

RETROGRADE REACTIONS OF PHENOLIC COAL
CONSTITUENTS: SELF-COUPLING REACTIONS
OF DIHYDROXY AROMATIC STRUCTURES

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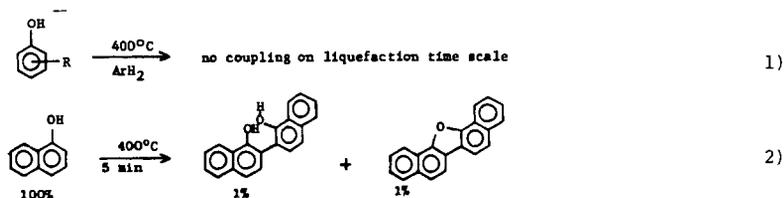
INTRODUCTION

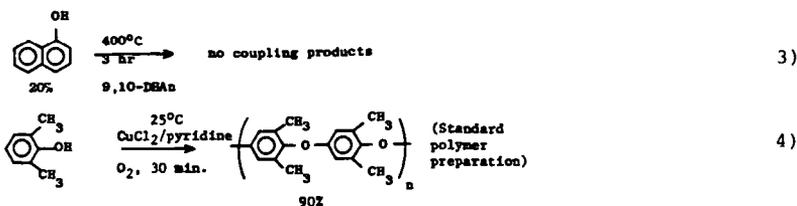
Importance of OH Groups in Coal Processing

It is generally agreed that the evolution of phenolic groups is a critical part of coal liquefaction. However, little is known about the homogeneous chemical reactions which, during liquefaction, bring about deoxygenation on the one hand, or coupling reactions on the other hand. This is particularly true for polyhydroxy aromatic structures. For instance, although polyhydroxybenzenes are a basic unit of lignin structures and are presumed to persist in low-rank coal structures, polyhydroxybenzenes are not substantial constituents of liquefaction products (1,2). In contrast, pyrolysis of low-rank coals under conditions that minimize secondary reactions of evolved volatiles produces large amounts of dihydroxy benzenes (3). In some cases, dihydroxybenzenes are even the dominant component of the volatiles (4). Thus, it is clear that under coal liquefaction conditions, these dihydroxyaromatics react either in "simple" dehydroxylations or in condensation processes to form high molecular weight products. Since the former process is highly desirable and the latter highly undesirable, it is important to understand the chemistry responsible for these processes. In this paper, we describe initial results of model compound and coal liquefaction studies designed to elucidate the self-coupling reactions of dihydroxyaromatics that may account both for the disappearance of Ar(OH)₂ structures during coal liquefaction and the degradation of liquefaction and pyrolysis properties that often occurs upon coal "aging" (5).

Self-coupling of ArOH

With simple, monocyclic phenols, coupling can be induced at room temperature by the presence of oxygen, base, and transition metal catalyst, as described in the literature for the preparation of polyphenylene oxide polymers (6). Simple, bicyclic phenols are known to couple to form biaryl or diaryl-ether linkages (7). However, in the absence of added oxidizing agents, the rates of these reactions are slow even at 400°C, and are generally not observable under the reducing conditions that are maintained during coal liquefaction.





These slow reaction rates notwithstanding, it is commonly assumed that the principal reaction involved in the loss of the c.a. 50% oxygen (as water) that occurs during pyrolysis between 350 and 400°C is the coupling of phenols to form diaryl ethers (8).

While searching for phenolic structures reactive enough to account for the rapid incorporation of THQ into coal structures, we observed that nonquinonoidal dihydroxyaromatics couple rapidly not only with THQ but also with themselves, even under the reducing conditions provided by reaction in hydroaromatic solvents. At 400°C, in the absence of donor solvents, this coupling can be sufficiently rapid so that after one hour, no starting phenol can be detected (99.9% reaction), and all coupling products have high molecular weights. With neat resorcinol, for example, the starting material was >99% consumed, but no product could be seen, either by capillary gc or by field ionization (FI) mass spectrometry with a high temperature inlet. The results described below indicate the nature of the products and provide information about the chemistry responsible for their production.

EXPERIMENTAL PROCEDURE

Catechol, resorcinol, 1,3-dihydroxybenzene, m-cresol, tetralin, 9,10-dihydrophenanthrene, and 9,10-dihydroanthracene were obtained from Aldrich Chemical Company and used without further purification. The polyphenylene oxide was obtained from Poly-science, Inc. The Wyodak coal, which was stored under water from the time of sampling until use, was obtained from Electric Power Research Institute. Most model compound reactions were conducted in sealed, 4-mm-od, fused silica ampoules that were loaded, together with some solvent (to equalize pressure), into a 3/8-in-od, Swagelok capped stainless-steel jacket. This assembly was heated for the prescribed reaction time in a molten salt bath whose temperature was controlled to within $\pm 0.3^\circ\text{C}$ and then quenched in a water bath. The hybrid experiments containing both coal and model compounds, and model compound experiments for which identical conditions were desired, were performed directly in 3/8-inch and 1/2-inch stainless-steel micro-reactors without a fused silica liner. Product mixtures were analyzed by GC, GC/MS, and by field ionization mass spectrometry (FIMS).

RESULTS AND DISCUSSION

Self-Coupling of Ar(OH)₂

The conditions, which result in the complete loss of resorcinol to high molecular weight products referred to in the introduction, are shown in Table 1. Lack of volatility under the high vacuum/450°C conditions of the FIMS inlet system generally

means a molecular weight well in excess of 600. In the case of resorcinol, with a molecular weight of 110, this would mean that there is no significant amount of polymer below hexamer. As seen in Table 1, dilution of the resorcinol with a hydrogen donor solvent changing the reactor from stainless steel to fused silica, and carrying out the reaction in the absence of atmospheric oxygen, all serve to decrease the resorcinol loss through coupling.

Table 1

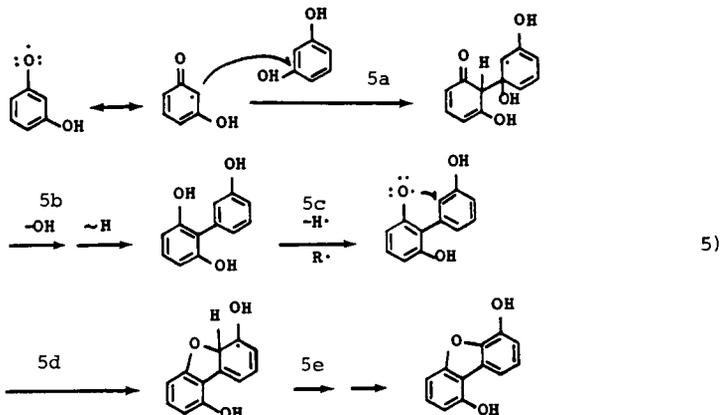
LOSS OF RESORCINOL TO HIGH MOLECULAR WEIGHT PRODUCTS
UNDER LIQUEFACTION CONDITIONS

	 $\xrightarrow{400^{\circ}\text{C}, 1 \text{ hr}}$			
100%	$\xrightarrow{\text{sst tube, air}}$	0	0	no products visible by GC or FIMS
100%	$\xrightarrow{\text{quartz, evac.}}$	44	0.3	no other products visible by GC
10%	$\xrightarrow{\text{90\% tetralin sst tube, N}_2}$	80	≤ 0.1	no other products visible by GC
50%	$\xrightarrow{\text{50\% Tetralin quartz tube, evac.}}$	90	≤ 0.1	no other products visible by GC

However, even when 90% of the resorcinol was recovered unreacted, no low molecular weight coupling products could be seen. Evidently, the reaction of initial coupling products with more resorcinol to form higher molecular weight materials is considerably more rapid than the reaction of resorcinol with itself to form more dimer. Ultimately, we were successful in seeing and identifying low molecular weight products of resorcinol by carrying out the reaction in the presence of reagents that could terminate the ends of the growing oligomer. However, the types of reactions responsible for the coupling were first and most clearly identified using a substrate where the ratio of dimer formation rate constant to dimer consumption rate constants was considerably higher. This involved use of 1,3-dihydroxynaphthalene (DHN) as the model compound. (With DHN, the formation of dimers and higher oligomers all involve attack on a polycyclic aromatic system, whereas with single ring $\text{Ar}(\text{OH})_2$, the formation of trimer, tetramer, etc., involves attack on polycyclic systems and is evidently more rapid than the initial step, dimer formation, which involves attack on the less reactive monocyclic system of resorcinol itself.)

Examination of the DHN product mixtures, which will be discussed below, reveals that the coupling involves formation of a dibenzofuran linkage between two resorcinol molecules. This coupling is shown for resorcinol as reactions 5a-e. The reaction is shown beginning with attack of the carbon-centered resonance form of a phenoxy radical, a reaction we consider likely. However, the actual mechanism is still a matter of speculation, and reactions 5a-e are intended primarily to show the stoichiometry of the coupling. The loss of OH in a unimolecular process can occur slowly at 400°C (9), but may nevertheless be less likely than an acid-catalyzed water elimination process.

The stoichiometry of $\text{Ar}(\text{OH})_2$ self-coupling shown above was obtained primarily from the product-mixture molecular ion profiles provided by field ionization mass spectrometry. Figure 1 shows the FI mass spectrum of the products obtained from the reaction of the bicyclic analog of resorcinol, 1,3-dihydroxynaphthalene (DHN), in the presence of meta-cresol.



Inspection of Figure 1 reveals groups of peaks that appear to form homologous series consisting of "dimers," "trimers," "tetramers," etc., and this is confirmed by the fact that the common increment in these series is 140 amu. 140 mass units corresponds to $160-18-2$, or to DHN monomer minus the elements of water, minus the elements of H_2 . Thus, each monomer unit is added to the growing oligomer by formation of one linkage with loss of water, and formation of the other with loss of $2(\text{H})$. Some products are exceptions to this coupling pattern, but the above stoichiometry and the geometrical coupling requirements of the 1,3-DHN system clearly indicate that the principal coupling is primarily through formation of dinaphtho-(or dibenzo)-furan linkages. These dibenzofuran-type couplings form very refractory materials, as will be discussed later.

The FI mass spectrum in Figure 1 shows groups of "dimers," "trimers," etc., rather than a single molecular weight for each oligomer. This is because of variations in the loss of additional hydroxy groups and in "capping" of the oligomers by coupling with cresol. These various kinds of coupling reactions are sufficiently rapid that unreacted starting material (m/z 160) accounts for less than 0.5% of the total ion intensity in Figure 1. Similarly, the peak at m/z 302 (which subsequent spectra will demonstrate to be the initial coupling product) accounts in Figure 1 for only 0.1% of the total ion intensity. Slightly more prominent, at 0.7%, is m/z 300, representing the dihydroxy-dinaphthofuran formed by elimination of $2(\text{H})$ from m/z 302. Still more prominent are m/z 284 and 268, the dehydroxylation products of m/z 300. Although, strictly speaking, the FIMS spectra only indicate the molecular weight of the various products, in a case like this where the starting materials are known and the chemistry invoked is reasonable, the molecular formulae of the products and the gross structure (e.g., phenol vs ketone) can often be assigned with reasonable confidence. An example where ambiguity is possible is m/z 408 in Figure 1. Here, two possibilities are shown, one a DHN trimer, and one a dimer capped by cresol. In fact, this particular ambiguity is largely resolved in favor of the cresol-capped dimer (and analogous peaks), since the intensities of the peaks in question are greatly reduced in the absence of cresol. Assignment of the positional isomers is significantly less

certain; those shown on Figure 1 are merely those that we consider likely from steric and electronic considerations.

Inhibition of DHN Coupling

From the considerations discussed above, it appears that the cresol serves to inhibit continued polymerization of DHN by "capping" reactive portions of the growing oligomers with a less reactive cresol fragment. (This could account for the beneficial effects of phenolic solvent constituents claimed under some coal liquefaction conditions.) However, Figure 2 shows that some solvent constituents inhibit DHN coupling without becoming incorporated in the coupling products. Figure 2a is the FI mass spectrum of a product obtained under conditions similar to those of Figure 1, except that the 1:1 DHN:cresol mixture has been diluted with 50% tetralin. Products obtained at similar concentrations and much shorter reaction times are shown in Figure 2b.

In Figure 2a, the coupling reactions are quite clearly inhibited by the solvent change: unreacted starting material is increased to ~ 5% of the total ion intensity (vs ~ 0.3% in Figure 1). Also, the proportion of trimers and tetramers is decreased relative to dimers. The intensity of m/z 302, the proposed initial coupling product, is increased from 0.1 to 14%, and the relative prominence of masses that most probably reflect capping by cresol (e.g., 408, 548) is markedly decreased. The decreased reaction time reflected in the products in Figure 2b resulted in a further decline in the yield of coupling products, particularly products beyond the level of dimers. Specifically, m/z 302 accounts for 30% of the total ion intensity and for virtually 100% of the products, and thus is quite clearly the initial coupling product.

The primary factor in diminishing the coupling seen in Figure 2a is actually the presence of the donor, rather than merely the dilution of the coupling substrate, because dilution of the DHN-cresol mixture with naphthalene rather than tetralin results in a less marked increase in the proportion of remaining starting material. Moreover, the addition of other hydroaromatics known to be more effective donor solvents (for coal liquefaction) than tetralin, as shown in Table 2, causes

Table 2

EFFECT OF DONOR SOLVENTS ON RECOVERY OF UNREACTED DHN AND ITS PRODUCTS

Initial Concentration, m%		m/z of Initial DHN		
10%	90% Naphthalene →	16%	1.8%	12.7%
10%	90% Tetralin →	29%	3.6%	12.3%
10%	90% 9,10-Dihydroanthracene →	~22%	26.3%	13.1%
10%	90% 9,10-Dihydrophenanthrene →	53%	7.4%	23.9%
10%	70% tetralin KM Fe-oxide →	~9%	16.9%	11.6%

a very marked increase in the amount of remaining starting material and a decrease in the total amount of material classified as dimeric or higher molecular weight. Two interesting observations are that 9,10-dihydrophenanthrene is substantially more effective at preventing coupling than is 9,10-dihydroanthracene, but that the latter is much more effective at promoting the deoxygenation of the monomer. The first observation is interesting in that dihydrophenanthrene is generally observed to be a more effective liquefaction solvent than is dihydroanthracene (10,11), even though dihydroanthracene, as a better radical scavenger, better fulfills the traditional radical "capping" requirement for donor solvents (12). Similarly, the observation of dehydroxylation is another reminder that during coal liquefaction many things happen that could not be accomplished if donor solvents were to function merely as radical capping agents (9).

Effect of THQ on DHN Self-Coupling

Because cresols appear to serve as capping agents that limit the size of the growing polymers, it was of interest to see what effect on the coupling process would be exerted by hydroaromatic amine solvents, such as 1,2,3,4-tetrahydroquinoline (THQ), that are known to be effective liquefaction agents and to couple with phenols (13). Additional reasons for testing THQ as a coupling inhibitor are that the Ar(OH)_2 self-coupling could be initiated by an acid catalyzed electrophilic reaction, and if so, should be suppressed by base. (It is already known, but not understood, that THQ does not promote the formation of dibenzofuran during the base-catalyzed cleavage of p-hydroxydiphenyl ether (14).) Figure 3 shows an FI mass spectrum of products obtained under conditions similar to those of Figure 1 (50% tetralin, 25% DHN, 25% cresol), except that the cresol was replaced by THQ.

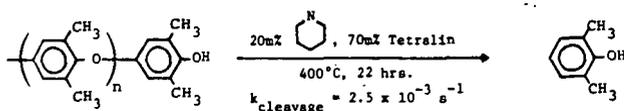
The amount of unreacted starting material is similar to that shown in Figure 1. The homologous series in Figure 2, also appear, at first glance, to have a similar character. However, inspection of the group nominally representing trimers (m/z 350 to 450) reveals that the most prominent masses are not the same as in Figure 1. Moreover, the most prominent new masses are odd. In other words, these "trimers" contain 1 nitrogen atom, and thus are not really trimers, but dimers capped by THQ. Similarly, many of the "dimers" are really the DHN-THQ nucleophilic condensation product (m/z 275) or secondary products derived from this material. Thus, THQ does indeed inhibit the formation of the higher oligomers, but it does so primarily by "capping" these products and becoming covalently bound into the coal structures, rather than by inhibiting the DHN self-coupling per-se.

Attempts to Reverse Ar(OH)_2 Coupling: The Stability of Dibenzofuran Linkages

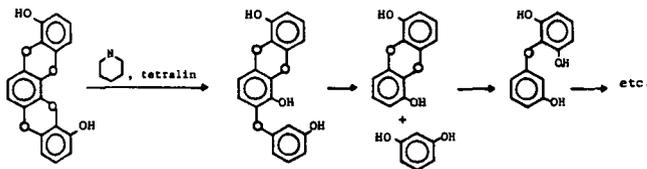
Dibenzofuran-type structures are well known to represent very refractory sinks for coal oxygen. A natural question, therefore, is, "Is there any simple, practical way, short of severe hydrotreating conditions, to reverse the coupling process?" Although dibenzofuran itself is very stable in donor solvents at 400°C, the presence of hydroxy groups ortho- or para- to the ether linkage provides a structure which might be more susceptible to bond cleavage. The reason for this increased susceptibility is that 1-hydroxydibenzofuran, for instance, is similar to para-hydroxydiphenylether. This latter compound, although very strongly bonded and resistant to thermolysis, is very susceptible to cleavage in basic donor solvent systems (13,14,15). For instance, in a tetralin-10% piperidine mixture at 400 C, para-hydroxydiphenyl ether decomposes to phenol with a half-life of less than 5 minutes, as compared with a half-life of 100 hours in pure tetralin.

However, tests with 1-hydroxydibenzofuran (as a monomeric model for Ar(OH)_2 self-coupling products) show it to be very stable in THQ-tetralin mixtures (less than 0.1% reaction in 1 hr at 400°C). Evidently, any opening of the ether linkage that occurs is readily reversed, since the two fragments are held in close proximity by the

biphenyl linkage. Because of the stability of hydroxydibenzofuran, and in order to test the presumption that the studies of base-promoted bond-cleavage rates of hydroxydiphenyl ether may apply to a polymeric system, we measured the rate of depolymerization of a commercial polyphenyl ether, 2,6-dimethyl polyphenylene oxide. This polymer consists of diphenyl ether units in which the terminal phenyl groups still bear a hydroxy group. The polymer should therefore be susceptible to an "unzipping" process in which the diphenyl ether unit bearing the hydroxy group is subject to base catalyzed cleavage. In fact, the rate of production of monomer was found to correspond very closely to that predicted on the basis of the measured rate for central bond scission in p-hydroxydiphenyl ether itself (13,14,15).



The stability of 1-hydroxydibenzofuran and the lability of both monomeric and polymeric hydroxybiphenyl ether systems allow us to make two conclusions. First, the opening of the relatively labile hydroxydiphenyl ether linkage in hydroxylated dibenzofurans does not provide an easy route to destruction of the entire dibenzofuran linkage. Second, it probably does not because the most favorable reaction following opening of the ether linkage is simply the reclosing of that linkage. In addition, the stability of the DHN-coupling products in basic donor-solvent systems provides additional proof that the coupling products are indeed joined by furan linkages (i.e., one diaryl ether link and one biphenyl link). The alternative would be dioxin linkages (two diaryl ether links). In this case all of the ether links would have an ortho- or para-hydroxy (or would have one generated when an adjacent ether link is opened), and therefore all linkages would be susceptible to base-catalyzed cleavage.



Presence in Wyodak Coal of structure of similar Reactivity to DHN

If 1,3- and other non-quinonoidal dihydroxyaromatics are significant in real coals, the above results clearly indicate that these structures are probable sources of rapid retrogressive reactions during coal liquefaction (and possibly during oxidative weathering). The structures of various lignin components do suggest that di- (and even tri-) hydroxy aromatics may be important in low-rank coal structures. This anticipation is confirmed by the pyrolysis-FI-mass-spectrum of a Wyodak coal, shown in Figure 4, in which the most prominent peak in the entire spectrum is that at m/z 110. Under non-fragmenting conditions, the predominant contributor to m/z 110 will be the molecular ion(s) of dihydroxybenzene(s). Almost as prominent are peaks at m/z 124 and 138, corresponding to C_1 - and C_2 -dihydroxybenzenes. Similarly, Meuzelaar and coworkers have previously reported prominent peaks in the 110, 124, 138 series in the pyrolysis-EI-mass spectra of other western coals (3). Given the abundance of dihydroxybenzenes indicated by these mass spectral analyses, the pertinent question becomes whether the dihydroxybenzenes and other $Ar(OH)_2$ are 1,2-, 1,3-, or 1,4-, isomers, and how their reactivity compares to that of the 1,3-DHN discussed above.

An indication of the range of self-coupling reactivities encompassed by mono- and bi-cyclic ArOH and Ar(OH)₂ is given by the measured and estimated half-lives shown in Figure 5. Half-lives in hours are shown for four phenolics under three sets of reaction conditions that are progressively less favorable for self-coupling. The first set of four bars shows the coupling half-lives under the conditions described in the literature for polyphenyl ether formation, where the coupling even of simple phenols takes place in only a few minutes (6), and the coupling of the three polycyclic or polyphenolic materials is presumed to be unobservably rapid on the time scale of Figure 5. The second and third sets of bars correspond to half-lives measured in this work. The second set of conditions is reaction of the neat phenols in the absence of any added oxidant. Under these conditions, the half-life for coupling of phenol itself exceeds 27 hours, and those for the three more reactive phenols become long enough to move onto the time scale of Figure 5. The third set of conditions is nominally the most relevant for coal liquefaction, in that the phenols are diluted in a hydroaromatic solvent (25% in tetralin). Under these conditions only the two dihydroxy compounds undergo measurable self-coupling on coal liquefaction time scales. From these data, we would conclude that 1,3-dihydroxynaphthalene structures in coals, if prominent, would certainly be subject to self-coupling reactions. For 1,3-dihydroxybenzene, coupling would appear possible, but not assured.

The data in Figure 5 give no information on quinonoidal dihydroxyaromatics. Literature data for low-temperature coupling reactions of quinones would suggest that under oxidizing conditions, they could be even more reactive than non-quinonoidal Ar(OH)₂ (16,17,18). However, separate experiments reveal that 1,4-dihydroxynaphthalene in donor solvents undergoes deoxygenation sufficiently rapidly to largely prevent self-coupling. On the other hand, 1,2-dihydroxybenzene (catechol), the most probable coal-derived isomer, does not undergo rapid deoxygenation and is subject to self-coupling at a slightly slower rate than resorcinol. In order to derive some additional information bearing on the question of the type, abundance, and reactivity of the "native" Ar(OH)₂ structures in low-rank coals, we carried out a series of "hybrid" experiments in which Wyodak coal was added to the 1,3-DHN-tetralin-THQ mixtures. These results, shown in Table 3, reveal the following: (1) formation of high molecular weight products from DHN is accelerated by the presence of the coal, and (ii) that the DHN self-coupling itself appears not to be accelerated by the presence of the coal.

Table 3

EFFECT OF COAL ON THE REACTION OF 1,3-DIHYDROXYNAPHTHALENE
IN DONOR SOLVENTS AT 400°C; 1 hr

Run No.					Products (m%)					
	DHN	Tetralin	THQ	Wyodak Coal	DHN		+ other dimers		ETHQ + Q	Nuc. Cond.
IV-75	25	75	—	—	1.7	5.4	2.6	43	—	—
IV-81	25	75	—	80 mg ^a	0	3.8	0.8	7	—	—
IV-41	5	75	20	—	0	5.7	1.2	5	62.4	17.9
IV-70	5	75	20	80 mg ^a	0	3.1	0.1	≤ 0.1	62.9	0

^a80 mg = wt of DHN.

These results suggest that Wyodak coal itself contains structures that couple more readily with DHN than DHN does either with itself or with THQ. Similar results were obtained when hybrid experiments were performed with 1,3- and 1,2-dihydroxybenzene. Thus, Wyodak coal contains structures that couple more readily with any of these three dihydroxyaromatics than they do with themselves. Given the prominence, discussed above, of dihydroxybenzenes in low-rank coals and certain low-severity products of such coals, it appears that dihydroxyaromatics, as a general class, emerge as very good candidates for the structures that undergo the retrogressive reactions that often rapidly degrade the convertibility of low-rank coals. Therefore, an improved understanding of the mechanism(s) of these couplings may aid in finding means of limiting the losses in convertibility.

Potential Effects of Water on Ar(OH)₂ Coupling

It may be significant that water is a product of the formation of benzofuran linkages and that the drying of low-rank coals before liquefaction often reduces the subsequent conversion yields (5). In real coals we would expect the Ar(OH)₂ structures (or their precursors) to be partially immobilized in the coal matrix, which, in its water-swelled condition, would have neighboring Ar(OH)₂ structures largely isolated from each other by a "gel" of hydrogen-bonded water molecules. Under these conditions, removal of these water molecules would then be very critical, because it would provide for sterically favored coupling reactions with very high bimolecular "A" factors.

Possible Mechanisms of Ar(OH)₂ Coupling

Although the results described above clearly indicate that Ar(OH)₂ couple first by eliminating water (presumably to form a biphenyl linkage) and second by eliminating the elements of H₂ (to form an ether linkage), the detailed mechanisms of these two steps are not certain. The formation of the linkage with loss of 2(H) is, by definition, an oxidative coupling. (Thus, when DHN couples in a donor solvent, we have an oxidation in the absence of any obvious oxidizing agent.) This coupling is presumably the step that benefits most from the presence of metal oxide surfaces and O₂. By analogy with polyphenyl ether formation mechanisms (19), we presume one of the functions of the transition metal oxide is to oxidize radical intermediates to cations so that hydrogens can be lost as protons, rather than as hydrogen atoms. However, there are a number of considerations that make direct analogy with reported phenolic coupling processes difficult. One is the fact that low temperature polyphenyl ether preparation tends to favor initial formation of carbon-oxygen bonds, which, being inherently weaker than C-C bonds (20), might not survive long enough to be stabilized at 400°C. Indeed, the work of Poutsma with naphthols has shown that at 400°C, the initial product coupling is an oxidative carbon-carbon coupling (7), not a condensation process that eliminates water, such as we see with the dihydroxyaromatics.

In the case of the dihydroxyaromatics, a number of low-temperature, acid-catalyzed benzofuran-forming reactions involving 1,4-hydroquinone and resorcinol are described by Högberg and coworkers (16,17,18). However, these reactions require one of the Ar(OH)₂ species to be in the oxidized (quinone) form, and therefore will not work for purely non-quinonoidal Ar(OH)₂ systems. Furthermore, neither the formation of an initial coupling product with water loss, nor the absence of inhibition by base, as seen in the present work, are consistent with the reactions seen by Högberg. Clearly, in reaction at 400°C, there are a number of mechanistic modes possible. Further experimentation is necessary to delineate, if possible, the mechanism, but in any case, to define the conditions under which this class of coupling reactions can be minimized during coal conversion.

CONCLUSIONS

Products:

The coupling products are generated primarily through formation of dibenzofuran-type linkages, which result from initial formation of a biphenyl linkage with elimination of water, followed by formation of the ether linkage and elimination of the elements of 2(H).

The size of the coupling products is limited by reagents, which cap the growing oligomer (such as cresols and THQ), and by donor solvents, which inhibit the coupling process without being consumed in capping the polymer.

Rates:

The self-coupling reactions of 1,3-dihydroxynaphthalene are so rapid that, at coal liquefaction temperatures and on coal liquefaction time scales, 20 mol% DHN in any donor solvent undergoes a substantial amount of coupling.

Resorcinol is significantly less reactive, and presence of a donor-solvent, and the absence of O₂ and stainless-steel surfaces easily enables recovery of 90% of the initial resorcinol unreacted.

Wyodak coal appears to contain structures that react more rapidly than either resorcinol, catechol, or DHN do with themselves, indicating that structures of very high reactivity are available for retrograde reactions. These reactive native structures are suggested to be polyhydroxyaromatics, but in any case, their demonstrated reactivity with added Ar(OH)₂, unequivocally shows that native Ar(OH)₂ (which are shown to present by MS analyses) are subject to rapid retrograde reactions even under the reducing conditions present during coal liquefaction.

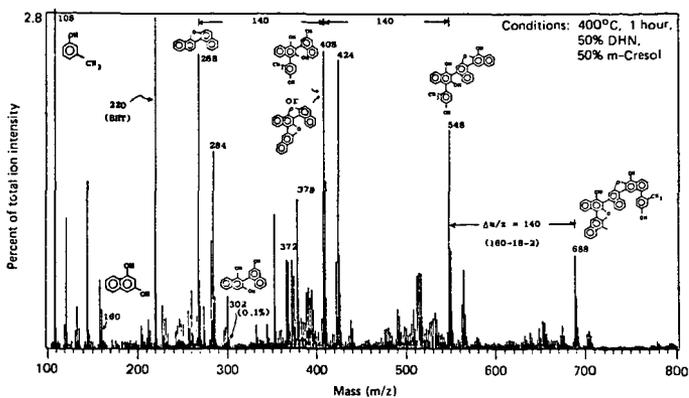
The order of decreasing effectiveness of solvents in preventing DHN coupling is 9,10-dihydrophenanthrene, 9,10-dihydro-anthracene, tetralin, m-cresol, naphthalene.

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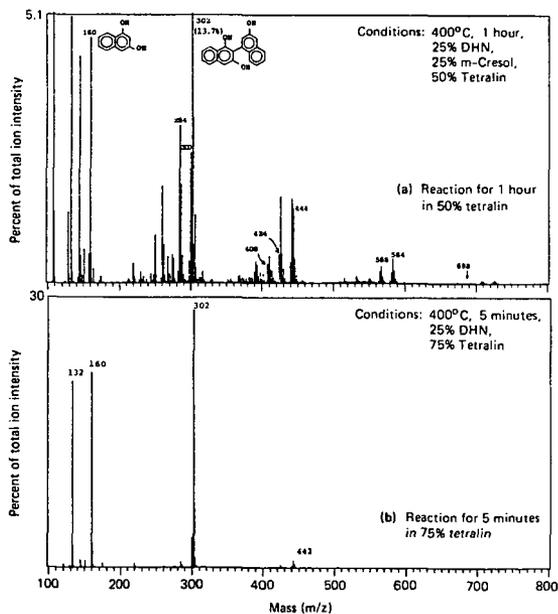
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Figure 1. FI-mass spectrum of 1,3-dihydroxynaphthalene coupling products. No donor solvent.



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Figure 2. FI mass spectra illustrating the effect of donor solvent and decreased reaction time on DHN coupling.

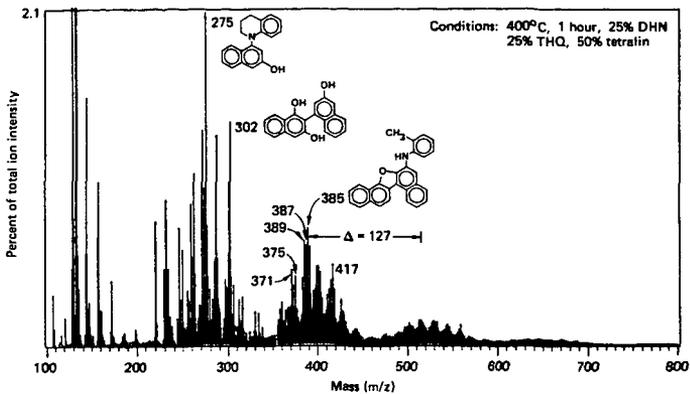


Figure 3. FI-mass spectrum of 1,3-dihydroxynaphthalene coupling products showing inhibition of DHN self-coupling by preferential condensation with THQ.

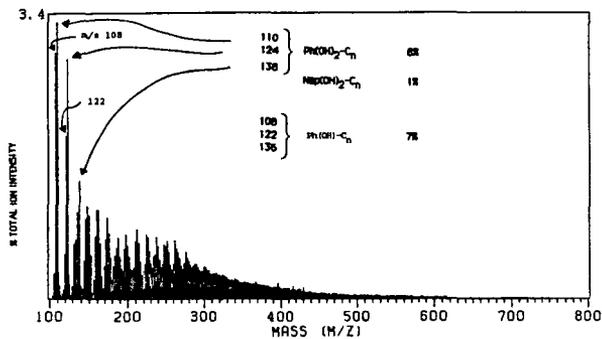


FIGURE 4 PYROLYSIS FI MASS SPECTRUM OF WYODAK COAL

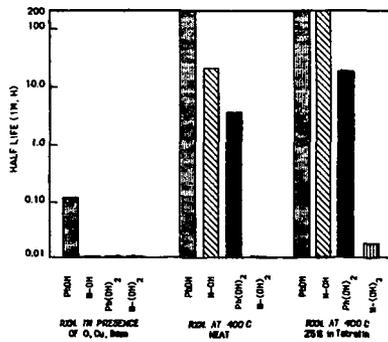


FIGURE 5 OBSERVED HALF-LIVES FOR ArOH SELF-COUPLING