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

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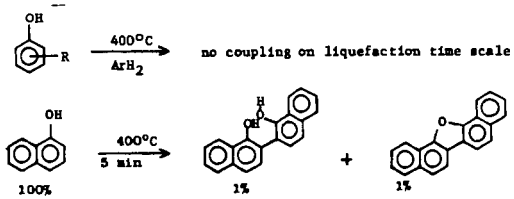
INTRODUCTION

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.



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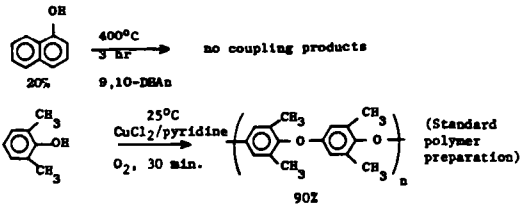


3)

4)

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 Polysciences, 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 ±0.3°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 microreactors without a fused silica liner. Product mixtures were analyzed by GC, GC/MS, and by field ionization mass spectrometry (FIMS).

RESULTS AND DISCUSSION

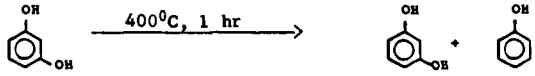
Self-Coupling of $Ar(OH)_2$

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

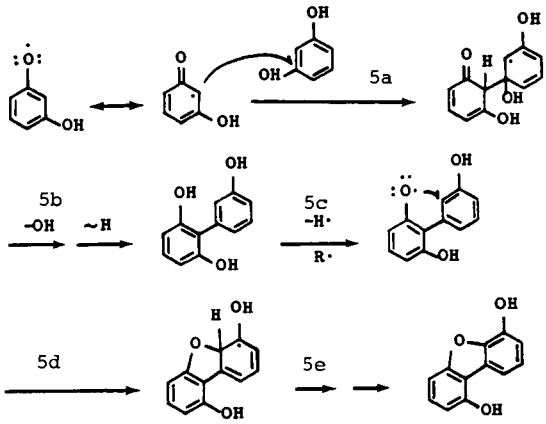


100%	sst tube, air	0	0	no products visible by GC or FIMS
100%	quartz, evac.	44	0.3	no other products visible by GC
10%	90% tetralin, sst tube, N_2	80	$\leq$ 0.1	no other products visible by GC
50%	50% Tetralin, quartz tube, evac.	90	$\leq$ 0.1	no other products visible by GC

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 considerbly 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 $Ar(OH)_2$, 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 of 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 $Ar(OH)_2$ self-coupling shown above was obtained primarily from the product-mixture molecular ion profilea 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.



5)

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(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(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

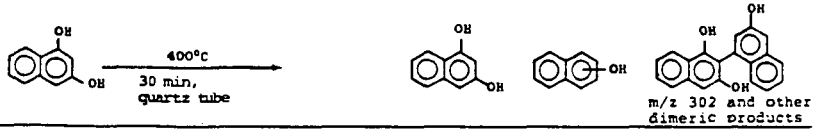
From the considerations discussed above, it appears that the cresol serves to inhibit continued polymerization of DHN by "capping" reactive portions of the growing oligomers with a less reactive cresol fragment. (This could account for the beneficial effects of phenolic solvent constituents claimed under 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% 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.

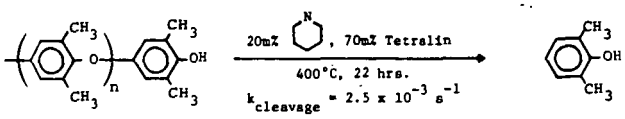
The amount of unreacted starting material is similar to that shown in Figure 1. The homologous series in Figure 2, also appear, at first glance, to have a similar character. However, inspection of the group nominally representing trimers (m/z 350 to 450) reveala that the most prominent masses are not 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

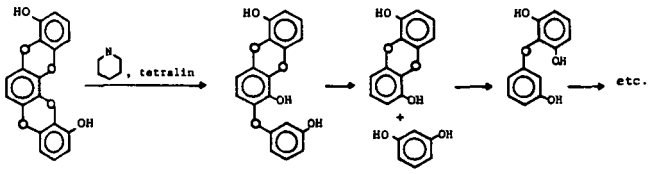
Dibenzofuran-type structures are well known to represent very refractory sinks for coal oxygen. A natural question, therefore, is, "Is there any simple, practical way, short of severe hydrotreating conditions, to reverse the coupling process?" Although dibenzofuran itself is very stable in donor solvents 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 beacause 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-dihydroxybnezenes. Similarly, Meuzelaar and coworkers have previously reported prominent peaks in the 110, 124, 138 series in the pyrolysis-EI-mass spectra of other western cosls (3). Given the abundance of dihydroxybenzenes indicated by these mass spectral anslyses, the pertinent question becomes whether the dihydroxybenenes 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 bicyclic 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 correspsond 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 measureable 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: (i) 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

					Products (m%)					
Run No.	DHN	Tetralin	THQ	Wyodak Coal	DHN			+ other dimers	ΣTHQ + 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	$\leq$ 0.1	62.9	0

[a]80 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 H_2 (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 O_2. 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 deliniate, 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 O_2 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, teralin, m-cresol, naphthalene.

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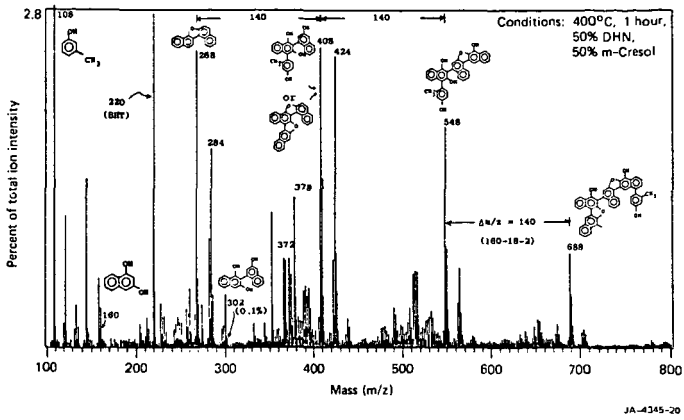

Figure 1. FI-mass spectrum of 1,3-dihydroxynaphthalene coupling products. No donor solvent.

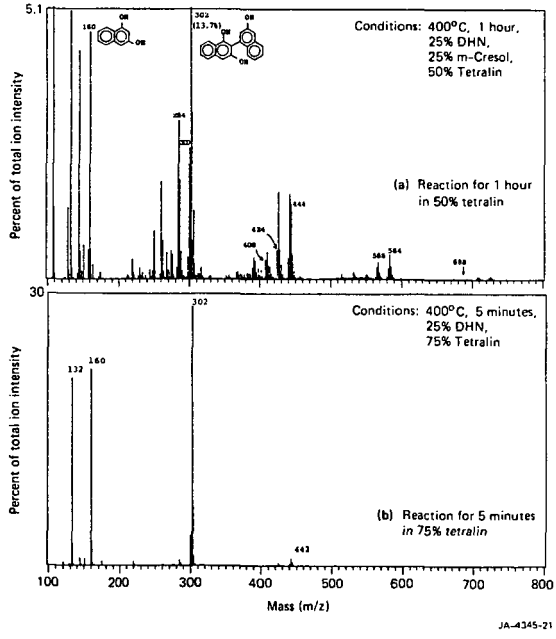

Figure 2. FI mass spectra illustrating the effect of donor solvent and decreased reaction time on DHN coupling.

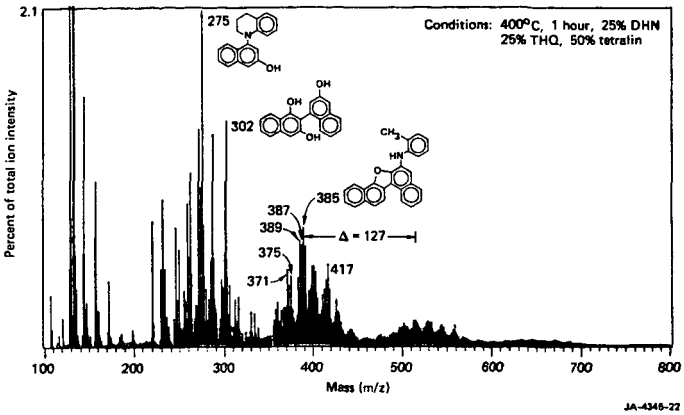

Figure 3. FI-mass spectrum of 1,3-dihydroxynaphthalene coupling products showing inhibition of DHN self-coupling by preferential condensation with THQ.

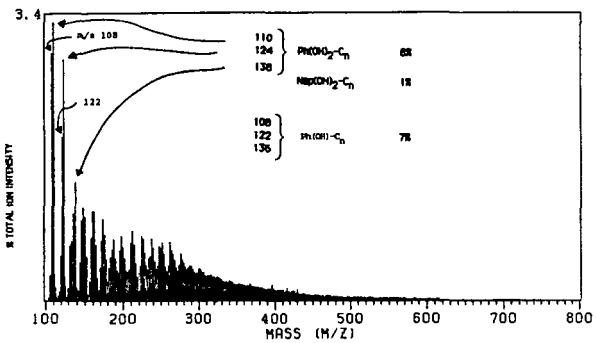

FIGURE 4 PYROLYSIS FI MASS SPECTRUM OF WYODAK COAL

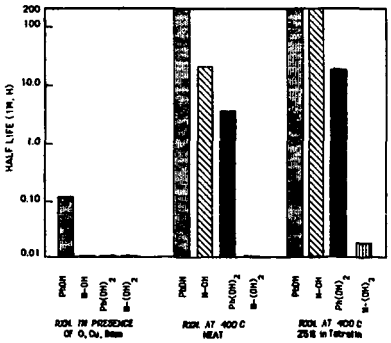

FIGURE 5 OBSERVED HALF-LIVES FOR ArOH SELF-COUPLING

PROBING COAL STRUCTURE WITH INVERSE GAS AND LIQUID CHROMATOGRAPHY.*

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Introduction

The objective of this study is to examine variations in coal structure using two inverse chromatography approaches. Inverse gas chromatography, a technique widely used for studying polymers, is being used to study phase transitions in coals upon heating. In contrast to classical GC, inverse chromatography probes the stationary phase, a coal, by determining the retention time of known compounds. This transposition of known and unknown in the GC experiment gives rise to the term "inverse chromatography". Inverse liquid chromatography, a new technique, is being used to examine coal surfaces. This approach is analogous to the GC method except that solvents are used. The coal samples will be chosen to examine variations with rank and to investigate structural changes in ground coals, both in air and in the absence of air, as a function of time. These approaches show promise for providing chemical information on subtle variations in coal structure. The initial experiments are described in this paper.

Inverse GC (1-3) has been applied to polymers to measure the glass transition temperature (4), the degree of crystallinity (5), melting point (6), thermodynamics of solution (4,7), and chemical composition (8,9). The first use of the term "inverse chromatography" is attributed to Davis and Peterson (8), who applied the technique to the determination of the degree of oxidation of asphalt. In later work, the experiments were extended to include measurement of thermodynamic properties of the asphalt.

Some other methods used to study the physical structure of coal and coal surfaces include measurements of heats of adsorption of organics on coal surfaces by GC, to probe the nature of solute-coal surface interactions (10); swelling indices, for the qualitative determination of the extent of cross-linking (11); initial swelling rates, to investigate the steric requirements of swelling (12); and microscopic observation of solvent diffusion through coal thin-sections (13).

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Experimental

Inverse gas chromatography: The coal used in the inverse GC experiments was an Illinois No. 2 hvC bituminous coal (analysis, dmmf basis: C 73.4%, H 5.3%, N 1.1%, S 1.6%, 18.1% (by diff.)), ground to -100 mesh and soxhlet extracted with an azeotropic mixture of benzene and ethanol, and dried under vacuum at 110°C. The coal was thoroughly mixed with non-porous glass beads (-40 to -60 mesh) to give coal/glass bead mixtures in the range of 2.5 to 30 w/w %. Stainless steel columns (1/4" od x 1 m) were packed with ca. 10 g of the coal/glass bead mixture.

The entire experiment was controlled by a DEC LSI 11/73 computer. The GC (Carla Erba, Model 4160), equipped with a single FID, was modified such that the oven temperature could be computer-controlled to within 1°C. The injector, a gas sampling valve, was housed in a thermostated box at 110°C. Carrier gas flow was provided by two controllers, one with a 0 - 5 mL/min element (low flow) and the second with a 0 - 60 mL/min element (high flow). The high flow controller was connected to the injector through a computer-controlled solenoid.

The probe sample, 5% methane in argon, is injected onto the column and its retention time at the specific temperature is determined. The column temperature is then increased and the FID signal determined. If the signal exceeds the baseline by more than four percent, the solenoid to the high flow controller is opened to give a carrier gas flow rate of approximately 20 mL/min. This extra flow is intended to purge the column of thermally released materials more rapidly, thus decreasing the time required for the experiment. Once the FID signal has returned to within four percent of the baseline signal, the probe sample is again injected and the process is repeated. The experiment was carried out at 3°C increments from 50°C to 450°C. A control experiment run with only glass beads in the GC column gives a slope of zero in a log t_{ret} - 1/T plot, when corrected for carrier gas viscosity.

Inverse liquid chromatography: The LC system consisted of a pump (Waters Model M-6000-A) equipped with a 10 μL sample loop, a differential refractometer detector (Waters), and a UV absorbance detector set at 254 nm (Schoeffel Model 770). Data were collected on a DEC LSI 11/23 interfaced through an A/D convertor. The mobile phase was high purity methanol (Burdick and Jackson), with a flow rate of 1.0 mL/min.

The stationary phase was prepared from an Upper Freeport medium volatile bituminous coal (analysis, dmmf basis: C 89.0%, H 5.2%, N 1.6%, ash 13.1%, S_{tot} 2.4%). The coal was ground to -100 mesh and extracted overnight with refluxing methanol. A 1 cm id x 10 cm stainless steel column was then slurry- packed with the coal at a flow rate of 2.0 mL/min. The column was jacketed and the column temperature maintained by a circulating bath. The void volume of the system was determined to be 3.4 mL by measurement of the retention volume of ethanol or of methanol-d_4.

Results and Discussion

Retention data from the inverse GC experiment are shown in Figure 1. There are three retention mechanisms likely to affect the inverse GC experiment. These mechanisms are molecular sieving, surface adsorption, and solution of the probe in the stationary phase. The observed retention behavior will be due to the combination of effects operating under the given conditions. The specific retention volume, V_g, is given by the sum of the retention terms:

$$V_g = K_d V_L + K_o A_L + K_s W_L \qquad 1)$$

where K_d, K_o, and K_s are the partition coefficients for gas-pore, gas-solid, and gas-liquid partition, respectively; V_L is the accessible pore volume; A_L is the accessible surface area; and W_L is the accessible mass of the stationary phase. It is largely the phase and physical state of the stationary phase which determines the retention mechanism. The retention volume may be related, through the partition coefficient, to the free energy or enthalpy of adsorption, and a plot of log t_{ret} vs. 1/T gives a slope proportional to ΔH_a. Changes in the thermodynamics of retention result in discontinuities or changes in the slope of the plot.

Three such changes in slope are shown enlarged in Figure 1. One, occurring at about 110°C, can be attributed to dehydration of the coal. An increase in retention is observed, which may be due to an increase in either the amount of accessible surface (A_L) or the volume of accessible pores (V_L). At temperatures below the glass transition temperature, gas-liquid partitioning will not play a major part in the retention of the probe molecule. The reproducible transition seen at 140°C may be due to the loss of tightly bound water and loss of other volatile species.

Other changes in the state of the coal are observed at ca. 350°C and 400°C. Similar transitions have been observed by other workers, with a variety of methods. For example, differential scanning calorimetry studies by Mahajan et al. (14) showed two endotherms in the 300-400°C range, which appear at increasing temperature with increasing coal rank (in the range hvA - hvC). Patrick, Reynolds, and Shaw (15) observed a transition to total anisotropic content at 370-420°C in optical anisotropy experiments on vitrains with C < 89%. In addition, several workers (16) have reported that, after heat treatment, both the amount of pyridine-soluble material and the average molecular weight of the material reach a maximum in the 300-350°C range.

It is also interesting to note the large change in slope of the log t_{ret} - 1/T plot at temperatures above 300°C. This is indicative of major changes in coal structure above this temperature.

Data from the inverse LC experiments are shown in Figure 2. As in the inverse GC experiment, retention behavior may be expressed by the sum of several retention terms, including those for liquid-liquid, liquid-solid, and size exclusion chromatography. In liquid chromatography, the capacity factor, k', is given by

$$k' = \frac{KV_s}{V_M} = \frac{t_r - t_m}{t_m} \qquad 2)$$

where K is the equilibrium constant of the retention mechanism, V_s is the effective surface area, volume, or pore volume of the stationary phase, and V_M is the mobile phase hold-up, or the void volume of the system. The capacity factor may be determined from the retention time of the solute (t_r) and the retention time of an unretained solute (t_m) or solvent front. The capacity factor may be related, through the equilibrium constant of the retention mechanism, to the thermodynamics of retention (17). A semi-log plot of k' vs. 1/T gives a slope proportional to the enthalpy of transfer between the stationary and mobile phases. Nonlinearities would be symptomatic of changes in the nature of coal-solute-solvent interactions. A van't Hoff plot for the retention of phenanthrene is shown in the lower part of Figure 2. Relatively good linearity is observed over the range 25-80°C.

A semi-log plot of k' vs. carbon number for the series of aromatic solutes benzene, naphthalene, phenanthrene, and triphenylene is shown in the upper part of Figure 2. This type of plot is useful for the comparison of the retention powers of different stationary phases. Data for the medium volatile bituminous coal indicate that this material is similar to some reversed-phase HPLC packing materials, particularly the porous carbon packings (18-20). One might expect pi-pi interactions between the coal surface and aromatic solutes to predominate in determining retention, so that the capacity factor increases with increasing solute surface area.

The initial results presented here demonstrate that these methods will provide reproducible results which can be interpreted. Coals from the Argonne Premium Coal Sample Program will be investigated using both approaches. We plan to examine possible changes of the physical structure of coals upon storage both in the oxygen and absence of oxygen.

Acknowledgments

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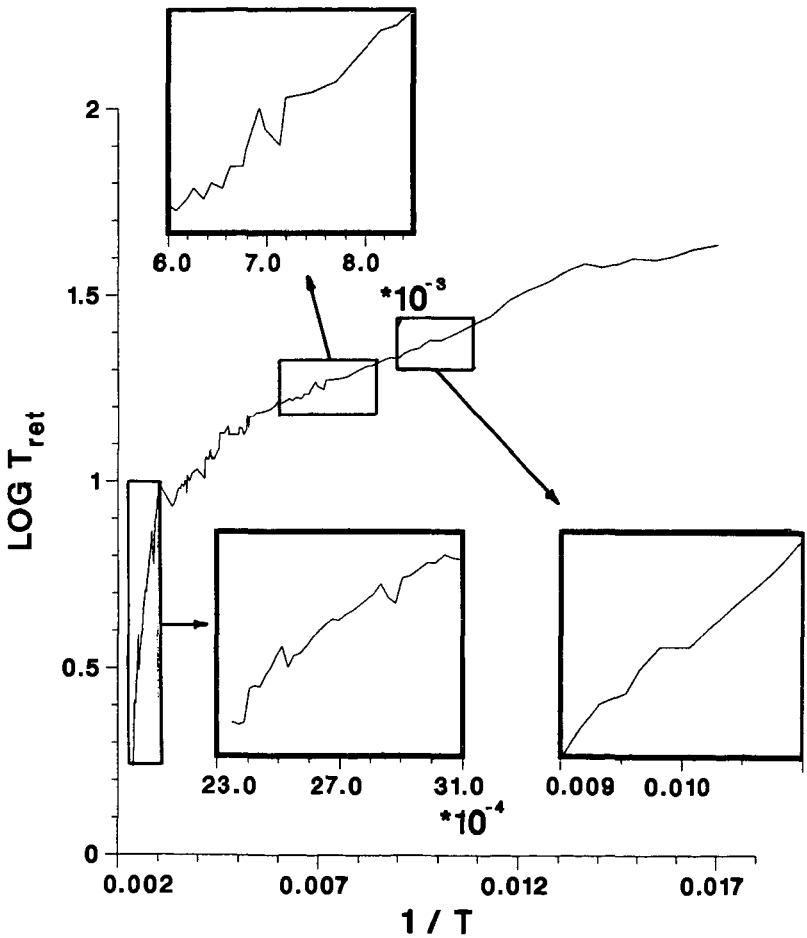

Figure 1. Inverse GC of Illinois No. 2 hvC bituminous coal. Top insert: 145°C region, lower left; 350-400°C region, lower right: 110°C region.

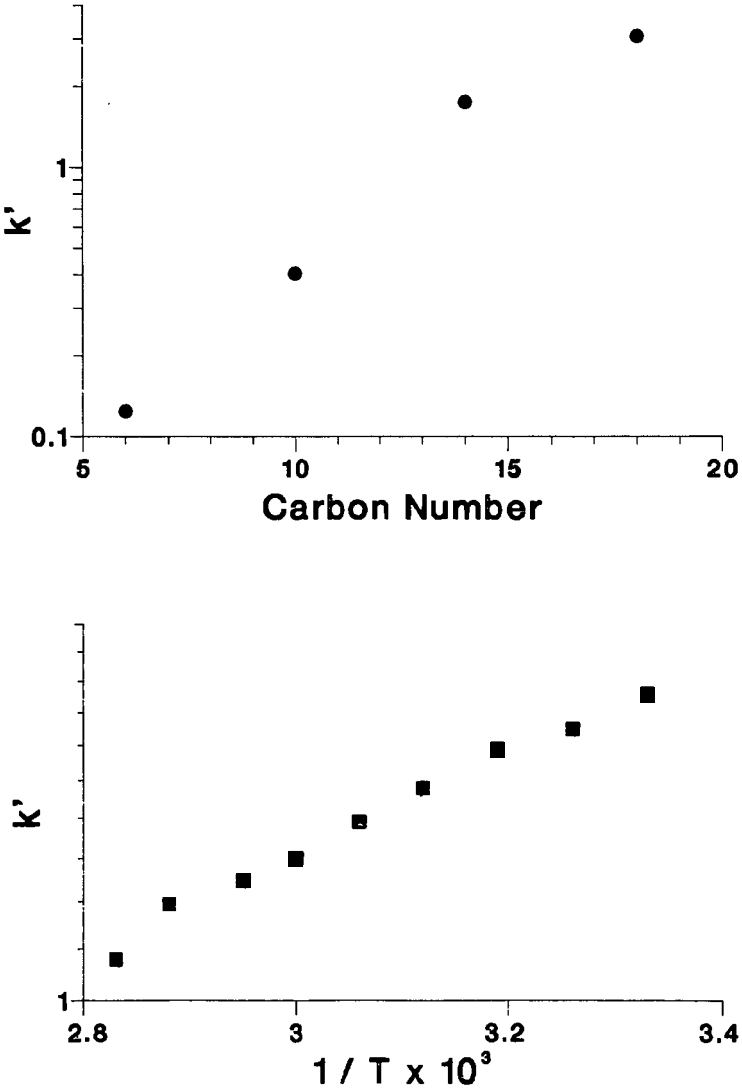

Figure 2. Inverse LC of Upper Freeport medium volatile bituminous coal. Top: retention data for benzene, napthalene, phenanthrene, and triphenylene. Bottom: retention data for phenathrene from 27.5-80°C.

Coal Swelling and Neutralization: Reactions within a Three-Dimensional Organic Matrix

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The physical transport of chemical reagents into cross-linked solids such as functionalized polymers, ion exchange resins, or coal is generally a slow process(1-3). Unlike reactions in solution, where bulk mass transport is limiting only for very fast reactions such as proton transfer, the rates of reactions within organic networks are often limited by diffusion through the solvent swollen solid. When coal contacts a base solution, the base diffuses into the solid, over the course of several hours, and reacts with the acidic sites that are present. As a result of this neutralization and the absorption of solvent, the coal physically swells to a greater volume. Under some conditions the volume increase can be on the order of 400%. The rate and extent of the swelling are highly dependent on the nature of the swelling solution. To study this diffusion process and learn more about the physical and chemical interactions of coal with solvents and reagents, we have examined and compared the rates and equilibria of coal swelling and neutralization as a function of base cation size, concentration, and solvent.

Coals are highly heterogeneous materials, with complicated three-dimensional structures(4-6) that contain entrained organic material known as bitumen(7). The connectivity, conformation, and topology of actual coal macromolecules are unknown. Connectivity refers to the fundamental atomic connectivity and includes the identity and quantity of cross-links, the arrangement and type of fused-ring systems, and the average molecular weight between cross-links. Collectively, these features comprise what is called the primary structure. The conformation of coal is related to the noncovalent cross-links which, in part, maintain the general shape of the macrostructure. These cross-links include the inter- and intramolecular associations in the form of hydrogen bonds(8-11), dipole-molecule interactions, and simple entanglements in the structure. Typically, low rank coals (subbituminous and lignitic) are characterized by significant quantities of phenolic and carboxyl groups (~4-8 per 100 carbons)(11). The ionization of these groups, depending upon their proximity and the degree of cross-linking in the organic network, will affect the overall acid-base equilibria as well as the degree of swelling of the material. The ion exchange properties of such coals in aqueous media have recently been discussed(12,13).

We have examined a bituminous coal (Illinois No. 6, Table I) which contains only five acidic centers per 100 carbon atoms. Most of these sites are represented by phenols(11). Our work has focused primarily on development of swelling as a macroscopic observable that relates the known chemistry of well characterized ion exchange resins to the chemistry of coal. Swelling measurements in conjunction with swollen polymer theories have been used to provide information about the macromolecular structure of bituminous coals (e.g., number average molecular weight per cross-link)(4,14,15). In general, we have found that bituminous coal, although a complicated heterogeneous organic material, possesses regular and predictable physio-chemical properties similar to weak acid ion exchange resins (polyelectrolytes).

RESULTS AND DISCUSSION

Swelling values (Q in units of mL/g) were obtained by mixing dry, powdered coal(16) with an appropriate base solution in graduated centrifuge tubes and reading the volume of the solid after centrifugation. Before conducting an experiment, the

coal was exhaustively extracted using pyridine to remove occluded organic material (25-30%)(17). Pyridine is known to disrupt hydrogen bonds in the coal and to swell the organic matrix. When the pyridine nonextractable component (PNE) of Illinois No. 6 coal was treated with methanolic solutions of a series of tetra-n-alkylammonium hydroxides(R_4NOH, R=methyl, n-propyl, n-butyl, n-hexyl, and n-octyl), the neutralization and concomitant swelling were found to be strongly dependent on the size of the ammonium ions. To obtain a convenient and useful correlation of our data, we use an empirical rate derived by treating the swelling process as a "first order" approach to equilibrium with a typical diffusion time dependence. The mass transport process is quite complex and the type of diffusion mechanism operating will depend not only on particle shape but also on particle size distribution(18). Figure 1 shows a plot of $-\ln[(Q_\infty-Q)/(Q_\infty-Q_0)]$ versus $t^{1/2}$ where Q_0 is the initial swelling value and Q_∞ is the final value after equilibration. The slopes of these lines give a measure of the swelling rate which was found to decrease with increasing base cation size(19). Swelling of the sample with tetra-methylammonium hydroxide was ~3.5 times faster than with the corresponding n-octyl substituted cation, a surprisingly large difference.

Examination of the final equilibrium swelling values Q_∞ for the series showed a uniform increase with the nonsolvated volume of the tetra-n-alkylammonium ions, ranging from 2.3 to 43 mL/g(20). This is analogous to the bulk volume increases observed for ion exchange resins in aqueous solution as a function of hydrated ion volume(21). The increase in volume of the coal upon contact with base is many orders of magnitude greater than the volume increase calculated for the absorbed quaternary ammonium ions.

Figure 2 shows a plot of the extent of reaction, expressed as $(V_0-V)/(V_0-V_f) \times 100]$ versus time (min.), for several base solutions studied with the PNE component of Illinois No. 6 coal. The value V is the volume of standard acid used to titrate an aliquot removed from the reaction mixture. The value V_0 was determined by titration of the starting base solution and the value V_f is the calculated volume for neutralization of the total number of acidic sites (phenols and carboxylic acids) in the coal based on previous alkylation experiments(9) using isotopically labeled methyl iodide. The data are, therefore, scaled so that 100% represents the total number of acidic hydrogens per gram of coal. By examining the initial slopes, it can be seen that the 0.25 M n-Bu_4NOH/methanol solution neutralizes the coal about seven times slower during the first twenty minutes than either the 0.20 M n-Bu_4 NOH/THF, H_2O (4:1) or the 0.25 M KOH/methanol solution. At constant ion size, the rate of neutralization is greater for n-Bu_4NOH in aqueous THF than in methanol and is apparently related to the solvent swelling potential. When the coal was placed in methanol, a swelling value Q(mL/g) of 2.3 was obtained while aqueous THF led to value of 4.0, a 74% increase in volume (typical swelling values for several solvents are given in Table II). The rate of neutralization was consistent with the previous findings that the size of quaternary ammonium ions was inversely related to the rate of their diffusion into coal as measured by swelling studies. We would expect that potassium ions should, because of their small size, diffuse into the coal at a faster rate than the n-Bu_4N^+ ion. However, a solvent mixture (THF/H_2O) that swells the organic matrix to a greater extent increases the diffusion rate of the tetra-n-butylammonium ions into the coal to a point where the order is reversed.

An empirical relationship (Equation 1) can be used to analyze the diffusion mechanism(22). We can write:

$$((V_o-V)/(V_o-V_f)) = kt^n$$

$$\ln((V_o-V)/(V_o-V_f)) = \ln k + n(\ln t) \qquad 1)$$

The quantities, V, V_0, and V_f are the same as described above. The value k is a

constant and n is an unknown exponent that defines the diffusion process (n= 0.5 for Fickian diffusion). A plot of $\ln[(V_0-V)/(V_0-V_f)]$ versus ln t gives a straight line with slope equal to n. Least squares treatment of the data for 0.2 M n-Bu_4NOH/THF, H_2O and 0.25 M KOH/methanol gave the results shown in Table III. The exponents 0.43 and 0.46 indicate that a diffusion limited mechanism is operating, the detailed nature of which will depend upon particle size distribution(18). Base uptake rates were not measured for the other tetra-alkylammonium ions.

The extent of neutralization at equilibrium falls below the theoretical neutralization point in all cases and is strongly dependent on cation size and solvent (Figure 2). Examination of the quarternary ammonium ion data in water as a function of ion radius shows a profound decrease in capacity as ion size increases. The capacity drops from 1.45 to 0.41 mmol/g for tetra-methyl and tetra-n-hexyl ammonium ions, respectively. The base capacity levels off as the size of the cation increases, apparently to some constant value independent of chain length. A similar leveling effect is seen in methanol for the ammonium ions, tetra-n-propyl through tetra-n-octyl. In this series, the change in base capacity was small, however, over the range studied. A decrease in base capacity with increasing cation size is typical for cross-linked polyacids(23). In polyelectrolytes, these trends are explained by increased chain (polyanion) potentials. As ion size increases, average charge separation distance will also increase leading to destabilization of the macro-ion and lowered ionization constants. Titration studies of linear polyacrylic acids with quarternary ammonium bases have demonstrated that pKa increases with cation size(24). Evidently, cross-linking limits the conformational mobility of the poly-anion, produces a higher density of charges in a given volume element, and again raises the potential of the macro-ion.

In coal, two explanations are possible for incomplete neutralization: 1) polyelectrolyte charging effects as discussed for cross-linked resins inhibit dissociation within the organic matrix or, 2) specific structural features such as in a o-phthalic acid or catechol lead to a substantial decrease in the dissociation constant for a second deprotonation (o-phthalic acid; $k_1/k_2=3.3 \times 10^4$ at 25°C in H_2O)(25). The latter explanation has been proposed based on evidence obtained from potentiometric titration(26).

Also consistent with a polyelectrolyte model for bituminous coal is the observation that the addition of electrolytes, potassium chloride and tetra-n-butylammonium bromide, to KOH and n-Bu_4NOH solutions, respectively, increases both the swelling volume and base uptake during neutralization. Table VI gives the equilibrium swelling values and base capacities for Illinois No. 6 (TNE) coal treated with 0.25 M base solutions in methanol and water. Base capacity for an aqueous KOH/KCl mixture increased 36% over a corresponding base solution containing no salt. This effect was greatly augmented for n-Bu_4NOH/H_2O mixtures where base capacity increased from 0.47 to 1.17 (mmoL/g) upon the addition of n-Bu_4NBr (four fold excess). A similar salt effect, although attenuated, was observed for n-Bu_4NOH/MeOH solutions. Such salt effects are expected for polyelectrolytes and have been observed in many macromolecular systems (synthetic resins, pectic acid, etc.)(27-29).

It is interesting to note that, although the measured base capacities for Na^+ and K^+ are 1.92 and 1.89 (mmol/g), respectively, and essentially the same, a significant increase in bulk swelling is observed for Na^+ (4.5 versus 3.8 mL/g). This is consistent with a greater solvated volume for Na^+ than K^+ ions. The solvation number for Na^+ in methanol is known to be greater than that for K^+(30). The increased swelling at constant capacity may indicate that sodium is well solvated in the coal.

Table IV also gives final swelling values Q_∞ (mL/g) and base capacities (mmoL/g) for 0.25 M potassium and tetra-n-butyl ammonium hydroxides as well as 0.125

M tetra-n-hexyl ammonium hydroxide in various solvents. For 0.25 M KOH, MeOH leads to a 67% increase in swelling over that observed for H_2O and the base capacity increases by 35%. This general trend , where better coal swelling solvents lead to increased swelling and base uptake capacity, persists for the three bases examined. Presumbably, a physical increase in the spacing of ionized groups via stretching of the cross-linked coal matrix (this could be a conformational change in the macromolecular structure) allows a greater base uptake. It must be noted, however, that changes in the dielectric of the medium with different solvents may act to stabilize the polyanion directly rather than via solvent-coal swelling.

Examination of bulk swelling versus time curves for several concentrations of tetra-n-butylammonium hydroxide in methanol revealed an unusual effect. Although the equilibrium swelling values increased with base concentration, an inverse dependence was observed with respect to initial swelling rate (estimated from the initial slopes). The swelling rate for the 0.25 M solution is about six times greater than the rate observed for the 1.0 M solution. One possible explantion involves osmotic pressure effects(31). Since the absorption of ions into the organic matrix is slow compared to the rate of solvent uptake, the swollen coal particles apparently behave as if enclosed in a semipermeable membrane. Solutions of high ionic strength "deswell" the coal or limit the amount of solvent that can be absorbed into the cross-linked matrix. Similar deswelling has been observed for weak acid ion-exchange resins(24). A dramatically decreased rate of swelling is also observed when excess electrolyte is added to a 0.25 M solution of tetra-n-butylammonium hydroxide; although a cross over in swelling value is observed at long times which leads to a substantial increase for the solution of higher ionic strength.

In Figure 3, a comparison between swelling and neutralization of the (TNE) component of Illinois No. 6 coal is presented. The figure shows a plot of reaction extent versus time for neutralization and swelling with 0.25 M potassium and tetra-n-butylammonium hydroxides in methanol. It is important to note that, although the extent of swelling for tetra-n-butylammonium hydroxide in methanol appears less than, or equal to, the swelling observed in KOH/methanol solution, these curves have been normalized to their own final states. At equal concentrations, the tetra-n-butylammonium hydroxide solution swells coal to a much greater extent (4.8 mL/g) than potassium hydroxide (3.9 mL/g). This is a greater than 20% increase in the bulk swelling, even though fewer sites have been reacted. With potassium hydroxide, the degree of swelling of the matrix is directly correlated with neutralization. An incremental increase in base uptake leads to a corresponding increase in the expansion of the organic matrix. This is not the case, however, for tetra-n-butylammonium hydroxide. At a given time the extent of swelling is greater than the extent of neutralization. Within one hour rapid swelling of the coal occurs (70% of Q_∞ while only half of the accessible acidic sites are neutralized). The large quaternary ammonium ions apparently act as a wedge in the organic structure and must lead to conformational changes in the matrix that do not occur with the smaller potassium ion. If hydrophilic regions exist in the coal, which contain clusters of the hydrogen bonded, acidic groups, the highly aliphatic character of the tetra-n-butylammonium ions may lead to strong hydrophobic interactions(32-34) that influence local structure. Such hydrophobic interactions would not be expected from solvated potassium ions and should be minimized if the acidic sites were uniformly dispersed throughout the the cross-linked structure. Similar speculations have been made regarding the structure of globular proteins(35).

CONCLUSION

The physio-chemical behavior of bituminous coal with base and salt mixtures has been shown to be in accord with a simple polyelectrolyte model, derived from more regular polymeric materials (functionalized, cross-linked resins). Bulk swelling measurements in conjunction with chemical probes have provided useful information

about neutralization rates and equilibria. The understanding of these properties for heterogeneous, organic solids, such as coal, is needed for the controlled processing of fossil fuels and more generally for the control of reaction chemistry within solvent swollen, three dimensional organic matrices.

EXPERIMENTAL SECTION

Materials. The pyridine and tetrahydrofuran nonextractable component of Illinois No. 6 coal, a high-volatile C, bituminous rank coal, was used in the studies described. Solvent fractionated coal was prepared using a Soxhlet extraction apparatus. The coal was extracted with pyridine until the solution filtering through the extraction thimble was clear (~four days), then with distilled tetrahydrofuran (~one day). Drying of the sample was accomplished using a vacuum oven (1-5 torr.) at 105-110°C for a minimum of twenty-four hours. In some cases the coal was pre-dried in a fritted funnel to remove most of the organic solvent under a stream of nitrogen before the final drying step. All solvents used were reagent grade and were not further purified before use unless otherwise specified. Tetra-n-butylammonium bromide (99%) was obtained from Aldrich Chemical Company and the tetra-n-alkylammonium hydroxides were obtained from Southwestern Analytical Chemical, Inc. (Austin, Texas).

Swelling Measurements. In a typical swelling experiment, a 15 mL graduated screwtop centrifuge tube (Kimax Cat. No. 45166) was charged with 1.0 grams of dry, fractionated coal and 14 mL of the appropriate swelling solution(36). The tube was sealed immediately using a Teflon-lined cap, taped to prevent solvent loss due to evaporation, and shaken at room temperature (24°C) at a rate of about 170 cycles per minute using an Ederbach Corporation sample shaker (Model No. 6000) equipped with a utility carrier tray (Model No. 5865). When shaking was begun, the time was noted; this was taken as t_0 for kinetic runs. During the experiment, tubes were removed from the shaker periodically, the time was recorded, and the samples were centrifuged at 2800 rpm (25 cm rotor, ~2200 G's) for five minutes using a Sorvall Instruments RC-3B refrigerated centrifuge at 24°C. The tubes were removed, briefly shaken to dislodge any solid material adhering to the upper portions of the tube, and spun down again at 2800 rpm for another five minutes. The samples were removed from the centrifuge, and the volume of solid was measured by visual inspection of the calibrated tubes. In some samples, darkening of the liquid layer and uneven settling of the coal during centrifugation led to small uncertainties in volume readings. Using repeat measurements, maximal errors were estimated to be ± 0.1 mL. When the volume measurements were completed, the tubes were shaken vigorously by hand to break up the solid plug of coal produced by centrifugation and placed back into the shaker to resume the kinetic run. Swelling volumes were recorded using the method described above until they were constant at long reaction times. Equilibrium swelling values were obtained in a similar fashion after a total shaking time of two weeks. To eliminate errors in swelling measurements due to differences in particle size from one experiment to the next, all samples compared were obtained from the same batch of well-mixed coal.

Neutralization Rate and Base Capacity Measurements. A typical neutralization study was carried out in the manner described below for THF fractionated coal. All experiments were conducted at ambient temperature (24°C). 1. Neutralization of the THF Nonextractable Component of Illinois No. 6 Coal. A 100 mL single-necked, round bottomed flask was equipped with a magnetic stirring bar and charged with 4.00 grams of THF insoluble Illinois No. 6 coal. The solid coal was stirred and 55.0 mL of 0.26 M KOH (1 equivalent assuming 3.5 meq. of acidic hydrogens per gram of coal) in methanol was added in one portion rapidly. When addition of the base solution was completed, a timer was started and the kinetics run begun. During the course of the neutralization, the solution was maintained under a positive pressure of nitrogen. Periodically, the slurry was sampled using a large bore calibrated glass tube and a Glasfirn "Pi-Pump" pipetting aid. A 2 mL aliquot was removed. Control experiments

showed that the slurry was well agitated and that equal portions of coal and solution were removed regardless of the sampling depth of the pipette. The removed aliquot was filtered using a sintered glass, medium frit filtration funnel. The coal was washed with 2 mL of methanol and the filtrate was diluted with 20 mL of de-ionized, degassed water. The aqueous methanol solution was then titrated with 0.020 M HCL to a pH of 7.0. Blank titrations, without coal, were done to determine the initial base concentration. Final base concentrations in the reaction mixture were determined after twenty-four hours. 2. Base Capacity Measurements. Equilibrium base capacities were measured after two weeks by titration of a known volume aliquot removed from the supernatant of the centrifuged swelling samples. The titration was conducted at room temperature with standard acid solution (0.020 M HCL) using a Beckman Potentiograph (E 536) and a Metrohm (655) Dosimat.

ACKNOWLEDGEMENTS

We would like to extend special thanks to Professor J. W. Larsen for insightful discussions and his instrumental contributions to the progress of our work. Appreciation is also given to M. L. Gorbaty, P. S. Hagan, J. S. Gethner and D. Brenner for valuable suggestions.

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TABLE I
Typical Analysis for Raw, Perdeuteromethylated, and Solvent Extracted Illinois No. 6 Coal

WT %	RAW	PNE	PE	PNE-CD_3	TNE-CD_3	RAW-CD_3
C	68.4	64.9	77.8	65.5	66.9	69.5
H	5.2	4.8	5.8	4.0	4.4	4.8
D	-	-	-	2.4	1.7	1.8
N	1.3	1.2	1.4	-	-	-
$S_{(SO_4^=)}$	0.01	0.01	-	-	-	-
$S_{(pyr)}$[a]	1.3	1.7	-	-	-	-
$S_{(org)}$	3.1	3.6	3.2	-	-	-
$S_{(total)}$	4.4	5.3	3.2	-	-	-
Ash	9.4	13.7	-	-	-	-
$O_{(NAA)}$[b]	14.4	17.2	-	-	-	-
MM[c]	11.2	16.3	-	-	-	-
$O_{(diff)}$	10.8	9.1	11.8	-	-	-

Empirical Formula on C_{100} Basis

C	100.0	100.0	100.0	100.0	100.0	100.0
H	91.8	89.1	89.2	73.0	79.6	82.2
D[d]	-	-	-	22.1	15.3	15.4
N	1.6	1.6	1.5	-	-	-
S	1.7	2.1	1.5	-	-	-
O	11.8	10.5	11.4	-	-	-
CD_3 Groups[e]	-	-	-	7.4	5.1	5.1

a PNE = pyridine nonextractable component, PE = pyridine extract, and TNE = THF nonextractable component

b % pyritic sulfur

c MM = mineral matter calculated as 1.13 (ash) + 0.47 (pyritic S)

d by combustion/mass spectral analysis

e alkylation procedure taken from References 9 and 11

TABLE II
Solvent Swelling Values for the Pyridine Nonextractable Component of Illinois No. 6 Coal

Solvent	Q(mL/g)
H_2O	1.8
MeOH	2.3
THF	3.6
THF/H_2O (3:1 by volume)	4.0
Pyridine	4.5

TABLE III
Least Squares Treatment (Eq. 1) of Neutralization Data for the Tetrahydrofuran Nonextractable Component of Illinois No. 6 Coal

Base	Concentration (M)	Solvent	n	k	r^2
n-Bu_4NOH	0.20	THF/H_2O	0.43	1.9	0.97
KOH	0.25	MeOH	0.46	2.1	0.99

TABLE IV
Base Capacities and Swelling Values Q as a function of Solvent, Salt Concentration, and Base for the TNE Nonextractable Component of Illinois No. 6 Coal.

Base (0.25 M)	Solvent	Salt (1.0 M)	Q(mL/g)	Base Capacity (mmol/g)
KOH	H_2O	-	2.2	1.40
KOH	H_2O	KCl	2.4	1.90
KOH	MeOH	-	3.8	1.89
n-Bu_4NOH	H_2O	-	2.0	0.47
n-Bu_4NOH	H_2O	n-Bu_4NBr	3.5	1.17
n-Bu_4NOH	MeOH	-	4.8	1.49
n-Bu_4NOH	MeOH	n-Bu_4NBr	5.4	1.83
n-Bu_4NOH	THF/H_2O(3:1)[a]	-	7.0	>1.65[b]
n-Hex_4NOH[c]	H_2O	-	2.1	0.41
n-Hex_4NOH[c]	THF/H_2O(3:1)[a]	-	5.8	>1.17[b]

a By volume

b Corrected for partial dissolution of the sample.

c 0.125 M

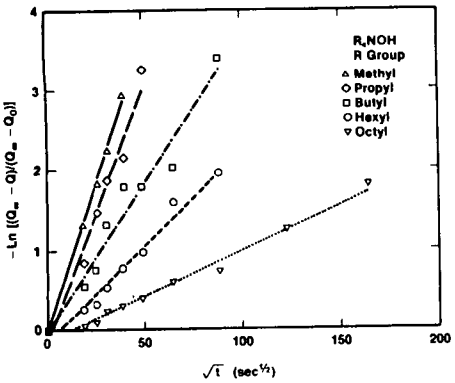

FIGURE 1

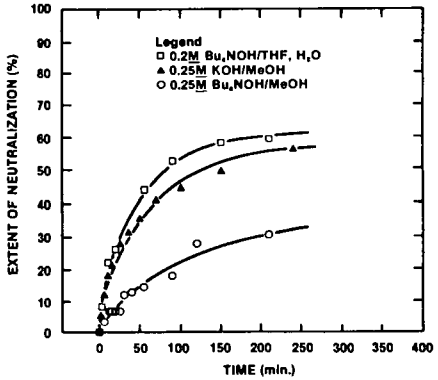

FIGURE 2

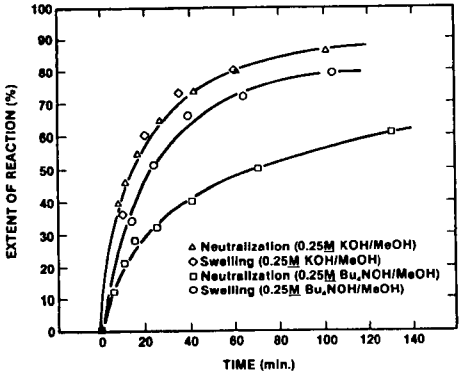

FIGURE 3

COAL: MACROMOLECULAR STRUCTURE AND REACTIVITY

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This paper will tie together results from two disparate studies of coal reactivity, studies whose only uniting feature is the reactant coal. They will be discussed in terms of a model for the macromolecular structure of coal. Two very different reactions have been chosen to illustrate the utility and appropriateness of the model under very different circumstances. Not all of the predictions made are correct, we have very far to go. The ability to make a definite prediction about coal reactivity from a model is an advance. I hope the power and utility of viewing coal as a macromolecular solid will be made apparent by the selected examples.

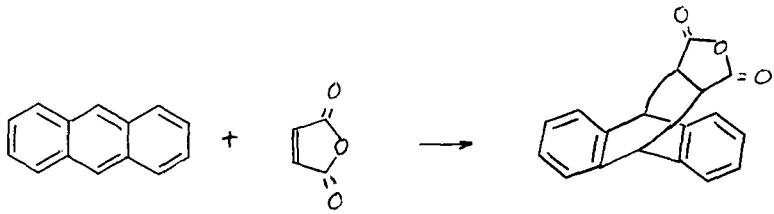
Coals are extraordinarily difficult materials to study, and, more than in most areas of science, progress is general and due to the efforts of the whole, rather than a few.
Progress has been rapid recently, due in part to new ideas and approaches rising from the general realization that coals are macromolecular gels and the concepts and techniques of polymer science apply.

A tiny beginning has been made in relating coal macromolecular structure to reactivity. The importance of macromolecular structure can be made clear by a consideration of the general factors which are important in the conversion of coals to soluble materials. The overall conversion rate will be a function of the number of bonds which must be broken to produce a soluble material, some mass transport terms, and the rates at which the individual chemical bond breakings occur. The first term is a simple function of the macromolecular structure. In principal, knowledge of the macromolecular structure will lead to a reasonable understanding of mass transport rates. Systematic study of mass transport in coals is just now beginning, despite the very important role it plays in many, if not most, coal reactions. The intrinsic chemical reactivity of individual bonds or groups, the third term, is not a function of the network containing those groups. Any attempt to understand coal reactivity in a fundamental way must include a macromolecular structure model of sufficient specificity to be useful for predictions. Neither the model nor the necessary theoretical framework yet exist, but progress is being made[1-6]. In this short paper a structural model will be presented and related to coal reactivity at both low and high temperatures. The discussion will cover important issues which we do not understand as well as a few we are beginning to understand.

The structural model is shown in Figure 1, and is for an Ill. No. 6 coal having the following composition (dmmf) $C_{100}H_{84}O_{11}S_{1.8}N_{1.4}$ and five hydroxyl groups per 100 carbon atoms. In drawing this model, we arbitrarily assumed a cluster molecular weight of 300. The extractable material, that not bonded to the network, has an average molecular weight of 900, close to experimental value for this coal[7]. The number average molecular weight between cross links (M_c) is 3000, higher than that given by our experiments[6]. There exists

evidence that the use of the Kovac model[8] underestimates M_c. The clusters which are network branch points, which are linked to more than two other clusters, are circled. The most startling feature of the model is the large number of network active hydrogen bonds, denoted by hash marks. In this native coal, hydrogen bond cross links (branch points) exceed covalent ones by a factor of four. This value was derived from solvent swelling measurements published elsewhere[7].

We will first use this model to make some qualitative predictions about the rate of the low temperature diffusion controlled reaction between maleic anhydride and coal. This has been established as a Diels-Alder reaction[9,10]. A consideration of the known reactivity of maleic anhydride in Diels-Alder reactions and current coal structural models leads to the conclusion that the reaction must be occurring between anthracene structure units and maleic anhydride. Neither benzene, naphthalene, or phenanthrene react. The linear anthracene structure reacts readily, either as anthracene itself as shown below or when this structure is imbedded in a larger polynuclear aromatic system (PNA). The evidence that the reaction is mass transport limited is: the reaction of coals is much slower than the reaction of anthracene itself, the reaction kinetics follow $t^{1/2}$, and the activation energy for the reaction in o-dichlorobenzene is 7.5 kcal/mole.



We anticipated that swelling the coal would increase the reaction rate. Particularly, as hydrogen bonds were broken by solvents like dioxane, the network would become more flexible and diffusion rates would increase. This did not happen as shown by the data in Table 1. We do not understand this, and plan further studies.

In other respects, the reaction seems normal. The effect of bulky groups on the reaction is to slow the rate, as illustrated by the data for fumarate esters shown in Table 2. Di-neopentyl fumarate does not undergo a Diels-Alder reaction with anthracene or with the coal.

This reaction can be used as an interesting probe of coal structure since it limited to structures containing the anthracene nucleus. The analysis of the Bruceton coal used is 78.6% C, 5.0% H, 1.6% N, 8.3% O (diff), 1.2% S, and 5.4% mineral matter. For every 78.6 g of carbon, 18 g of maleic anhydride were added. Since a minimum of 14 carbon atoms are required for the reaction, at least 39% of this coal's carbon atoms are in reactive PNA structures. With an f_a (measured by Dr. Ron Pugmire, Univ. of Utah) of 0.73, a bit more then half of the aromatic carbons must be contained in reactive PNA systems. This is a startling result, and deserves both further checking and elaboration. Work on this reaction continues.

The next reaction to be discussed is pyrolysis of a lignite and a bituminous coal. Details are to be published elsewhere[11]. We studied the emission of volatile products from coals rapidly pyrolyzed (1000 K/sec) and cooled (200 - 400 K/sec) on a wire mesh. These data were combined with measurements of the cross-link density of the chars by solvent swelling with pyridine. As shown in Fig. 2, the cross-link densities of the chars increase parallel with the loss of CO and CO_2. With no more evidence than this, we cannot say that the pyrolytic loss of the carboxyl groups leads directly to the formation of new cross-links in the coal. The data certainly are consistent with this.

The situation is very different with the bituminous coal. As shown in Figure 3, the pyridine swelling does not begin to decrease due to cross-link formation until about 2/3 of the tar formation has occurred. Cross linking occurs at a late stage of pyrolysis, as must be true if a coal is to melt and form a good metallurgical coke. The measurement of char cross-link densities makes the very different pyrolysis behavior of lignites and bituminous coals very clear and allows a quantitative comparison between them.

Coals are macromolecular solids; this has long been known. But only recently has the systematic application of classical polymer physics and chemistry techniques to coals occurred. All of the hopes we had for the power and success of these techniques have been exceeded. We are a very long way from a fundamental understanding of the relationships between coal structure and reactivity, but progress is being made and the problem can be solved.

Acknowledgements. I am grateful to the Department of Energy, the Gas Research Institute, and the Exxon Education Foundation for financial support of the research described. The names of my collaborators and students appear in the references. Their contributions have often been crucial and I could not wish for a finer group of associates.

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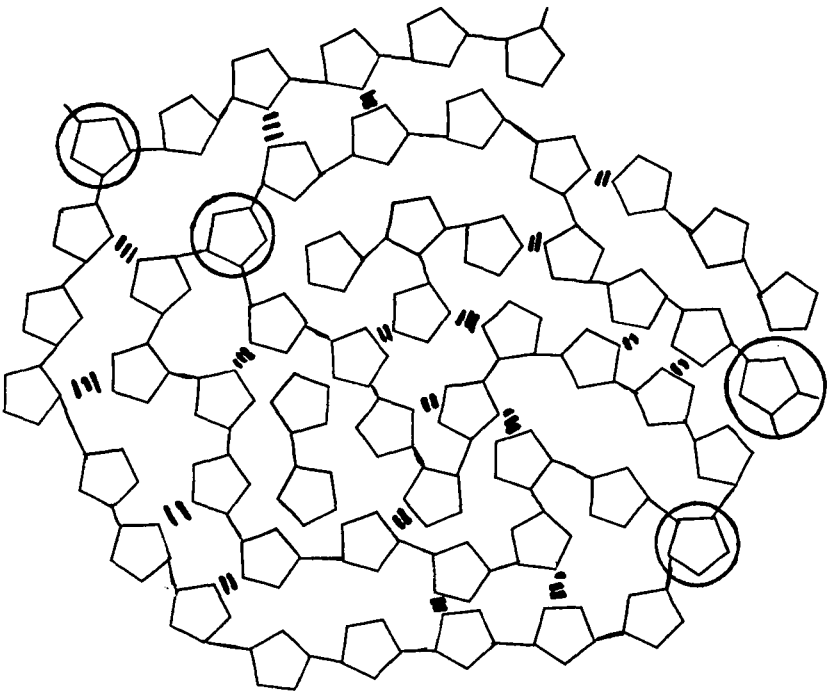

FIGURE 1. Macromolecular Structural Model for An Illinois No. 6 Coal

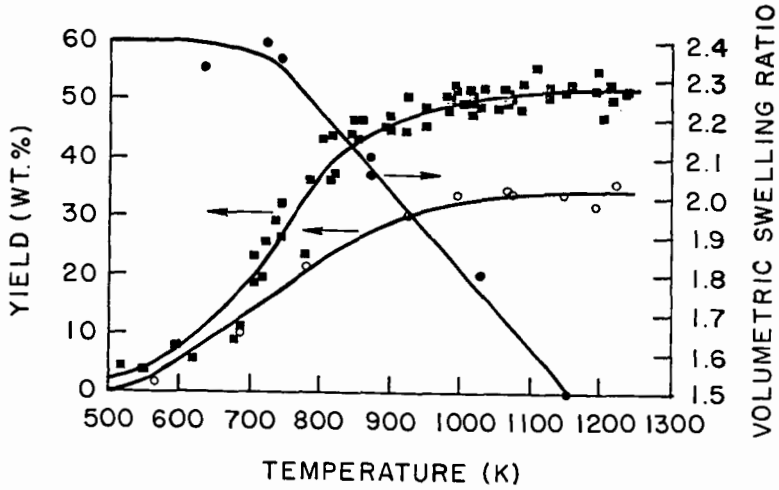

FIGURE 2. Yields of Carbon Monoxide (o), Carbon Dixoide (o), and the Ratio of Initial to Final Number Average Molecular Weights Between Crosslinks (M_0/M) in North Dakota Lignite Char

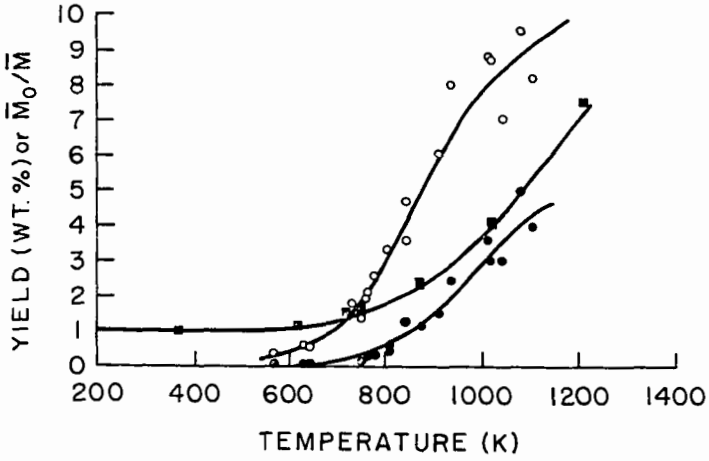

FIGURE 3. Total Volatiles Yield ( ), Tar Yield (o), and Char Volumetric Swelling Ratio in Pyridine (o) as a Function of Pyrolysis Peak Temperature for Bruceton Coal

TABLE 1. Influence of the solvent on the rate of addition of maleic anhydride to Bruceton coal at 90 ± 3°C

Solvent	Slope[a] (g $h^{1/2}$)	Swelling ratio
1,2,4-trichlorobenzene (TCB)	0.0018	1.16
o-dichlorobenzene (oDCB)	0.0018	1.22
m-dichlorobenzene (mDCB)	0.0018	1.42
p-dichlorobenzene (pDCB)	0.0025	1.06
Nitrobenzene (ϕNO_2)	0.0016	1.56
o-xylene	0.0015	1.33
Dioxane	0.0015	1.62
Chlorobenzene	0.0017	1.43

[a]Slope of a plot of mass of coal product versus $\sqrt{t}$ (h)

TABLE 2. Ratio and extent of reaction of fumarate esters with Bruceton coal swollen with xylene at 200°C

Dineophile	Slope ($\Delta g/hr^{1/2}$, $X10^{-4}$)	Rel. Rate[a]
Dimethylfumarate	22	1
Diethylfumarate	25	0.95
Di-n-hexylfumarate	32	0.73
Diphenylfumarate	36	0.87
Dineopentylfumarate	0	0
Maleic Anhydride	80	5.3

[a]Normalized to a moles $hr^{-1/2}$ basis. All reactions are diffusion controlled