

**DENSITY SEPARATION OF CHEMICALLY MODIFIED COAL MACERALS.
A TWO DIMENSIONAL SEPARATION METHOD FOR MORE HOMOGENEOUS MACERALS.**

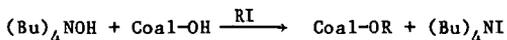
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INTRODUCTION

That coal is a very physically and chemically heterogeneous substance is one of the few facts about coal that has not been contested in the long history of coal research. However, the extent and nature of that heterogeneity is not at all clear. Coal heterogeneity is due to several elements: The varied diagenesis and catagenesis of the original organic plant constituents, specific associations and interactions of macerals from different paleo-environments, and the different mineral constituents of coal. Even though the heterogeneity is practically self-evident and is a major obstacle to defining the structural elements of coal, remarkably little work is directed toward exploring methods to reduce the heterogeneity prior to structure elucidation. Density gradient centrifugation (DGC) appears to be one of the most effective separation methods for reducing the heterogeneity of coal by separating the three maceral groups, and concomitantly provides some idea of the range^{1,2,3} of physical and chemical variation that exist within a coal sample. However, this still represents only a first order separation. We rarely can resolve the individual macerals that make up the maceral groups because their density distributions overlap. The maceral density ranges may overlap so closely, that no matter how finely we fractionate a density gradient, we will not resolve the various species. Thus, some additional treatment or separation method is necessary to resolve individual macerals or sub-maceral species.

Chemical modification of the coal maceral particles coupled with density gradient centrifugation is one approach to higher maceral resolution. For this two dimensional type of treatment to be useful, we must use a reaction which exhibits selectivity towards the macerals, and can cause an observable change in the density of the product. For our initial efforts, we felt that the reaction should be mild and not extensively alter the maceral particles, since petrographic analysis was needed to understand any changes in the separations. O-alkylation of the coal appeared to meet our requirements. The alkylation reaction utilizes tetrabutylammonium hydroxide and an alkyl iodide to alkylate hydroxyl groups⁵:



This reaction is carried out under mild conditions and is relatively non-destructive towards the coal. Since we know that at least the maceral groups have different oxygen contents and probably³ hydroxyl contents, this reaction system seemed most appropriate to our needs.

EXPERIMENTAL

Alkylation

The alkylation conditions were slightly modified from that indicated by Liotta.⁵ Under nitrogen, the sample (~20 mg) was stirred in 5 ml of THF for 10 minutes and then 50 ul of 40% aqueous tetrabutylammonium hydroxide was added. After an hour, the alkyl iodide was added, and the solution stirred for seven days. The solution was neutralized with HCl and the volatile organics removed on a rotary evaporator at 60°C. Water was added and the mixture dispersed in a sonication bath. The solid was collected on 0.8 micron polycarbonate filter and washed with 50% aqueous methanol. The alkylated coal was dried under vacuum at 64°C.

Density Gradient Centrifugation

The density gradient centrifugation procedures in aqueous CsCl/Brij-35 solutions devised by Dyrkacz and co-workers were used as described.¹⁻³ Each coal was ground to less than 10 microns, and chemically demineralized before any further separation or chemical modification. The preparative level separations were done either on two gram levels (Preparative I) or on maceral sink-float concentrates (Preparative II). Analytical density gradient runs of the alkylated coal maceral fractions (1-25 mg) were done in 50 ml centrifuge tubes. The amount of coal at various densities in the analytical runs was inferred from the absorbance response at 660 nm in a flow through cell when the gradient was being fractionated.

Each density distribution has been normalized to the highest peak.

RESULTS AND DISCUSSION

Two high volatile A bituminous coals, PSOC-732 and 726, obtained from Pennsylvania State University were used in this study. The elemental and maceral analyses are shown in Table 1. All the data that will be presented is based on the chemically demineralized coals. This is necessary to maximize the resolution of the macerals.

Figures 1 and 2 present the DGC separations for the untreated, methylated and n-butylated coals. In the unalkylated coals, the lowest density band is the exinites and the mid-density band is the vitrinite. The highest density inertinite band is obvious in PSOC-732, but not in the PSOC-726 coal. For both inertinites the density at which there is 50% vitrinite and 50% inertinite is close to 1.31 g cm^{-1} . Relative to the untreated coals, all the alkylated coals exhibit a shift in their density distributions to lower densities, which is in accord with previous findings.⁶ We also see that the butylated coal density patterns are shifted more than the methylated coal; this is expected from molecular volume considerations.^{2,7} Looking at the density distributions in more detail, we see rather complex changes are occurring with alkylation. If each of the maceral groups were responding in the same way to alkylation, we would expect that the overall density pattern would not change. Maceral analyses of the density fractions confirmed the

notion that the macerals are changing density in a manner too complicated to follow easily by just petrographic analysis.

In order to understand the behavior of the macerals in the alkylation/DGC separation, we approached the separation from the opposite sense. We first density separated the unalkylated coal by DGC, alkylated the individual macerals and then DGC separated this new material. The results are shown in Figures 3-5. In each case a single density gradient derived fraction, covering approximately a 0.01 g cm^{-1} range, was methylated or butylated and then separated on an analytical density gradient. The maceral density fractions that were used in these studies are at least 95% pure in a single maceral group by petrographic analysis. From analytical data the amount of alkylation per 100 carbons increases in the order: inertinite < exinite < vitrinite.

In the case of the alkylated exinites, for PSOC-732 the expected shift to lower density occurs as the size of the alkyl group increases (Figure 3). However, the methylated PSOC-726 exinites material shows a higher density distribution, while the butylated material shows a lower density relative to the untreated coal fraction. The reason for this behavior is not clear. It could be due to extraction of a highly aliphatic material from the exinite, which is more than compensated for by the molecular volume added by butyl groups, but cannot be compensated by the smaller molecular volume of the methyl groups. Alternatively, the alkylation reaction may be opening up pores which were closed to the density gradient solution in the original coal. Another possibility is that the alkylation alters the surface of the the exinites and changes the behavior of the particles in the complex density solution.

The alkylated vitrinite macerals from both coals show the expected behavior of shifting to lower density upon alkylation. However, all four alkylated vitrinites show broadening of the band. In the case of the butylated PSOC-726 there is even a distinct shoulder present. The exinites also show this behavior which implies that there may be subspecies of maceral particles which have different reactivities towards alkylation.

The alkylated inertinites show some remarkable changes in density distribution relative to the original maceral density distribution. All the alkylated inertinites show large band broadening and, in the case of the butylated materials, show the presence of multiple bands. It should be held in mind that particularly in the case of the alkylated inertinites, we have found that the relative absorbance that is plotted versus density does not necessarily reflect the true weight distribution of material; this is because of a complex relationship between absorbance and particle size for these altered materials.⁸ Nevertheless, the overall character of the patterns is still correct. Not only do the alkylated inertinites show a band broadening compared to the original material, but particularly in the butylated inertinites we see the development of new bands. The fact that specific bands emerge upon alkylation can be explained if there are classes of inertinite particles in the untreated maceral fraction with quite specific reactivity towards alkylation. The precise identity of these particles is not clear. They may represent monomaceral inertinite particles such as semi-fusinite, fusinite or micrinite within the inertinite group. On the other hand, they may represent a chemically different sub-species of an individual maceral.

To try and understand the nature of these new bands, several further experiments were done. In the case of the PSOC-732 inertinite fraction, the three bands were separated from several small scale analytical separations. The C, H, N analysis were done on the original fraction and the three new bands. Using the original data as a base, the bands contain: 3.0, 1.7 and 0.3 butyl groups per 100 carbon atoms, as a function of increasing density. In addition, FT-IR spectra of the three inertinite density bands show large increases in the aliphatic C-H stretching band in accordance with the increase in butyl groups. These results suggest that the differences in the density pattern are definitely related to selective chemical modification of different species.

CONCLUSIONS

Although we do not yet understand the nature of the species that have been separated, there is little doubt that we have achieved a higher level of separation than possible with density gradient techniques alone. The presence of new bands can only indicate that there are at least several specific classes of particles that have quite specific behavior towards alkylation.

The two dimensional separation of coal, consisting of density gradient separation and chemical modification, represents a new approach to resolving the heterogeneity of coal and possibly other maceral sub-species that may not be petrographically identifiable. It should be obvious that this approach can be used with any mild chemical treatment, O-alkylation being only one example. Even further maceral resolution might be achieved by chaining various functional group selective reactions with density gradient separation to do a multi-dimensional separation.

ACKNOWLEDGEMENTS

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3. Dyrkacz, G.R., Bloomquist, C.A.A., Ruscic, L. Fuel 1984, 63, 1367.
4. In a few rare cases alginites or resinities can sometimes be separated from sporinite in the exinite maceral group, because of a very large difference in density between the constituents.
5. Liotta, R., Fuel, 1979, 58, 724.
6. Liotta, R., Rose, K., Hippo, E.J., Org. Chem., 1981, 46, 227.
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8. The alkylation reaction in some cases leads to fragmentation of some particles so that the original fairly narrow particles size distribution becomes larger. It is also possible there is selective swelling of certain maceral particles. Thus, the new material does not necessarily have a uniform size throughout the density band.

TABLE 1. Analytical Data for Coals.

Coal	C	H	N	S	O	Ash	
	% wt (daf)					(dry)	
PSOC-732	84.5	4.72	1.65	0.82	8.2	18.7	
PSOC-726	87.5	5.20	1.30	0.65	5.3	4.8	
Pet. Anal.							

Coal	Sp	Re	Cu	Bi	Vit	S-fus	Mi	Fus	Id
	% volume ^a								
PSOC-732	10.2	0.4	0.0	1.5	63.0	27.9	3.1	2.8	3.7
PSOC-726	10.6	1.4	0.5	0.0	50.4	10.9	3.8	2.6	7.2

a. Sp = sporinite; Re = resinite; Cu = cutinite; Bi = bituminite;
 Vit = vitrinite S-fus = semi-fusinite; Mi = micrinite; Fus = fusinite;
 Id = inertodetrinite.

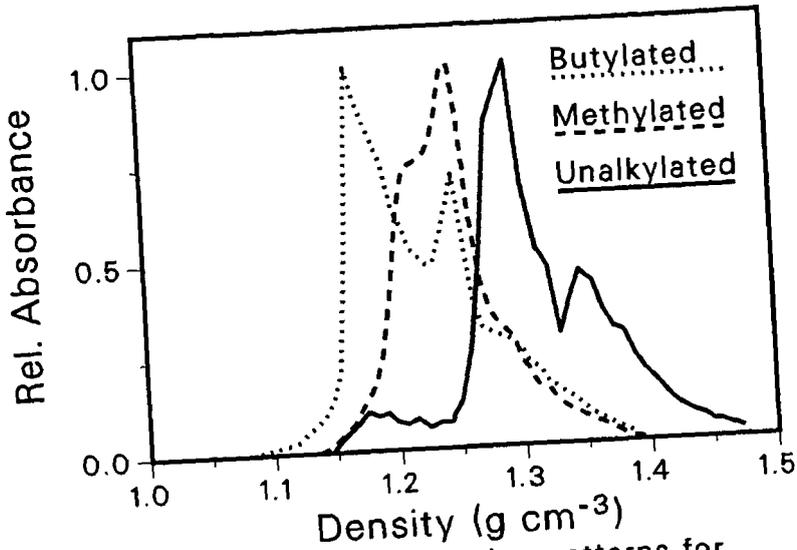


Figure 1. Density distribution patterns for alkylated and unalkylated PSOC-726; 25° C.

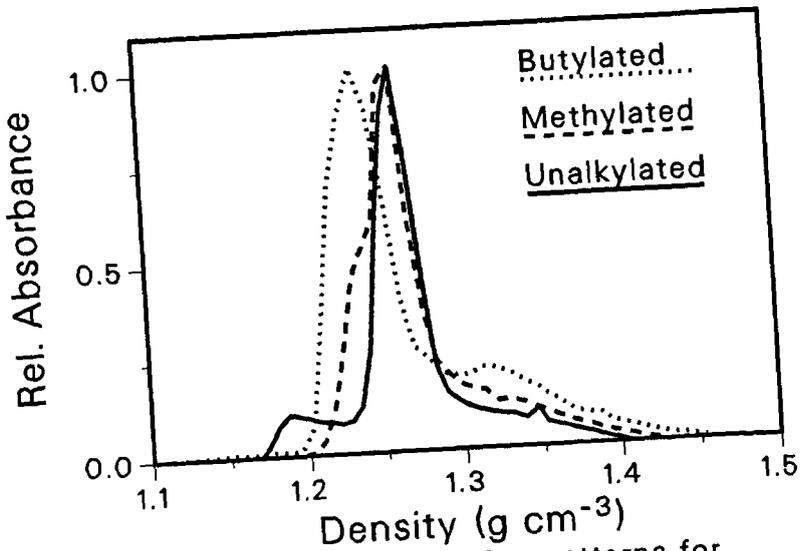


Figure 2. Density distribution patterns for alkylated and unalkylated PSOC-732; 25° C.

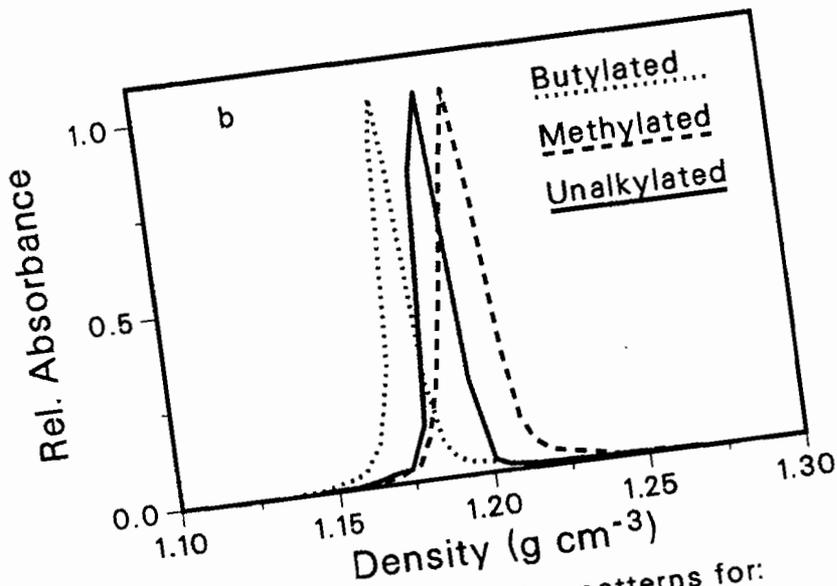
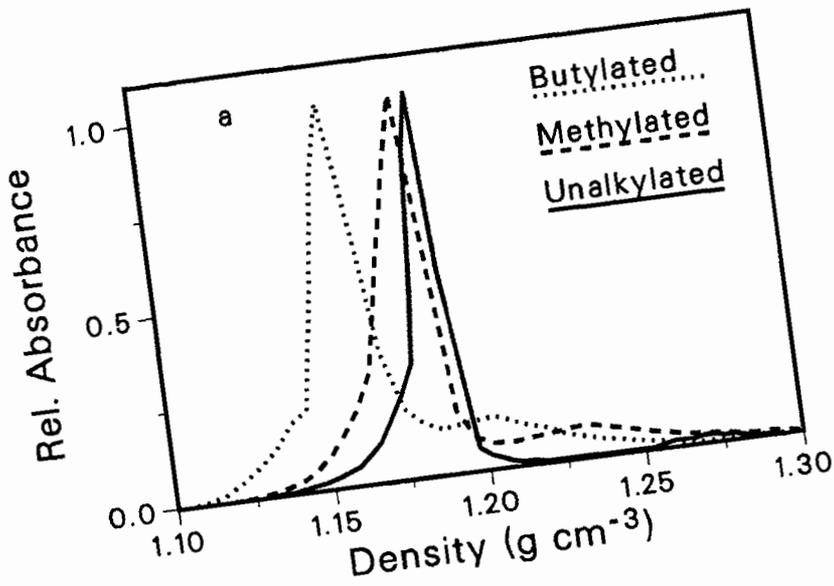


Figure 3. Exinite distribution patterns for: (a) PSOC-732; (b) PSOC-726.

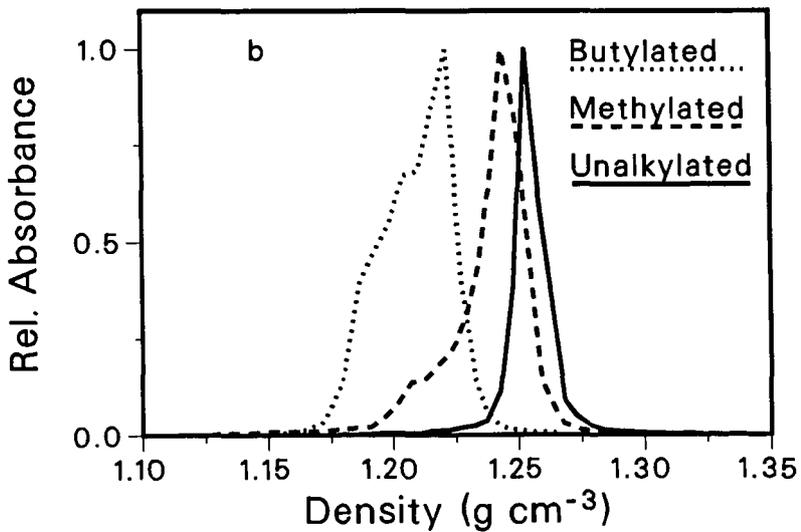
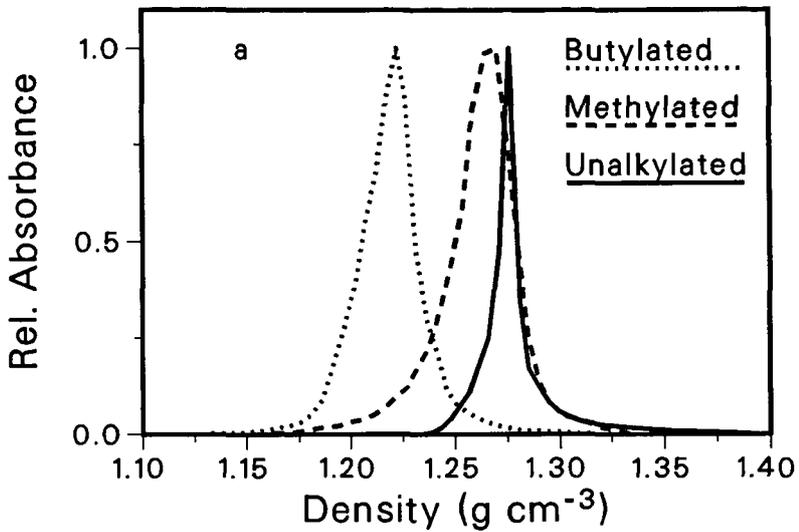


Figure 4. Vitrinite density distribution patterns for: (a) PSOC-732; (b) PSOC-726.

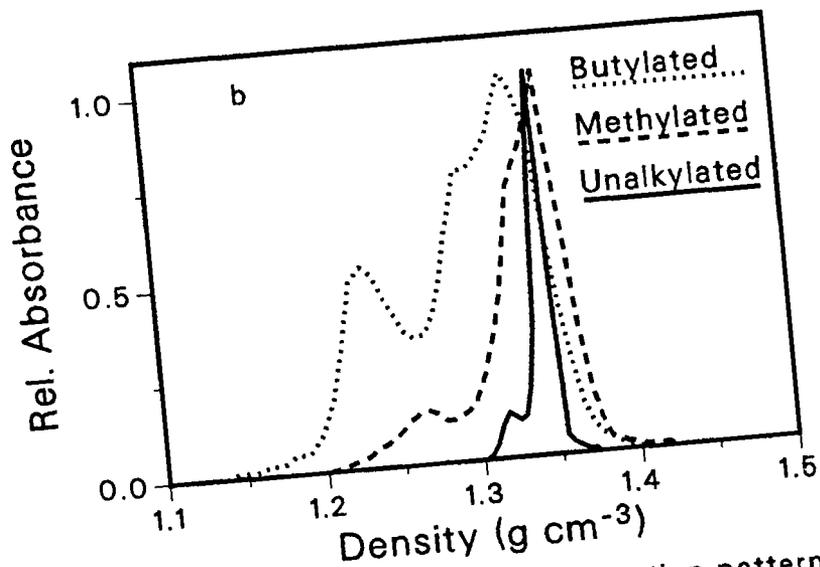
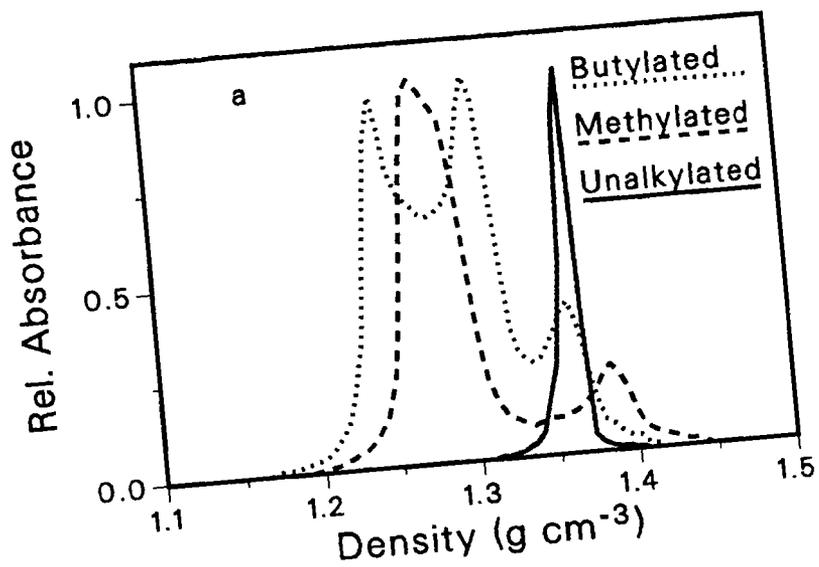


Figure 5. Inertinite density distribution patterns for: (a) PSOC-732; (b) PSOC-726.

TWO DIMENSIONAL SOLID STATE NMR METHODS APPLIED TO WHOLE COALS AND CHEMICALLY MODIFIED COALS

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Introduction

Carbon-13 solid state NMR spectroscopy of coals and chemically modified coals using the combination of cross polarization and magic angle spinning (CPMAS) has proven an extremely useful method for characterizing the organic structures present in these systems.^{1,2} In addition to providing a direct measure of carbon aromaticity, the method gives some further indication as to the different types of organic functionalities present from the characteristic shoulders usually observed on the two principal bands in these spectra. Unfortunately it is not possible to quantitatively assign any of these features in coal CPMAS spectra to single functional types because of severe spectral overlap. For instance in the aromatic region there are typically three overlapping bands centered roughly at 127, 138 and 155ppm from TMS. As a rule of thumb the 155 band is often taken as attributable to phenols or aryl ethers, the band at 138 as alkyl substituted aromatics and the band at 127 as both protonated aromatic carbon and nonprotonated carbon in fused rings. This qualitative interpretation of CPMAS coal spectra is supported by studies using CPMAS to follow the maturation of coal.³ As rank increases the general trend observed is that oxygenated aromatic carbons disappear first followed by loss of alkyl groups and the aromatic band becomes progressively narrower. This picture should however not be taken too literally as many other types of carbons that are to be expected in coals also resonate in these regions. The inclusion of heteroatom substitution in the unsaturates produces a wide range of carbon-13 shifts making it especially difficult to identify these important constituents of coal by solid state NMR.

These difficulties of interpretation are similar to those encountered in the study of complex biomolecules by NMR in solution. Because of the large number of resonances and the resultant spectral overlap, unambiguous assignment of the spectra is not simple. Most often in solution NMR this problem is handled by application of one of the many two dimensional (2D) NMR methods developed over the last decade.⁴ In general the 2D methods used in solution are not applicable to coal because of the strong internuclear dipolar interactions present in organic solids. Our research has been concerned with the development and application of new 2D methods for solids that overcome these difficulties. We have previously reported the successful application of a version of the heteronuclear shift correlation method for solids to a whole coal.⁵ This experiment permits assignment of carbon-13 resonances on the basis of the chemical shift of any directly bonded proton. In this way the protonated carbon-13 resonances in the aliphatic portion of a coal can be separated and clear distinctions made between methylenes, methyls bonded to carbon and methyls bonded to heteroatoms. In this type of experiment the idea is to produce a pulse sequence that removes the complications of the solid state to yield a result similar to the analogous experiment in solution. A much more productive approach has been to use the magnetic interactions present in solids as the basis for 2D NMR. Two such methods being studied which hold much promise for structure analysis in coals are asynchronous dipolar shift correlation spectroscopy (ADIPSHIFT) and zero field NMR

(ZFNMR).⁶ These methods yield spectra with much better resolution than typically observed by CPMAS spectroscopy and provide for a more complete accounting of functional groups. Recent work in this laboratory has also indicated that 2D methods which can correlate carbon-13 resonances on the basis of connectivity are possible in solids. These methods will determine how functional groups are connected to one another and be especially applicable to chemically modified coals.

ADIPSHIFT NMR

In ADIPSHIFT NMR the resonances in a complex carbon-13 CPMAS spectrum can be separated on the basis of the number of directly bonded protons using the carbon-13/proton dipolar interaction. All types of carbon are observed in this experiment at once and it is inherently as accurate as CPMAS spectroscopy itself. This is a significant advantage over the dipolar dephasing method which cannot distinguish methines from methylenes and requires empirical corrections if semi-quantitative results are to be obtained. The experimental setup and pulse sequence used in the ADIPSHIFT experiment has been described elsewhere. In brief the experiment produces a 2D spectrum with the decoupled carbon-13 CPMAS spectrum along the ω_2 axis and a proton dipolar coupled carbon-13 MAS spectrum along the ω_1 axis. To identify the types of carbon resonating at a given point in the normal carbon-13 CPMAS spectrum the dipolar sideband pattern in ω_1 for that point is simulated. The basis of the method is that a CH_2 group will give about twice as wide a sideband pattern as a CH group and both of these patterns are very much wider than those for nonprotonated carbons or rotating methyl groups. The sideband patterns are determined by a number of factors including C-H distances, H-C-H angles, chemical shift anisotropies and the relative orientation of the chemical shift anisotropy to the C-H vectors. In extensive computer simulations it has been found that under conditions of fast MAS rotation the sideband patterns are dominated by the number of protons attached. Reasonable variations in the C-H distance, chemical shift anisotropy, H-C-H angle and shift tensor orientation have only small effects on the calculated sideband intensities. Average values for relative sideband intensities can therefore be used as a basis for simulating experimental spectra. All that is necessary is to find a linear combination of the standard sideband patterns to determine the ratios of CH_2 :CH:CH₃ and nonprotonated carbons contributing to a particular resonance.

In application to model systems the method gives excellent agreement with known structures. For cholesterylacetate the CPMAS spectrum is quite complex giving as many as three lines for each carbon in the molecule due to solid state effects. From the ADIPSHIFT sideband pattern for the 80-10ppm region of the spectrum the relative percentages of the three types of carbon are calculated to be 42% CH_2 , 27% CH and 31% CH_3 plus nonprotonated carbons. This compares quite well with the actual numbers of 42.1%, 27.2% and 30.7% respectively. The method has also been applied to three coals: PSOC-284, PSOC-1135 and an air-oxidized Illinois#6 coal. The results from the sideband analysis for these three coals are contained in Table 1. Even though the air-oxidized coal and PSOC-284 give essentially identical CPMAS spectra, measurable differences exist in the breakdown of carbon types. The numbers in Table 1 can be used to calculate the H/C ratio for the organic portion of the coal. In each case the number is somewhat lower than that measured by analysis. For example in PSOC-284 the H/C ratio by ADIPSHIFT NMR is 0.83 and is measured by analysis to be 0.87. This difference is to be expected as the NMR measurement accounts only for hydrogen attached to carbon, that associated with heteroatoms is not accounted for.

Chemical shift spectra for the different sidebands in the ADIPSHIFT spectra also make for an interesting comparison between these coals. In the

centerband the spectra are dominated by nonprotonated and methyl carbons. The first and successive sidebands are due to CH and CH₂ groups with the latter dominating the outermost sidebands. Significant differences are observed in these coals, especially in the low field aromatic region. In the first and second sideband spectra resonances attributed to protonated sp² carbons are observed which are normally obscured by the resonances from phenol or phenolic ether carbons. This is a rather unique shift range for protonated carbon and is most likely attributable to carbons in furan derivatives alpha to the oxygen. Another interesting feature is a shoulder sometimes seen in CPMAS spectra of coals at ~108ppm which is now clearly resolved. These carbons are also protonated and probably are due to carbons beta to the heteroatom in phenols, furans or pyrroles. Some types of olefins will resonate in this area of the spectrum as well. In the aliphatic region the spectra clearly distinguish methyl carbons and CH₂ groups. For the poorly resolved region where ethers resonate there is now clear evidence for a substantial portion of methylenes attached to oxygen.

Zero Field NMR

While CPMAS based methods are useful for spin 1/2 nuclei such as carbon-13, they are of limited utility for nuclei with spin greater than 1/2 because of the nuclear quadrupole interaction. This same interaction is put to good use in ZFNMR which can produce exceptionally well resolved solid state spectra.⁷ For coal the most important applications of ZFNMR will be to nitrogen-14 and deuterium nuclei with indirect detection via the abundant protons for sensitivity enhancement. ZFNMR of these nuclei is essentially Fourier transform pure nuclear quadrupole resonance. Because of the large variation in quadrupole coupling constants associated with changes in functionality, the ZFNMR spectra of these nuclei in coals are expected to be especially informative. ZFNMR is basically a 2D technique which correlates the high field NMR spectrum with the spectrum in zero applied field. In a typical ZFNMR experiment the zero field evolution is accomplished by removing the sample from the NMR magnet to a region in the fringe field which can then be conveniently compensated for by a set of pulsed magnet coils. The difficulty with this approach is that the relaxation times T₁ for the nuclei being observed must be longer than the time needed to move the sample out of the NMR magnet and back. Typical pneumatic shuttling times are currently 100msec which is the order of T₁ for the protons in most coals. In order to make ZFNMR applicable to coal, methods are being developed to lengthen the proton T₁'s and shorten the sample shuttling times. One approach has been to remove all oxygen from the coal sample and to lower the temperature which we have found can produce T₁'s as long as 800msec in coals. Another way around this problem is to not shuttle the sample and electronically switch the main magnet field instead. Switching times the order of 30msec are currently achievable with fields as large as 1.4T. This method is faster and more reproducible than pneumatic sample shuttling and much easier to combine with low temperature operation.

Connectivity by Solid State NMR

The advanced NMR methods outlined above come close to extricating all the structural information possible by NMR alone at present. Another approach to increasing the information content of NMR spectra is to combine NMR spectroscopy with chemical treatment. Some elegant work along these lines has been done using alkylation chemistry.^{8,9} By incorporating a spin label in the alkylating reagent in the form of isotopic enrichment or another NMR active nucleus, the structure of the reaction site can be conveniently studied by solid state NMR methods. Previous studies have been especially informative as

to the types of sites that may be O-alkylated in coals. In particular the chemical shifts for aryl ethers are quite sensitive to sterics. This makes it possible to determine the ratio of aryl ethers formed with no substitution at adjacent carbons to those with substitution. Such chemical treatment can also be used to good advantage in 2D NMR studies. The principal piece of information that the other 2D techniques discussed here lack is connectivity, i.e., how are the functionalities observed attached to one another? The functional analysis provided by ADIPSHIFT and ZFNMR only tells us what types of carbons, protons, or nitrogen are present, not how they are linked. By using carbon-13 labeled alkylating reagents it should however be possible to establish connectivity in the area of the alkylation site using 2D NMR methods such as COSY and NOESY.⁴

The basic idea in the COSY and NOESY methods is that spin-spin couplings and internuclear dipolar couplings are short range interactions which can be used to correlate the resonances for carbons in close proximity to one another. For a number of reasons such carbon-carbon connectivity experiments may not be expected to work well in solids and this has slowed their development. One potential problem is that for pairs of carbon-13 nuclei the size of the direct dipolar coupling and the chemical shift differences may be comparable giving rise to second order effects which are observed to be pronounced in powder spectra.¹⁰ This might be expected to give rather complicated scalar coupling patterns for bonded spins making COSY methods difficult to interpret in complex systems. In addition spin exchange mediated by direct dipolar couplings in second order systems under MAS may make it difficult to quantitate the results from NOESY type experiments and thus internuclear distances derived from such methods may not be reliable. However under MAS conditions it has been observed that these factors do not necessarily result in second order COSY or NOESY spectra and for the purposes of establishing connectivity the techniques work quite well if certain precautions are followed.

The model system studied here is the pair of phosphorus-31 nuclei in 1,2-bis[2,4,6-tri-tert-butylphenyl]diphosphine. This system was chosen for study because of the high sensitivity of phosphorus-31 NMR, the conclusions drawn are applicable to any pair of spin 1/2 nuclei with similar dipolar couplings and chemical shift anisotropies. Therefore similar behaviour is expected for pairs of carbon-13 nuclei in organic solids. In solution the phosphorus-31 spectrum displays a single line under proton decoupling for the two magnetically equivalent phosphorus nuclei. In the solid state the CPMAS spectrum is somewhat different showing two lines with barely resolved fine structure. One line has the appearance of a triplet and the second has an ill defined shape with noticeable shoulders. The nature of the fine structure has been determined to be due to ³¹P-³¹P scalar coupling in the solid which is not observable in solution. This was accomplished by a homonuclear J 2D experiment using CPMAS and strong proton dipolar decoupling. In addition it was found necessary to increment the t_1 period synchronously with the MAS rotation rate ω_r to ensure that the π pulse in the middle of t_1 did not interfere with the MAS process. The resultant J spectrum gives a reasonable value for J ³¹P-³¹P of 200Hz. The patterns in the 2D J spectrum suprisingly are observed to be very close to first order. To determine the connectivity of the transitions a COSY experiment was performed again restricting the increment in t_1 to $1/\omega_r$. The resulting 2D spectrum shows that the two lines in the ³¹P spectrum are in fact not coupled to each other, rather they are actually two pairs of closely spaced resonances which are internally coupled. This is somewhat perplexing as the resonance which has the appearance of a triplet is seen to actually be a doublet of doublets with J close to the isotropic chemical shift difference. The reason that the pattern is not highly second order as would be observed

for this case in solution is subtle. Even though the average shift difference for these two nuclei is small, the instantaneous shift difference at many points during the MAS rotation apparently is large. This is a consequence of the fact that the two ^{31}P nuclei have anisotropic chemical shifts ($\Delta\sigma=110\text{ppm}$) and that the shift tensors are not coparallel. Thus the J spectrum and the COSY patterns are first order even though the isotropic shift difference is close to J over a MAS rotation. While this situation may seem to be fortuitous, it will in fact be the usual case in most systems of this type. Only in the case where of a pair of nuclei are related by an inversion center will scalar couplings not be observed. In carbon-13 alkylated coals it is then expected that the identification of C-alkylation sites should be possible using this solid state COSY method. All that is required is the observation of cross peaks in the 2D spectrum with the natural abundance carbon-13 at the site of attachment and these should be observed with the same sort of sensitivity as ADIPSHIFT spectra.

A second type of connectivity is also nicely demonstrated in our model system. In a typical NOESY experiment nuclei spatially close to one another are correlated via dipolar mediated cross relaxation. In the solid the experiment is conceptually similar except that the correlation is achieved directly with the dipolar couplings present rather than through relaxation processes. In the model diphosphine studied the results of the NOESY experiment are similar to those for the COSY experiment. The same first order COSY peaks are observed but now additional cross peaks are seen due to the mixing period during which the dipolar interaction correlates the resonances. This spectrum shows that although the two principal ^{31}P lines are not through bond connected, they are in close proximity to one another. Again the patterns are close to first order and of good intensity. These results lead us to conclude that there are at least two inequivalent molecules in the unit cell for this compound and that the molecules do not have inversion centers. In addition the sample used has an impurity of the analogous primary phosphine present. No cross peaks are observed between the diphosphine and the primary phosphine indicating that they are in separate phases, i.e. the two compounds crystallize out of solution separately. When applied to O-alkylated coals this method should be quite informative. Since there will be no large scalar couplings to other carbon-13 centers all cross peaks that will be observed will be NOESY peaks and indicate the identity of the carbons alpha to the oxygen or otherwise very close to the labeled center.

Summary

Two dimensional NMR methods have been shown to provide a much finer accounting of the functional types present in coals than by CPMAS spectroscopy alone. The ADIPSHIFT method has been shown to be at least as quantitative as CPMAS both in theory and experimentally. The method gives reliable distributions of carbons with differing multiplicities which is useful in identifying different functionalities that overlap in chemical shift. Recent studies of a model system indicate that the connectivity of the different groups in chemically modified coals should be obtainable from solid state COSY and NOESY experiments. This type of information will provide a very accurate picture of the structure of the alkylated sites and the substitution patterns surrounding them.

Acknowledgments

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TABLE 1

ADIPSHIFT Analysis for Three Coals

Coal	Aliphatics			Aromatics		f_A
	%CH ₂ , C	%CH	%CH ₂	%C	%CH	
PSOC-284	17	39	44	62	38	0.68
Air Ox. II. #6	22	43	35	63	37	0.69
PSOC-1135	27	48	25	70	30	0.81

COAL ALKYLATION AND PYROLYSIS

Leon M. Stock

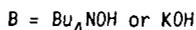
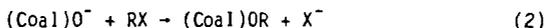
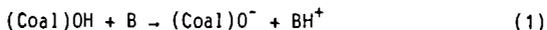
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INTRODUCTION

Investigations employing alkylation, reductive alkylation, and related kinds of chemical transformations have provided new information concerning the structural characteristics of representative bituminous coals (1). The nature of the oxygen functional groups in coals are of rather special interest because they strongly influence the reactions of the coal. Accordingly, we determined the relative abundance these groups during a study of the alkylation and reductive alkylation of Illinois No. 6 coal (2). The availability of information of this kind, especially the hydroxyl group content, led us to consider a new approach for the evaluation of the factors governing the reactions of coal molecules. Specifically, knowledge of the hydroxyl group distribution provided an opportunity to introduce new organic groups into coal at selected, known locations. Once alkylated, the modified coals could be investigated in a variety of ways to gain more information on their structure and reactivity. The presentations of G.R. Dyrkacz (3) and K.W. Zilm (4) illustrate some aspects of this activity. We, in collaboration with R.F. Zabransky of the Institute of Gas Technology, have examined the pyrolytic reactions of the modified coals.

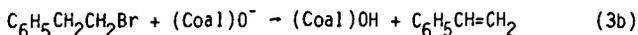
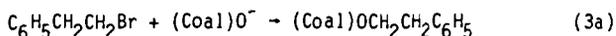
RESULTS AND DISCUSSION

Preparation. At first, we contemplated using reductively alkylated coals in studies of liquefaction and gasification. Work with such kinds of modified coals is attractive because the reductively alkylated materials are significantly soluble in ordinary organic solvents. However, the achievement of solubility is realized at the cost of carbon-carbon bond cleavage reactions, as well as extensive O- and C-alkylation reactions (1). It appeared that the reactivity patterns of these modified coals might not be entirely representative of the original coals. Therefore, we elected to use simple alkylation procedures to modify the coals. The O-alkylation reaction worked out by R. Liotta and his associates (5) proved very suitable for our requirements. Illinois No. 6 coal and other coals can be very selectively alkylated using this reaction scheme, equations (1) and (2).



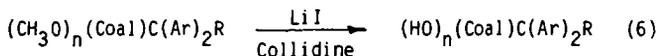
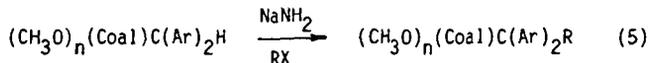
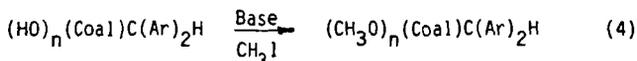
R = Primary alkyl halide or tosylate

In the course of the study, it became clear that tetrabutylammonium ions could be tenaciously retained in the modified coals and could produce unwanted by-products during the pyrolytic reactions. Potassium hydroxide was used to circumvent this problem. Certain primary alkyl halides, for example, the 2-phenylethyl bromides, selectively undergo elimination reactions rather than etherification reactions, equation (3). This difficulty was avoided by the



substitution of alkyl tosylates for alkyl bromides (6).

C-Alkylation was accomplished as outlined in equations (4) to (6).



Using techniques of this kind, we prepared many modified coals including derivatives with simple alkyl and allyl groups, arylmethyl and arylethyl fragments and compounds with aromatic and hydroaromatic structures, for example 9,10-dihydrophenanthrene. In order to trace the chemistry, H-2 and C-13 labels were introduced into the modified coals. Space limitations do not permit a discussion of the methods employed for the preparation and characterization of these compounds, but it should be noted that infrared and magnetic resonance spectroscopy as well as elemental analyses have been used extensively to establish their structures.

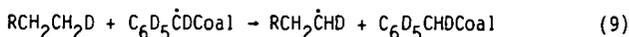
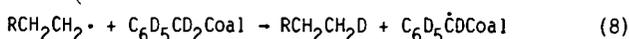
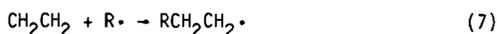
Pyrolysis. The pyrolysis experiments were carried out on a wire screen in a reactor of the type described by Anthony and his coworkers (7). In a typical experiment, 10-15 mg of coal was placed on a preconditioned 325 mesh, 316 stainless steel screen. The reactor was flushed with high-purity helium. Then, the pressure in the reactor was adjusted to 0.12 MPa and the sample was heated at $1000^\circ\text{C s}^{-1}$ to the desired final temperature usually between 600 and 850°C . After the reaction system had cooled, the gaseous products were absorbed on a Tenax column. The reaction vessel was then opened and the char and tar yields were determined gravimetrically.

The Tenax column containing the gaseous products was heated to transfer the absorbed materials to a calibrated vessel. The volatile products were analyzed using a Finnigan Model 4510 GC-MS system. The material balances in

these experiments were very good.

The isotopic composition of the gaseous products was also determined by GC-MS analysis. The procedures for the analyses of the labeled products were developed on the basis of the study of pure labeled compounds.

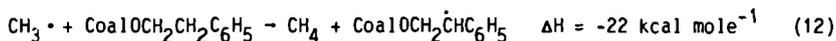
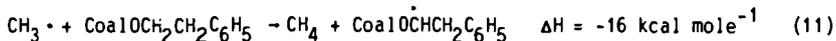
Methylated and Benzylated Coals, A Perspective of Pyrolysis.--The study of the O-methyl and O-benzyl coals established several pertinent points (8-10). First, the modified coals are more reactive than the unmodified starting materials. This enhanced reactivity is particularly evident in the increased yields of carbon monoxide and methane. The enhanced yields of these materials suggests that the increased radical density resulting from the modification of the coal promotes other secondary radical reactions that lead to demethylation or decarbonylation. Hence, the results strongly imply that the extent of small-fragment molecule formation depends in a direct way upon the concentration of radicals within the coal particles. The enhancement of the production of methane may, in part, be attributed to the increased concentration of effective hydrogen donor groups which terminate reactions that would otherwise lead to undesirable char-forming reactions. Second, the exchange patterns strongly suggest that many reactions occur reversibly and that radical addition reactions compete favorably with fragmentation and substitution reactions. Deuterium-labeled ethene, propene and butenes are formed during the rapid pyrolyses of the O- and C-benzyl-d₇ coals. Similar, significant amounts of deuterium are incorporated in the ethene produced from each coal. It seems unlikely that ethene is produced by the dehydrogenation of ethane under the experimental conditions. The most plausible pathways for the formation of ethene-d involve exchange reactions prior to the formation of ethene via pericyclic processes, β-scission reactions, and rapid addition-elimination reactions. These formulations all require that the primary reactive products formed in the original decomposition reactions undergo secondary reactions within the small coal particles, even in this reaction system where the secondary reactions of the initial products are minimized.



Third, the non-random distribution of the isotopic labels in the products, for example, the selective abstraction of hydrogen from the benzylic ether, indicates that the reactions within the coal particle are kinetically controlled even at temperatures near 850°C.

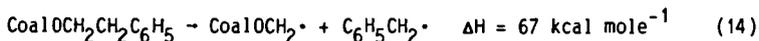
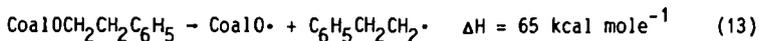
Phenylethylated Coals, The Origins of Ethene.--Next, we turned our attention to the reactivity of O-2-phenylethyl coals. The results can fruitfully be discussed on the basis of the calculated energy requirements (11) for several key reactions. The hydrogen atom abstraction reactions of the 2-phenyl-

ethyl fragment by alkyl radicals, equations (11) and (12), are thermochemically very favorable.



The yields of the simple gaseous paraffins are enhanced and these materials are extensively labeled when 0-2-phenylethyl- d_2 and - d_4 derivatives are used. These observations may be attributed to the occurrence of reactions (11) and (12). Moreover, it is evident that the transient alkyl radicals abstract hydrogen atoms from both the 1 and 2 positions of the 0-(2-phenylethyl) fragment. The methane-d/methane ratios 0.05, 0.09, and 0.17 for the 1,1- d_2 , 2,2- d_2 , and 1,1,2,2- d_4 compounds imply that hydrogen (deuterium) is selectively abstracted from the 2 position of the 2-phenylethyl fragment. This observation is in accord with the differences in bond energies noted in equations (11) and (12).

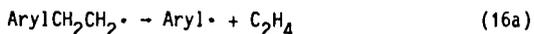
The predominant homolytic fragmentation pathways through which radicals could be formed from the 2-phenylethyl groups are shown in equations (13) and (14).

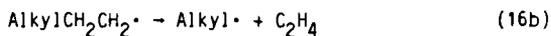


The results for labeled compounds establish that such reactions play a role. Specifically, the formation of significant amounts of toluene- d_2 from the 0-(2-phenylethyl-2,2- d_2) and 0-(2-phenylethyl-1,1,2,2- d_4) derivatives clearly indicates the involvement of benzyl-1,1- d_2 radical in the reaction sequence. In addition, labeled ethylbenzenes are found among the reaction products. Indeed, 2-phenylethane-1,1,2,2- d_4 is the most abundant form of 2-phenylethane. Ethene- d_2 and ethene- d_4 are prominent products of the thermal decomposition of the 0-2-phenylethyl-1,1,2,2- d_4 coal. We postulate that 2-phenylethyl radical undergoes fragmentation to yield ethene and phenyl radical, equation (15).



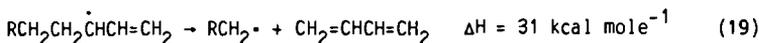
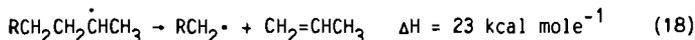
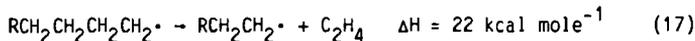
Although endothermic, this reaction apparently occurs readily under the experimental conditions. This observation provides strong support for the view that dealkylation reactions, equations (15) and (16), play a prominent role in ethene formation.



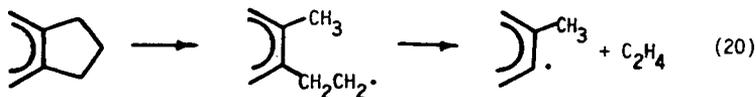


Our results provide strong support for the suggestions of Calkins and his co-workers who pointed out that there was a relationship between the yields of ethene, propene, and butadiene obtained in flash pyrolysis and the quantity of paraffinic hydrocarbons in the coal and proposed that such substances were the precursors of the low molecular weight hydrocarbons (12,13).

It seems reasonable to postulate that ethene, propene, and butadiene are produced from long chain alkyl radicals, equations (17) to (19)



Ethene and propene are also obtained from hydroaromatic constituents, equation (20). The high energy requirements notwithstanding, the available evidence

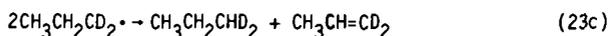
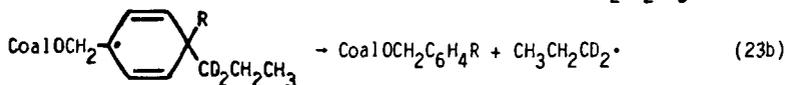
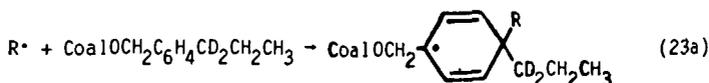
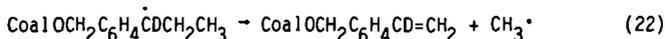
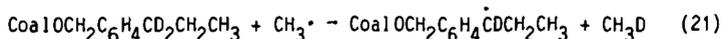


points to the importance of β -scission reactions of 2-arylethyl and 3-aryl-2-propyl radicals and their derivatives for the production of ethene, propene and related substances.

(4-Propylphenyl)methylated Coals. Ipso Replacement.--Ipso substitution reactions also occur. Vernon and his associates showed that such reactions were important for the dealkylation of aryl alkanes under the conditions of coal liquefaction reactions (14). This feature of the chemistry was confirmed by examination of the reactions of labeled and unlabeled 4-propylben-

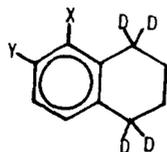


zene derivatives. These compounds provide rather high yields of C₂ and C₃ hydrocarbons. Indeed, the yield of ethane and ethene triples and the yield of propane and propene doubles when these fragments are present in coal. Even more significant, very large quantities of propane-d₂ are formed from the labeled derivative. In brief, the side-chain fragments are good hydrogen donors, equation (21), and undergo demethylation, equation (22). Ipso substitution chemistry accounts for the high yields of propane-d₂ and propene-d₂, equation (23).



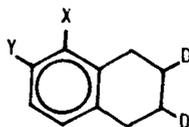
Tetralin Derivatives, Pericyclic Processes.--Our most recent studies have focused on the role of pericyclic processes in the thermal decomposition reactions of coals. Although there is ample evidence that such kinds of reactions occur readily under the conditions employed for the pyrolysis of coal, most workers in the field with the notable exception of Virk and his group (15) have adopted the view that coal decomposition is, with the exception of water-forming reactions, a free radical process (16). Although the early searches for pericyclic reactions during the thermal decomposition of coal have not been successful (17,18), we reconsidered the issue because the energy requirements for many pericyclic reactions are known to be modest.

Illinois No. 6 coal samples modified with labeled tetralin fragments, 5- and 6-(1,2,3,4-tetrahydronaphthyl-1,1,4,4-d₄)methyl bromide and 5- and 6-(1,2,3,4-tetrahydronaphthyl-2,3-d₂)methyl bromide, were pyrolyzed to determine



X = CoalO, Y = H

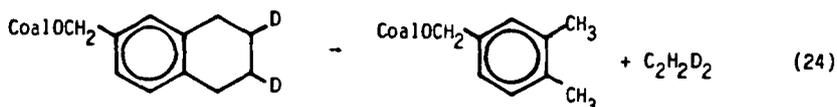
X = H, Y = CoalO



X = CoalO, Y = H

X = H, Y = CoalO

the fate of the grafted fragments and the labels within the fragments. The preliminary results strongly suggest that concerted reaction pathways contribute to the formation of low molecular weight hydrocarbons. More ethene was produced from the modified coal samples than from the reference sample. More importantly, the coal samples modified with 5- and 6-(1,2,3,4-tetrahydronaphthyl-2,3-d₂)methyl bromide produced significantly more ethene-d₂ than the samples with 5- and 6-(1,2,3,4-tetrahydronaphthyl-1,1,4,4-d₄)methyl bromide. These observations imply that molecules such as tetralin decompose via concerted pericyclic pathways within coals, equation (24). Presumably other retro



ene and retro addition reactions also occur during pyrolysis. Thus, theories of coal pyrolysis based exclusively on free radical reactions may be quite misleading.

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