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O-Alkylation Chemistry of Coal and Its Implications for the Chemical and Physical Structure of Coal

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The O-alkylation of coal by the use of a quaternary ammonium hydroxide base and a primary alkyl halide is a general method for the preparation of coal derivatives. These derivatives differ from the starting coal because the weakly acidic protons, primarily those associated with the hydroxyl and carboxylic groups, are replaced by alkyl substituents. The two coals described in this study are Illinois no. 6 coal (Monterey Mine No. 1) and Rawhide coal (Smith Seam in Wyoming). The Illinois no. 6 coal has five and the Rawhide coal has eight weakly acidic protons per 100 carbon atoms, respectively.[1] For each of the two coals, five O-alkylated derivatives were prepared, namely, the methyl, *n*-butyl, benzyl, *n*-heptyl, and *n*-octadecyl coal derivatives. The complete O-alkylation of these coals (the reaction of all the available acidic protons) was achieved under ambient conditions and remarkably short reaction times. Infrared analyses of these O-alkylated coals are consistent with ether and ester derivatives of hydroxyl and carboxylic acid functionalities. High-resolution ^{13}C NMR spectra of the tetrahydrofuran-soluble *O*-methyl coal derivatives are used to estimate the quantity of extracted ethers and esters. The physical properties of these uniquely modified coals were drastically altered. The elemental composition of each coal derivative accurately reflected the weight percents expected based on the complete alkylation of all acidic sites of starting coal. Helium density and mercury porosimetry measurements revealed that the secondary structure (intermolecular associations) of the O-alkylated coals was significantly reduced. There was also a dramatic increase in the extractability of coal molecules after O-methylation.

In a previous study,[1] it was demonstrated that methyl groups can be selectively incorporated into coal by using a quaternary ammonium hydroxide and iodomethane. The phase-transfer reaction proceeds quantitatively under mild conditions and is specific to the acidic proton sites contributed almost exclusively by hydroxyl and carboxylic acid functionalities in coal. Alkylation of these acidic sites generates the corresponding methyl ethers and methyl esters and dramatically changes the properties of coal by significantly reducing the degree of secondary structure, especially hydrogen bonding.

The selective "capping off" of acidic hydroxyls in coal is not new; O-silylation[2] and O-acetylation[3] reactions, for example, are known to produce derivatized oxygen functionalities. These methods are expected to add an equivalent number of substituents to a particular coal since the same acidic protons in the coal are presumably reacting. There are limitations to silylation and acetylation reactions, however, which are not observed in the O-alkylation procedure discussed here. All published conditions for silylation and acetylation reactions require pyridine which acts both as a base and as a good swelling solvent for coal. In the O-alkylation procedure, the aqueous solution of tetrabutylammonium hydroxide used to slurry the coal appears to be superior to pyridine for swelling coal[4] and is a stronger base. Unlike pyridine solvent, the tetralkylammonium salt byproduct is easily removed from the coal material after completion of the reaction. Although the silylation reaction can be modified to produce something other than trimethylsilyl derivatives, the necessary reagents are not readily available, are usually quite expensive, and require special handling. Acetylation of coal does not permanently derivatize the carboxylic acid groups in coal (since anhydrides are easily hydrolyzed) but is specific for conversion of phenols and alcohols to the corresponding esters. Unlike these procedures, O-alkylation quantitatively derivatizes hydroxyl and carboxylic acid groups in a single step under reaction conditions which are so mild that side reactions are avoided.

Alternatively, carbon alkylation procedures have been extensively reported which use olefins and strong acids to modify and solubilize coal. The common feature in these methods, which include the $HF-BF_3$ reaction,[5] Friedel-Crafts alkylation,[6] and to some extent the Heredy–Neuworth treatment,[7] is the use of a Lewis acid. Lewis acids readily cleave aliphatic bridges in the coal structure and initiate a series of isomerization reactions. For example, the Lewis acid can react with aliphatic bridge carbons to produce benzyl-type carbonium ions. These carbonium ions can then undergo aromatic electrophilic substitutions on aryl positions in the coal structure.[8] By such a series of cleavage and condensation reactions, the primary structure or original covalent backbone of coal is drastically altered. Although the yield of solubilized products is quite good, analysis of the Lewis acid reaction products provides little reliable information on the structural precursors of coal.

The O-alkylation procedure described in this study readily proceeds under ambient conditions and does not suffer from the side reaction previously mentioned. The reaction is specific to acidic protons in the coal structure and generates reaction products which are structurally unchanged with the exception of the alkyl terminating groups added to hydroxyl and carboxylic acid functionalities. In fact, only one structural linkage, naturally existing esters which may be present at low levels in low-ranked coal, is labile under O-alkylation conditions. Any esters which are present in the starting coal are readily hydrolyzed in aqueous base to produce both a hydroxyl

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(1) Liotta, R. *Fuel* **1979**, *58*, 724.

(2) Friedman, S.; Kaufman, M. L.; Steinger, W. A. and Wender, I. *Fuel* **1961**, *40*, 33.

(3) (a) Blom, L.; Edelhausen, L.; Van Krevelen, D. W. *Fuel* **1957**, *38*, 537. (b) Abdel-Baset, Z.; Given, P. H.; Yarzab, R. F. *Ibid.* **1978**, *57*, 84.

(4) Liotta, R., unpublished results.

(5) Hodek, W.; Meyer, F.; Kolling, G. *ACS Symp. Ser.* **1977**, No. 55, 411.

(6) Reference 5, page 408.

(7) Heredy, L. A.; Neuworth, M. B. *Fuel* **1962**, *41*, 221.

(8) See ref 5, Chapter 25.

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Table I. Composition (wt %) of Illinois No. 6 and Rawhide Coal and Five O-Alkylated Derivatives

	C[a]	H[a]	N[b]	S_{ORG}[c]	O[d]	mineral[e] matter
		(a) Illinois No. 6				
Illinois no. 6 coal	67.85	4.78	1.23	2.96	9.2	14.0
methylated	69.76	5.41	1.17	2.68	8.4	12.6
butylated	71.25	6.32	1.04	2.27	8.1	11.0
benzylated	74.38	5.33	0.98	2.01	7.3	10.0
heptylated	72.83	7.04	0.95	1.99	7.3	9.9
octadecylated	77.30	8.92	0.65	1.83	5.1	6.2
		(b) Rawhide				
Rawhide coal	66.85	4.79	0.88	0.47	19.5	7.5
methylated	69.49	5.60	0.85	0.38	17.5	6.2
butylated	71.66	6.83	0.73	0.35	14.9	5.5
benzylated	76.70	5.49	0.62	0.31	12.3	4.6
heptylated	74.21	7.73	0.60	0.32	12.2	4.9
octadecylated	78.01	9.96	0.36	0.21	9.1	2.4

[a] Determined on a Perkin-Elmer Model 324 analyser. [b] Determined on a Mettler nitrogen analyser. [c] Difference of the pyritic plus sulfate S from the total S. [d] Difference of the other columns. [e] Calculated according to equation 1.13ASH + 0.47pyrite S.

and carboxylic acid functional group. Subsequent O-methylation converts these groups to the corresponding methyl ether and methyl ester. Fortunately, infrared and NMR analyses of the Illinois no. 6 and Rawhide coals used in this study indicate extremely low concentrations of native ester groups. Thus, the O-alkylated coals are virtually unaltered in their primary structure. Finally, since the organic reagents which are used in the O-alkylation reaction can be removed by mild washing, alkylated coal derivatives can conveniently be prepared which differ in chemical structure from the starting coal only in the absence of acidic protons.

The alkylation procedure has now been extended to alkylating agents other than iodomethane. The reaction appears to be general for primary alkyl halides although longer chain alkylating agents such as *n*-octadecyl bromide and *n*-heptyl bromide react more slowly than iodomethane. For example, under the experimental conditions employed here, the O-alkylation of a slurry of –80-mesh bituminous coal with *n*-heptyl bromide is complete in 18 h. Subbituminous coal alkylates somewhat slower.[9] Although the reaction time varies with the alkylating agent, five and eight alkyl groups are added per 100 coal carbon atoms for Illinois no. 6 high-volatile C (hvc) bituminous coal and Rawhide subbituminous coal, respectively, regardless of the size of the alkyl group. Since these reactions can be conducted on a relatively large laboratory scale (several hundred grams), a variety of analyses were permitted on these materials in order to more fully explore the chemical and physical properties of coal.

Results and Discussion

Methyl, *n*-butyl, benzyl, *n*-heptyl, and *n*-octadecyl, O-alkylated derivatives of Illinois no. 6 and Rawhide coals were prepared by following the procedure outlined in ref 1. The results discussed below, when compared to that of the starting bituminous and subbituminous coals, are consistent with five and eight alkyl groups added to Illinois no. 6 and to Rawhide coal, respectively, per 100 coal carbon atoms.

A. Elemental Analysis. The weight percents of the elements carbon, hydrogen, nitrogen, sulfur, and oxygen were completely consistent with the values expected for addition of five and eight alkyl groups added to Illinois no. 6 and Rawhide coals, respectively, per 100 carbon atoms present in each coal. These analytical data are reported in Table I. The H/C ratio and the weight percent of carbon and hydrogen increase and the percentage of the other elements and the mineral content decrease as the size of the added alkyl group increases. By use of the elemental analysis for the starting coal the theoretical hydrogen to carbon ratio for each alkylated coal can be calculated by assuming that one hydrogen is replaced by one alkyl group. The comparison of the theoretical and actual H/C ratios is presented in Table II. The agreement between the expected and experimentally derived values is very good.

Table II. Comparison of the H/C Ratios of O-Alkylated Illinois and Rawhide Coals, Assuming the Complete Reaction of All the Acidic Functional Groups, with the Experimentally Found H/C Ratios of the Derivatized Products

	hydrogen to carbon ratio			
	Illinois no. 6 coal		Rawhide coal	
	calcd[a]	found	calcd[b]	found
untreated		0.85		0.86
methylated	0.90	0.92	0.94	0.97
butylated	1.04	1.06	1.14	1.14
benzylated	0.85	0.86	0.86	0.86
heptylated	1.15	1.16	1.27	1.25
octadecylated	1.39	1.39	1.53	1.53

[a] Assuming 5.00 alkyl groups added per 100 carbon atoms of starting coal. [b] Assuming 8.00 alkyl groups added per 100 carbon atoms of starting coal.

Elemental analysis of the inorganic portion was performed on both starting coals and each of their five O-alkylated derivatives. This data was determined on an ignited basis for ten specific elements. As noted by the mineral content which was reported in Table I, the inorganic component of the alkylated coal decreased with increasing size of the added alkyl group. However, the composition ratios of the elements in each of the five alkylated derivatives of Illinois no. 6 coal were practically identical. The data presented in Table IIIa show the change in the inorganic composition that takes place during O-alkylation. The corresponding data for Rawhide coal and the O-alkylated Rawhide coals are presented in Table IIIb. The chemical treatment and handling of these coals produced some minor changes in the inorganic composition of the resulting O-alkylated coals. In particular,

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(9) The O-heptylation of Rawhide coal was found to be complete in about 30 h.

Table III. Normalized Mineral Analysis (Percent) of Ten Elements on an Ignited Basis for Illinois Coal or Rawhide and O-Alkylated Coal

(a) Illinois

	Illinois no. 6	alkylated		Illinois no. 6	alkylated
P_2O_5	0.30	0.13	CaO	6.38	0.81
SiO_2	46.02	55.83	MgO	1.03	0.80
Fe_2O_3	20.31	20.41	SO_3	1.17	0.64
Al_2O_3	16.05	17.31	K_2O	1.48	1.20
TiO_2	6.24	0.86	Na_2O	1.18	1.15

(b) Rawhide

	Rawhide	alkylated		Rawhide	alkylated
P_2O_5	0.42	0.49	CaO	23.18	13.98
SiO_2	30.02	41.43	MgO	6.18	5.72
Fe_2O_3	5.40	5.40	SO_3	13.61	13.94
Al_2O_3	15.21	15.54	K_2O	0.13	0.14
TiO_2	5.55	1.13	Na_2O	0.57	0.43

the titanium and calcium concentrations are reduced. It is likely that these minerals are solubilized and washed out of the coal during the treatment and workup.

B. Infrared Analysis (See Supplementary Material for Figures). Although elemental analysis agrees with the number of alkyl groups added in every case, it gives no indication as to the chemical alteration which must have occured in order to achieve these results. One method of analysis which does supply such information is infrared (IR) spectroscopy. In Figure 1a, the IR spectra of Illinois no. 6 coal and the five O-alkylated derivatives are presented. There is a strong and broad absorption feature in the 3300–3600-cm^{-1} region in the spectrum of the unalkylated Illinois no. 6 coal. This band is attributed to the acidic hydroxyl groups present in the coal. In each spectrum of the five treated coals this hydroxyl band is missing, indicating that the O–H bonds have been chemically altered during the course of the alkylation. The aliphatic region of the IR spectra of the five alkylated coals has much more intense C–H bands than the starting coal, especially for the O-heptylated and O-octadecylated Illinois no. 6 coals. This observation is consistent with the tremendous increase in percent carbon and hydrogen which was found from elemental analysis. There is also a small peak in the 1730-cm^{-1} region of the alkylated bituminous coals which does not appear in the unalkylated bituminous coal. This band may be due to the esterification of the small numbers of carboxylic acids which are present in the C-ranked bituminous coal. On the other hand, this band may have resulted from the O-methylation of native ester groups which underwent hydrolysis, although the concentration of native esters is probably low. In Figure 1B the IR spectra of Rawhide subbituminous coal and the spectra of five of its O-alkyalted derivatives are presented. As previously described for Illinois no. 6 coal, the broad hydroxyl band (3300–3600 cm^{-1}) is not present in the O-alkylated Rawhide coals, and there is an increase in the intensity of the aliphatic C–H bands (2800–3000 cm^{-1}). One major difference in the IR spectra of the O-alkylated derivatives of the subbituminous coal as compared to the O-alkylated derivatives of the bituminous coal is the carbonyl peak centered at 1730 cm^{-1}. In each of the IR spectra of the five treated subbituminous coals there is an intense carbonyl peak which is far more pronounced than in the corresponding spectra of the bituminous coals. The chemical implication of this confirms what is well-known[18] about these different rank coals: subbituminous coal has a much greater carboxylic acid content than a bituminous coal. Under the alkylation conditions these acids have been converted into carboxylic esters. The carbonyl stretching frequency of the carboxylic acids that is present in the subbituminous coal is obscured by the large peak centered at 1600 cm^{-1}. This peak is assigned to the aromatic carbon–carbon linkage and is sufficiently broad so that it extends into the carboxylic carbonyl region (1665–1700 cm^{-1}). Since carboxylic esters have a higher carbonyl stretching frequency than the corresponding acid (1720–1740 cm^{-1}), the carbonyl band is resolved from the aromatic band after the coal is O-alkylated.

C. Carbon-13 NMR Analysis (See Supplementary Material for Figures). High-resolution carbon-13 NMR spectroscopy is also sensitive to the products of O-alkylation; for these experiments, the O-methyl derivatives of Illinois no. 6 and Rawhide coals are particularly advantageous. The methyl ethers and esters generated by phase-transfer alkylation of the hydroxyl and carboxylic acid functionalities resonate between 49 and 65 ppm with respect to tetramethylsilane, a region of the ^{13}C chemical shift range which is normally unobstructed by other coal extract resonances. Since naturally occurring methyl ethers and esters are below detectability in the solution NMR spectra of underivatized Illinois no. 6 and Rawhide coal extracts, methyl resonances in this shift region which appear after alkylation can unambiguously be attributed to reaction products. No additional carbon resonances are contributed by alkylation to the aromatic and aliphatic chemical shift regions so that aromaticity determinations can be made on extracts from derivatized coals.

Ether and ester methyl groups are insulated by an oxygen atom and a carboxyl group, respectively, from the sources of chemical shift dispersion which so seriously limit resolution in coal-extract NMR spectra.[10,11] As a result, the added methyl groups cover a comparatively small range of chemical shift values and are resolved according to methyl ether (54–61 ppm) and methyl ester (49–52) derivatives. Thus, NMR investigation of methylated coal extracts permits a measurement of hydroxyl and carboxylic acid functional groups which are present but unresolved in the carbon-13 spectra of underivatized samples.

Carbon-13 NMR spectra are presented in Figures 2A and 3A for the tetrahydrofuran extracts of O-methylated Illinois no. 6 and Rawhide coals, respectively.[12] Aromaticities determined from these spectra are 0.65 for Illinois no. 6 extract and 0.55 for Rawhide extract. Only the more rotationally mobile components of the coal extracts provide narrow and resolved resonances such as the long paraffinic segments at 29.8 ppm. Additional peaks are observed between 49 and 65 ppm which may be assigned to the methyl derivatives of hydroxyl and carboxylic acid functionalities. Only methyl esters are clearly observed in the extracted sample from Illinois no. 6 coal while a detectable quantity of methyl esters (49–52 ppm) are apparent in the Rawhide coal extract spectrum. This observation is consistent with expectations on these representative bituminous and subbituminous coals and with the infrared results presented in section B. The number of added methyl groups per 100 coal extract carbons is

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(10) Retcofsky, H. L.; Schweighardt, F. K.; Hough, M. *Anal. Chem.* 1977, *49*, 585.

(11) Maekawa, Y.; Yoshida, T.; Yoshida, Y. *Fuel* 1979, *58*, 864.

(12) Carbon-13 NMR spectra were accumulated on a HEOL FX-90Q spectrometer under gated proton decoupling for NOE suppression. Acquisition conditions were chosen which consistently provide quantitative results, including a delay between pulses at 2.5× and a 0.8-data acquisition period in the gated decoupling sequence. Tetramethylsilane and 0.035 M chromium(III) acetylacetonate were also added to 2 mL of chloroform-*d* solutions of the coal extracts. Overnight accumulations were generally used to obtain good signal to noise ratios.

Table IV. Percent Volatile Matter, DMMF,[a] from Pyrolysis at 900 °C

	Illinois no. 6	Rawhide
untreated	37	44
methylated	40	48
butylated	56	59
benzylated	49	55
heptylated	60	66
octadecylated	69	75

[a] DMMF = dry mineral matter free.

estimated to be 7.7 and 12.5 groups for Illinois no. 6 and Rawhide extracts, respectively.

Moderate carbon-13 enrichment of the alkylating agent used in the phase-transfer alkylation procedure significantly improves the NMR sensitivity to added groups and unambigously demonstrates which resonances have been incorporated by reaction.[13] Illinois no. 6 and Rawhide coals were methylated by using methyl iodide which was 9.5% and 5.6% enriched in carbon-13, respectively, as described in ref 13. The reacted coals were subsequently extracted with tetrahydrofuran and examined by ^{13}C NMR spectroscopy. The results obtained on these selectively enriched extracts are presented in Figures 2B and 3B; the vertical scales are approximately identical between unenriched and enriched extract preparations. NMR sensitivity to the methyl ether and ester resonances is now significantly enhanced. Although methyl ethers predominate in the bituminous coal extract, a small but measurable quantity of methyl esters is also observed, a result which is consistent with the infrared analysis of the methylated whole coal. Methyl esters of carboxylic acids contribute only 10% of added methyl groups in this sample; esters are more prevalent in the Rawhide extract comprising nearly 30% of added methyl groups.

The methyl ethers in the selectively enriched extract spectra are base-line resolved into resonances at 54–56 ppm and 57–61 ppm. The 54–56-ppm resonances are consistent with a variety of methyl ethers of aryl and cycloalkyl molecules including phenol, naphthol, and cyclohexanol. The downfield resonances are less easily classified but are consistent with the methyl ethers of some acyclic alcohols, benzyl alcohols, and furfuryl alcohols.

Only the NMR results for methyl derivatives are presented here, although extracts from several of the other alkyl derivatives were also examined by solution ^{13}C NMR. In all extract samples that were studied, resonances assignable to OCH_2R functionalities were observed. Determination of the sample aromaticities was more difficult in these cases due to those resonances in the aromatic and aliphatic chemical shift regions contributed by incorporated groups.

D. Proximate Analysis. The mineral content of Illinois no. 6 and Rawhide coals and their O-alkylated derivatives is presented in Table I. With the exception of the benzylated coal derivatives, the percent volatile matter on a dry mineral matter free (DMMF) basis increases with increasing size of the added alkyl group. These data are summarized in Table IV. Each butylated coal has a significantly higher volatile component than the corresponding benzylated derivative, an observation which perhaps can be attributed to the relatively higher hydrogen content of the butyl group. Nevertheless, as expected, the four normal alkyl substituents impart a monotonic increase in the volatile matter with increasing chain length.

Table V. Weight Percent of Coal Extracted on a Dry Mineral Matter Free (DMMF) Basis by Exhaustive Soxhlet Extraction Using THF, Benzene, and Chloroform Solvents

	weight percent extracted (DMMF)		
coal	THF	benzene	chloroform
Illinois no. 6	14.4	0.7	3.2
O-methylated Illinois no. 6	22.1	14.7	21.7
Rawhide	6.5	2.2	2.4
O-methylated Rawhide	16.1	12.2	18.1

E. Soxhlet Extractability. The reduction of the secondary structure of coal by O-methylation results in higher coal extractability. The hydroxyl and carboxyl functional groups which are present in untreated coals are responsible for much of the secondary structure because these groups are probably engaged in hydrogen bonding with neighboring molecules. Such attractive forces between coal molecules are likely to reduce coal extractability due to an effective increase in apparent molecular weight. Replacement of such hydrogen-bonding protons by alkyl substituents is expected to improve coal extractability in nonpolar solvents because of decreases in molecule polarity leading to decreases in the coal's secondary structure.

Large alkyl substituents make a significant weight contribution to an O-alkylated coal product. As a result, this contribution must be considered when determining the effective change in solvent extractability between starting and O-alkylated coals. For methyl substituents, however, the weight contribution to the starting coal material is small, only about 6.8 and 4.2 wt % added methyl groups for Rawhide and Illinois no. 6 coals, respectively. Because of this small weight factor for added methyl substituents, we can neglect this weight contribution to the percent of coal extracted.

Exhaustive Soxhlet extractions were performed on the two untreated coals and their O-methylated derivatives with three different solvents. The weight percent extracted on a dry mineral matter free (DMMF) basis for these systems is presented in Table V. According to these data, benzene is a relatively poor solvent for the two untreated coals. However, there is a dramatic increase in the benzene extractability of each coal after O-methylation. This is to be expected since benzene, a nonpolar solvent, should better solubilize the relatively less polar molecules of the O-methylated coal derivatives than the more polar native coal molecules themselves. A similar explanation can be used to describe the extractability differences between untreated and O-methylated Illinois no. 6 and Rawhide coals with the other two solvents, THF and chloroform. Since these latter two solvents are somewhat more polar than benzene and have better solubility parameters, higher extractabilities were achieved.

F. Density Measurements. Attempts to measure the true specific gravity of O-alkylated coals by standard water-air displacement techniques proved difficult. Since these coal derivatives are highly aliphatic, they do not wet readily, casting some doubt as to whether the density values determined by water-air displacement are truly representative of these samples. it was highly advantageous, therefore, to employ a Model 1302 helium–air pyrnometer (Micrometrics Instruments Co.) to obtain the true specific gravity for each coal alkylate by helium-air displacement. These values are presented in Table VI. As expected, the longer the added alkyl chain the lower the

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[13] Rose, K. D.; Melchior, M. T.; Elliott, J. J., submitted for publication in *Anal. Chem.*

Table VI. Density[a] of Illinois and Rawhide Coals and Their O-Alkylated Derivatives (Mineral-Containing Basis)

	Illinois no. 6	Rawhide
untreated	1.53	1.47
methylated	1.43	1.36
butylated	1.32	1.27
benzylated	1.33	1.30
heptylated	1.24	1.18
octadecylated	1.14	1.14

[a] In grams per cubic centimeter.

density in the resultant coal product. The trend in the density measurement of the O-alkylated coals may be viewed, at least in part, as a diluent effect of the added substituent.

These results were used to calculate the total porosity in the next section.

G. Porosity Measurements. A Quantachrome continuous-scanning mercury porosimeter was used to obtain the apparent densities and pore-volume distributions.[14] The samples of dried but otherwise untreated Illinois no. 6 and Rawhide coals as well as their O-alkylated derivatives were placed in a tared penetrometer of known volume. The penetrometer and sample were weighed and then placed in a filling chamber. The unit was then evacuated to less than 100 μm and outgassed for 15 min. The filling chamber was tilted so that the bottom of the penetrometer was immersed in mercury. The chamber was gradually filled with air, causing the mercury to fill the evacuated space. The filled penetrometer was then reweighed. The pore-volume distributions were determined by placing this filled penetrometer in the scanning porosimeter and pressurizing the unit while measuring the volume as a function of pressure. The sample volume was calculated by using eq 1, where V_s = the sample volume (cm^3), V_f =

$$V_s = V_f = \frac{(W_p + W_s + W_{Hg} + W_g) - (W_p + W_s + W_g)}{P_{Hg}} - V_{psi} \quad (1)$$

the free space volume of penetrometer (cm^3), W_p = the weight of the penetrometer (g), W_s = the weight of the sample (g), W_{Hg} = the weight of the mercury (g), W_g = the weight of the grease (g), V_{psi} = the volume of intruded mercury at a specific pressure (cm^3 for a given sample weight), and P_{Hg} = the density of the mercury (g/cm^3). The density was calculated by dividing the weight of the sample by its volume, V_s. Pore-volume distributions and porosities were determined by established procedures[15] with the assumption of a 140° wetting angle between mercury and the coal surface. The IUPAC convention[16] was employed to determine the pore-volume distribution as a function of pressure. At 3.5 MPa the mercury fills all pores having a radii greater than 2200 Å. By increasing the pressure to 15 MPa the mercury now is assumed to occupy all pores greater than 500 Å in radii. The mercury penetration into the pores in the range 18–500 Å occurs when the pressure is increased to 400 MPa. Total (transitional porosities plus microporosities) and microporosities are calculated for each sample by computing the differences between the reciprocal helium density and the reciprocal mercury densities measured at 3.5, 15, and 400 MPa, respectively. The percent porosity in pores with radii less than 2200, 500, and 18 Å has been calculated in accordance with this convention. The results of the porosity determinations for Illinois no. 6 and Rawhide coals and their O-alkylated derivatives are presented in Table VII.

Table VII. Percent Porosity of Illinois No. 6 and Rawhide Coals and Their O-Alkylated Derivatives Measured in Pores Less Than 2200, 500, and 18 Å[a]

	% porosity in pores less than		
	2200 Å	500 Å	18 Å
(a) Illinois No. 6			
untreated	23.1	20.8	9.8
methylated	25.3	22.6	21.0
butylated	24.2	23.2	12.0
benzylated	14.9	11.0	3.8
heptylated	20.3	17.3	0
octadecylated	12.3	9.3	0
(b) Rawhide			
untreated	13.3	12.0	3.9
methylated	15.6	12.7	7.8
butylated	16.5	14.7	7.5
benzylated	14.8	11.5	1.8
heptylated	16.3	9.6	0
octadecylated	11.2	11.3	0

[a] Results are on a mineral-containing basis.

Results and Interpretation of the Porosity Measurements. According to Gan, Nandi, and Walker,[15] coals vary widely in their total porosity. For the lower rank coals, porosity is primarily due to the presence of macropores. The contribution of the microporosity to the total porosity becomes more significant as the rank of the coal increases. Although the increase in microporosity as a function of increasing rank has been known for some time, an explanation of trend has been lacking. The examination of the pore-distribution data for Illinois no. 6 and Rawhide coals as well as their O-methylated derivatives has given us new insight into this observed phenomenon.

The total porosity (less than 2200 Å radus) is 23.1% for Illinois no. 6 coal and 13.3% for Rawhide coal. The higher ranked bituminous coal has a substantially greater total porosity than the subbituminous ranked coal. The microporosity (less than 18-Å radus) of the Illinois no. 6 coal is 9.8%, or about 42% of the total porosity. Rawhide coal's microporosity is only 3.9% or about 29% of the total porosity of this coal. This is entirely consistent with the results from previous workers;[15] lower rank coals have lower microporosity and higher rank coals have higher microporosity.

Microporosity is an important parameter since it is governed to some extent by the short-range intermolecular forces which contribute to the secondary structure of coal. Hydrogen bonding, for example, holds two or more polar functional groups in close proximity; of course, the molecules to which these groups are attached must also be in close proximity to one another.

Rawhide coal has about twice the oxygen content as the Illinois no. 6 coal. Furthermore, Rawhide coal has about 40% more acidic hydroxyl groups (eight vs. five per 100 carbons) as compared to the higher ranked Illinois no. 6 coal. Subbituminous Rawhide coal also has an appreciable concentration of carboxylic acid functionality which is not present in the Illinois no. 6 coal. Thus, it is likely that Rawhide coal has a more formidable secondary which holds the molecular network in a tight array. It seems reasonable, therefore, that the microporosity of Rawhide coal should be lower than that of Illinois no. 6 coal, and this was found to be the case.

It was instructive to see what effect O-alkylation had on the pore structure of these two coals. The two O-

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(14) Service performed by Quantachrome.

(15) Gan, H.; Nandi, S. P.; Walker, P. L. *Fuel* **1972**, *51*, 272.

(16) Juntgen, H. *Carbon* **1978**, *15*, 273.

methylated coals are highly representative, at least in terms of weight percent, of the starting coal. That is to say, well over 90 wt % of each O-methylated coal is attributed to the original coal. Therefore, the diluent effect of the added methyl groups is not appreciable.

The total porosity for each of the two O-methylated coals was greater than that of the corresponding untreated coals. This difference was more pronounced for Rawhide coal and its O-methylated derivative than for Illinois no. 6 coal and its O-methylated derivative. The important difference, as noted in the pore distribution, reveals that after O-methylation there is a tremendous increase in the microporosity. In fact, the microporosity of the O-methylated Rawhide coal is 50% of the total porosity; the microporosity of the untreated Rawhide coal is about a factor of 2 less than this. A similar situation holds for the Illinois no. 6 coal. However, the microporosity of O-methylated Illinois no. 6 coal is, remarkably, 83% of the total porosity, compared to 42% for the corresponding untreated coal.

The dramatic increase in the microporosity of the O-methylated coals relative to the two underivatized coals indicates that there is a more open arrangement in the area of short-range molecular interaction due to a decrease in attractive forces. Of course, in a chemical sense the transformation of the polar hydroxyl and carboxyl groups into methyl ethers and methyl esters would lead to an overall decrease in the secondary structure of the coal.

Higher rank coals lack the very polar carboxylic acid functionalities and also have a low concentration of total polar functional groups relative to subbituminous rank coals. Is is apparently the relative concentration of the polar functional groups in coals which governs the extent of microposity. Since coal rank is also governed by the relative concentration of the polar functional groups (hydroxyl and carboxyl), it seems reasonable that microporosity should increase with increasing rank.

Any discussion of the porosity measurements which were performed on the other O-alkylated coals would have to take into account the diluent effect of the added alkyl substituent. In the extreme case, for example, O-octadecylated Rawhide coal, the coal represents only 40 wt % of the derivative. Qualitatively, however, we can see that these two coals which were O-alkylated with the larger alkyl groups still have substantial porosity in the macro and transitional pore-volume range. Although the microporosity seems to disappear in the coal derivatives which contain the largest alkyl groups, the reason for this not entirely clear. Perhaps the large paraffin groups are somehow blocking off the micropore openings and preventing the penetration of helium. This would result in the low helium density that was found and in turn would account for the loss in microporosity. Alternatively, the high mercury pressures (~400 MPa) which are experimentally required to determine the sample porosity may have been great enough to actually cause these highly paraffinic coals to flow. This would naturally result in zero microporosity since the samples were no longer true solids. If either or both of these proposed alternatives are valid, the O-alkylated coals listed in Table VII as having no microporosity may indeed have microporosity which the experimental probe failed to reveal.

Conclusion

A facile procedure for the O-alkylation of coal has been developed. The reaction is conducted successfully under amazingly mild conditions. The alkylation appears to be versatile as illustrated by the fact that the alkylating agent can be varied considerably. The physical properties of these chemically modified coals reveal the importance of the secondary structure of coal. The fact that the O-alkylation process works so well for such a variety of alkyl halides is evidence that coal is more reactive and susceptible to ambient solution chemistry than is generally accepted.

Experimental Section

Preparation of Representative Coal Samples. The two coals used in this study were identically prepared before chemical treatment.

A fresh consignment of coal, sized to pass a $^3/_4$ in. mesh screen, was secured from each mine. One was from the Monterey Mine No. I in Illinois, the so-called Illinois no. 6 hvcb coal. The other barrel was from the Smith Seam in Wyoming. This latter coal was mined from the Rawhide Mine and is very similar to other Wyodak subbituminous coal of the region. Each coal consignment was stored under water until just before being ground. The coals were first surface dried under a stream of nitrogen. Then, while still blanketed with a nitrogen atmosphere, each coal was entirely reduced to pass an 80-mesh screen. The ground coals were transferred to large plastic bags and shaken to ensure homogeneity. At this point sample bottles were filled and sealed with weighed amounts of each coal from the plastic bags. All of this was conducted under inert atmosphere in a glovebox. These samples were used in all of the studies described in this report.

General Procedure for Coal O-Alkylation. I. Illinois No. 6 Coal. Method A. Illinois no. 6 coal (25.00 g, −80 U.S. mesh, or 87.5 mmol of active sites as determined by titration)[17] was placed in a 500-mL, round-bottomed flask under a nitrogen atmosphere. Tetra-*n*-propylammonium hydroxide solution [25 wt % in water and weighing 74.71 g (91.9 mmol), or a slight excess over the available acidic protons] was charged into the flask. Tetrahydrofuran (150 mL) which was freshly distilled from lithium aluminium hydride was also added. Finally, 1-bromobutane (24.54 g, 179.13 mol) was combined with the other reagents with vigorous mixing. The mixing was maintained for 72 h to ensure complete O-alkylation. O-Alkylation of coal using tetrapropylammonium hydroxide was found to be somewhat slower than that using tetrabutylammonium hydroxide. But this propyl derivative is still very useful as a base in these reactions since the byproduct, tetrapropylammonium bromide, is much more water soluble than the corresponding tetrabutylammonium bromide. Thus, it is easier to wash out this reagent from the O-alkylated coal during the workup step.

The workup step was as follows. The pH of the reaction mixture was tested and found to be slightly basic. Just enough 1 M HCl solution was slowly added to lower the pH to 7. The mixture was distilled under vacuum to remove the THF and the excess alkylating agent. Hot water (250 cm^3) was added to the flask and mixed to aid in the dissolution of the quaternary ammonium salts. The contents of the flask were filtered through a steam-jacketed filter flask equipped with a porous (74 μm) Teflon membrane. The product was washed with more hot water (4–6 L) and then dried under a stream of nitrogen until enough water was removed to transfer the material to a Soxhlet thimble (60 × 150 mm). The Soxhlet extraction apparatus was set up and maintained under a static atmosphere of nitrogen, and the flask was charged with water. A rapid turnover of water through the thimble chamber was reached at about 12 extractions/h. The siphon liquid was periodically tested with silver nitrate to check for the presence of halide ion. After 5 days the alkylated coal was completely free of byproduct. At this point the solid contents of the thimble were washed onto a filter and dried under a stream of nitrogen. Then the surface-dried material was placed in a

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(17) A known amount of excess tetra-*n*-butylammonium hydroxide base is mixed with the coal, and then a standard HCl solution is used to back-titrate. A pH meter was employed to follow the neutralization to the end point.

(18) Van Krevelen, D. W. "Coal"; Elsevier: New York, 1961; Chapter IX.

vacuum oven at 100–110 °C overnight.

Method B. The same O-alkylation procedure may be employed with a 25% solution of tetrabutylammonium hydroxide. Two modifications are required in the previous experiment if this base is used. First, the reaction time is less than 1 day, and second, during the workup sodium nitrate (3-fold excess) is added just after neutralization to produce an anion-exchange reaction with the tetrabutylammonium salt. Since the quaternary ammonium nitrate is more water soluble than the corresponding halide derivative, the sodium nitrate addition lessens the time required to wash out the tetrabutylammonium byproduct. The sodium salts were readily removed by the hot water extractions. The Soxhlet extraction time is about the same with this modified procedure as before.

Method C. Octadecylation Reaction. The octadecylation of a coal requires a special workup as well as twice the reaction time as the general procedure already described. For removal of excess octadecyl bromide, methanol was used instead of water throughout the entire procedure. Methanol is an excellent solvent for tetrabutylammonium halides. Fortunately, O-octadecylated coal is virtually insoluble in methanol. Thus, all the reagents can be easily removed from the alkylated coal product.

II. Rawhide Coal. The same general procedure used for Illinois no. 6 coal works equally well for Rawhide with some modifications.

Method A. Rawhide coal (50.00 g of −80 U.S. mesh, or 250 mmol of active sites) was placed in a 2-L, round-bottomed flask under a nitrogen atmosphere. Tetra-*n*-butylammonium hydroxide (1.00 M in water, 260 mL, 260.0 mmol, or a slight excess over the available acidic protons) was charged into the flask. Tetrahydrofuran (500 mL) which was freshly distilled from lithium aluminium hydride was also added. Finally, iodomethane (198.26 g, 1396.79 mmol) was added with vigorous mixing to the reaction vessel. The reaction was complete in a few hours, but it was allowed to stir overnight. The workup is the same as that used for the Illinois no. 6 coal.

Note: In O-alkylation of coals only a slight excess of base is used. The use of a 2-fold excess does not have any appreciable effect on the rate of alkylation. It serves only to complicate the workup because it becomes necessary to wash out the additional quaternary salts from the product. There is also a competing side reaction in the presence of excess base, a slow hydrolysis of the alkylating reagent to produce an alcohol which in a subsequent step undergoes O-alkylation to produce an ether. Obviously, this ether would have to be removed from the coal product. This would be most troublesome for the larger alkylating reagents since the ether produced from a C_1 to C_4 alkylating agent is easily distilled out of the product during normal workup conditions. Fortunately, this hydrolysis alkylation is relatively very slow and was not a problem in the course of this study except for the O-benzylation reaction since benzyl bromide hydrolyzes more readily than normal alkyl halides. Therefore, in this case the benzyl bromide was added dropwise to the stirred reaction mixture, and only a slight excess of alkylating agent was used in order to minimize the competing side reaction. Methanol was used during the workup instead of water.

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Supplementary Material Available: Infrared spectra of Illinois No. 6 coal, Rawhide coal, and alkylated derivatives thereof; ^{13}C NMR spectra of methoxyl derivatives of the above two coals (8 pages). Ordering information is given on any current masthead page.

Effects of Structure on the Ease of Electron Removal from *o*-Phenylenediamines. 2. Photoelectron Spectra of *o*-Phenylenediamines

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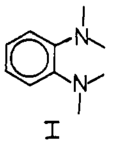
Photoelectron spectra are reported for *o*-phenylenediamine and 14 acyclic and N,N′-monocyclic alkylated derivatives, as well as for 2,3-benzo-1,4-diazabicyclo[2.2.2]oct-2-ene (**14**) and its 3′,6′- and 4′,5′-dimethyl derivatives and 9,10-benzo-1,5-diazabicyclo[3.3.2]dec-9-ene (**15**). Photoelectron spectroscopy does not appear to be useful for the determination of conformations in these compounds because of the strong interaction between the effects of bending and twisting at nitrogen on ionization potentials. Comparison of photoelectron and cyclic voltammetry data leads to estimates of 5.3 and 14.1 kcal/mol, respectively, for the destabilization of *N,N,N′,N′*-tetramethyl-*o*-phenylenediazine radical cation and $15^{+\cdot}$ relative to an unstrained, planar tetraalkyl-*o*-phenylenediamine radical cation.

We previously reported a cyclic voltammetry (CV) study of several *o*-phenylenediamine derivatives (I) in butyronitrile solution.[1] In most cases formal potentials for reversible electron transfer (here called $E^{\circ\prime}$) were measured for removal of both the first and second electron from I. Values of $E^{\circ\prime}$ (I, $I^{+\cdot}$) were observed to vary over a range of 1.1 V, corresponding to a ΔG° range of 25 kcal/mol. We report here photoelectron spectroscopy (PES) measurements on the same compounds. PES measurements provide vertical, vapor phase, I,$I^{+\cdot}$ energy differences, which make an interesting comparison with the adiabatic, solution values provided by the CV work. PES measurements have proven useful in determining the amount of rotation about the NN bond of hydrazines,[2,3] and we wished to



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[1] Nelsen, S. F.; Clennan, E. L.; Echegoyan, L.; Grezzo, L. A. *J. Org. Chem.* **1978**, *43*, 2621.

[2] (a) Rademacher, P. *Angew. Chem.* **1973**, *85*, 410. (b) Rademacher, P. *Tetrahedron Lett.* **1974**, 83. (c) Rademacher, P. *Chem. Ber.* **1975**, *108*, 1548. (d) Rademacher, P.; Koopman, H. *Ibid.* **1975**, 1088, 1557.

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