketone formation as a function of the H-donor content of the solvent.

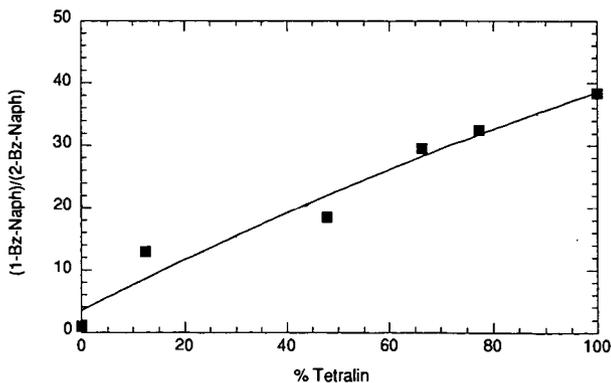


Figure 3. Ratio of 1-benzyl-naphthalene/2-benzyl-naphthalene as a function of the donor content of the solvent.