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Coal. Kinetics of O-Alkylation

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Abstract: The kinetic reactivities of the acidic hydroxyl groups in coal were measured. The chemical action of quaternary ammonium hydroxide bases in the presence of alkylating agents was used as the probe. Both Illinois No. 6 bituminous and Rawhide subbituminous coals contain aromatic and aliphatic hydroxyls as well as lesser amounts of carboxylic acids. Illinois coal was found to O-alkylate at a faster rate than Rawhide coal. The reactivities of the acidic functional groups in the coals were correlated to the reactivity of acidic groups in model compounds. This was accomplished by both relative and absolute kinetic rate measurements on each coal and a series of model systems. It was discovered that the activation energy associated with the nucleophilic displacement determined the rate of O-alkylation of the coal. Therefore, the rate of this reaction is not limited by mass transport of the chemical reagents into the coal structure. In this sense, O-alkylation of coal is a most unique reaction.

Introduction

The applications of tetraalkylammonium hydroxide bases to etherification and esterification reactions have been well studied.[1-4] The first report[5] of a quaternary ammonium hydroxide base reacting with coal demonstrated that even an insoluble material like coal (which contains many acidic hydroxyl groups) is quite reactive. This reaction was shown to be a general coal O-alkylation procedure. In the second report,[7] the nature of the alkylating agent was varied considerably, and, for example, it was demonstrated that coal could be n-octadecylated to the same extent as it could be methylated. The amazing feature of this reaction was its fast rate. The rate of the chemical reactions of coal invariably suffer from mass transport limitations, due to the insolubility of coal.[6] The quaternary ammonium base transports hydroxide ion from the solution to the solid coal (presumably diffusion controlled.[7] The carboxylic acids and the phenols which are both native to the coal are converted to the corresponding quaternary ammonium carboxylates and phenates, respectively. The reaction of these coal anions with the alkylating agent proceeds with a rate that is not mass transport controlled.

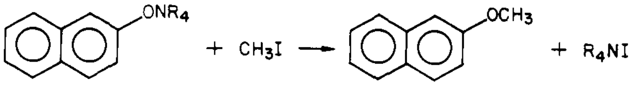
The ^{13}C NMR spectra (see Figures 1 and 2) of the O-methylated coals, using ^{13}C-enriched CH_3I, confirmed that almost all the added methyl groups were bound to oxygen. Methylation of nitrogen, sulfur and carbon centers constituted only a few percent of the added methyl groups.

In the first section of this study the intrinsic reactivities of "model compounds" were explored and their absolute and relative reactivities determined. This information was then used to interpret the behavior and explain that the rate of O-alkylation of coal was not hampered by mass transport limitations. Previous work[5] showed esters and ethers were formed, and, therefore, phenols and carboxylic acids were chosen to be model compounds.

Table I. Comparison of the Second-Order Rate Constants (25 °C) for the O-Methylation with Iodomethane and the O-Heptylation with 1-Iodoheptane of the Tetra-*n*-butylammonium Salts of 2-Naphthol and 2-Naphthoic Acid

	O-methylation, $M^{-1}\,s^{-1}$	O-heptylation, $M^{-1}\,s^{-1}$
2-naphthol	9.4×10^{-3}	1.9×10^{-4}
2-naphthoic acid	4.3×10^{-4}	8.8×10^{-6}

Table II. Comparison of the Second-Order Rate Constants (25 °C) for the O-Methylation of 2-Naphthol with Various Quaternary Alkylammonium Hydroxides



R group	second-order rate constant, $M^{-1}\,s^{-1}$	R group	second-order rate constant, $M^{-1}\,s^{-1}$
n-C_6H_{13}	5.0×10^{-2}	C_2H_5	3.1×10^{-4}
n-C_4H_9	9.4×10^{-3}	H	0

Results

I. Model Compound Alkylations. A. Phenols and Carboxylic Acids (Second-Order Rate Constants).

Quaternary ammonium hydroxide bases react with phenols and carboxylic acids to produce the ammonium salts of these weak organic acids and 1 equiv of water (eq 1a,b). Both the quaternary ammonium phenate and

$$ArOH + R_4N^+OH^- \rightarrow R_4N^+OAr^- + H_2O \quad (1a)$$

$$R'CO_2H + R_4N^+OH^- \rightarrow R_4N^+O_2CR'^- + H_2O \quad (1b)$$

carboxylate undergo O-alkylation when treated with an alkylating agent $R''X$ (eq 2a,b). The reaction of a phenol or carboxylic

$$R_4N^+OAr^- + R''X \rightarrow R_4N^+X^- + ArOR'' \quad (2a)$$

$$R_4N^+O_2CR'^- + R''X \rightarrow R_4N^+X^- + R'CO_2R'' \quad (2b)$$

acid with a quaternary ammonium hydroxide is complete essentially upon mixing, whereas O-methylation of a phenate, for example, takes on the order of 20 min (see O-methylation of 2-naphthol in Experimental Section).

In the first set of experiments, the second-order rate constants (25 °C) for the O-methylation and O-heptylation of 2-naphthol and 2-naphthoic acid were compared (Table I). The values which are presented represent the rate constants for the reaction of the tetra-*n*-butylammonium salt of 2-naphthol and the corresponding salt of 2-naphthoic acid with the iodoalkanes. In each case, methylation was some 50 times faster than heptylation. The steric requirements of 1-iodoheptane relative to iodomethane were apparently great enough to cause this rate difference. The quaternary ammonium salt of 2-naphthol was only slightly more reactive (about a factor of 3) to O-alkylation than the corresponding 2-naphthoic acid derivative.

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(1) Dehmlow, E. V.; Dehmlow, S. S. "Phase Transfer Catalysis"; Verlag Chemie: Weinheim, 1980; p 86.

(2) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis, Principles and Techniques"; Academic Press: New York, 1978, pp 29, 128.

(3) Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: Berlin, 1977; pp 73, 85.

(4) Keller, W. E., Ed. "Compendium of Phase Transfer Reactions and Related Synthetic Methods"; Fluka AG, CH-9470 Buchs: Switzerland, 1979; p 70.

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

(6) van Krevelen, D. W. "Coal"; Elsevier: Amsterdam, 1961; Chapter IX.

(7) Liotta, R.; Rose, K.; Hippo, E. *J. Org. Chem.* **1981**, *46*, 277.

(8) Recent work performed in conjunction with J. W. Larsen, University of Tennessee, revelaed that tetraalkylammonium hydroxides reacted with –80 mesh coal in water solvent in minutes.

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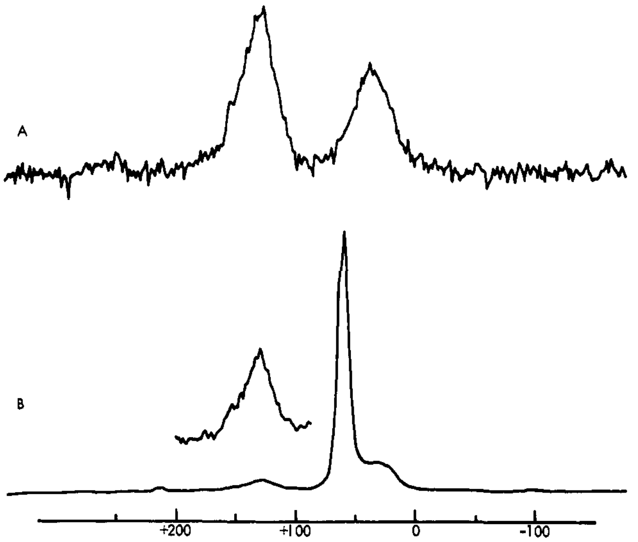

Figure 1. (A) The ^{13}C NMR spectrum of Illinois no. 6 coal. (B) The ^{13}C NMR spectrum of carbon-enriched O-methylated Illinois no. 6 coal.

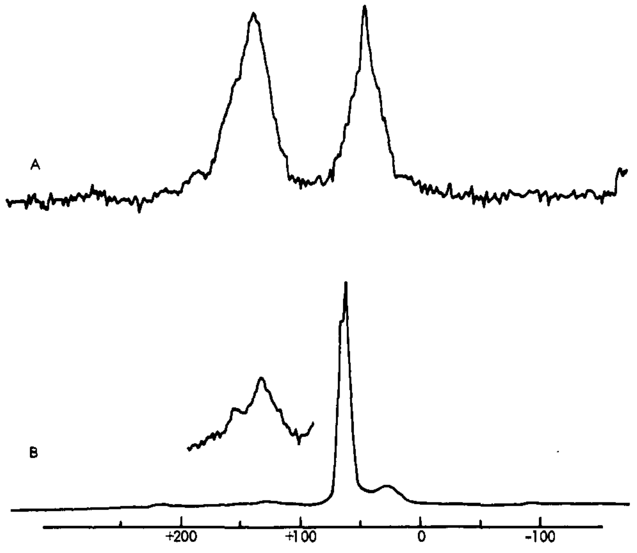

Figure 2. (A) The ^{13}C NMR spectrum of Rawhide coal. (B) The ^{13}C NMR spectrum of carbon-enriched O-methylated Rawhide coal.

The data shown in Table I involved the use of the same quaternary ammonium hydroxide base. However, the nature of the base had a profound influence on the rate of O-alkylation. Rate measurements (25 °C) for the O-methylation of 2-naphthol were performed in a manner identical with the previous experiments, except four different bases were employed. The comparisons of the second-order rate constants are presented in Table II. The tetra-*n*-hexylammonium salt of 2-naphthol was O-methylated about 5 times faster than the tetra-*n*-butylammonium salt of 2-naphthol. The tetraethylammonium salt was more recalcitrant than the corresponding butyl derivative by a factor of 30. Finally, ammonium-2-naphthoxide failed to methylate. Only a very slow hydrolysis of iodomethane to methanol was noted.

The decrease in reactivity from a large cation like $(n\text{-}C_6H_{13})_4N^+$ to a relatively small one like H_4N^+ can be explained by an increased cation–anion electrostatic binding energy (E_{+-}).[9] According to Coulomb's law, this energy is inversely proportional to the square of the distances between the ionic centers. Therefore, the free energy of activation for a displacement by the 2-naphthoxide was lower in the case of a larger ammonium cation. In a qualitative sense, this explains the decreasing trend found for the O-methylation of the four 2-naphthoxide quaternary ammonium salts, and that the simple ammonium derivative was so stable that it failed to undergo nucleophilic displacement at all.

Table III. Reactivities Relative to Phenol of Tetra-*n*-butylammonium Salts of Representative Weak Acids toward O-Methylation

cyclohexanol	8/92	*p*-cresol	56/44
2-naphthol	49/51	4-methoxyphenol	58/42
2-isopropylphenol	57/43	4-fluorophenol	44/56
2-*tert*-butyl-6-methylphenol	70/30	4-nitrophenol	5/95
2,6-di-*tert*-butylphenol	38/62		

B. Phenols: Steric and Electronic Effects (Relative Rates). A series of competitive reactions with pairs of substituted phenols was conducted. Steric crowding about the O–H group and electronic considerations played roles in governing the relative reactivity.

Five millimoles of each phenol was mixed together with 10 mmol of tetra-*n*-butylammonium hydroxide base to produce the corresponding ammonium salt of both phenols. Five millimoles of iodomethane was then added to this mixture. The extent to which each phenoxide reacted was determined by GC using the internal standard technique. These data are presented in Table III.

Phenol and 2-naphthol reacted at about the same rate. Surprisingly, the salts of the more sterically encumbered phenols, like 2-isopropylphenol and 2,6-xylenol, were somewhat more reactive than the corresponding phenol salt. Furthermore, a highly hindered phenoxide (2-*tert*-butyl-6-methylphenoxide) was even more highly reactive compared to sterically unhindered phenoxide. The enhanced reactivity of these ortho-substituted phenoxides is attributed to the increased cation–anion separation. This is the same explanation which was used to account for the trend in reactivities shown in Table II. In that case, the greater cationic radius produced a weaker electrostatic binding energy and resulted in enhanced reactivity toward nucleophilic displacement. Similarly, the ortho-substitution of phenoxides also weakened the cation–anion binding energy. This too, resulted in enhanced reactivity. There is a point of diminishing returns. Too much steric crowding, as in the example of 2.6-di-*tert*-butylphenoxide, resulted in a decrease in the rate of O-alkylation relative to phenoxide. Yet, this difference in reactivity was still small. The phenoxide reacted 62% of the time compared to 38% for the 2,6-di-*tert*-butylphenoxide.

In addition to the steric considerations, electronic factors play a role in reactivity. It is not easy to assess the individual contributions of electronic and steric factors in those cases. Electronic factors were treated separately by studying the reactivity of para-substituted phenols. For example, the *p*-methylphenoxide was slightly more reactive than phenoxide. The quaternary ammonium salts of *p*-cresol and 4-methoxyphenol were only slightly more reactive than phenoxide. On the other hand, 4-fluorophenoxide was slightly less reactive than phenoxide. A strongly electron-withdrawing group such as nitro has a profound effect on the relative reactivity. 4-Nitrophenoxide was not prone to undergo O-alkylation. Thus, the electronic nature of a para substituent on a phenoxide governs the rate of the S_N2 reaction in a predictable fashion.

C. O-Alkylation of Cyclohexanol. The tetra-*n*-butylammonium salt of phenol is O-alkylated at a faster rate than the corresponding salt of cyclohexanol. A relative rate measurement was performed on an equimolar amount of the two materials with only 1 equiv of iodomethane in aqueous THF solvent (Table III). In this experiment, phenol and cyclohexanol were allowed to mix with the base for 30 min before the addition of iodomethane. Phenol was converted to anisole 92% of the time, and only 8% of the alcohol was converted to cyclohexyl methyl ether.

The reaction of tetra-*n*-butylammonium hydroxide with cyclohexanol has a small K_{eq}. In contrast, the reaction of this same base with phenol has a large K_{eq}. This, of course, follows from the fact that the K_a of phenol is some 8 orders of magnitude lower than that of cyclohexanol. If there was even a modest equilibrium

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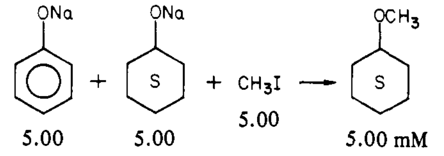
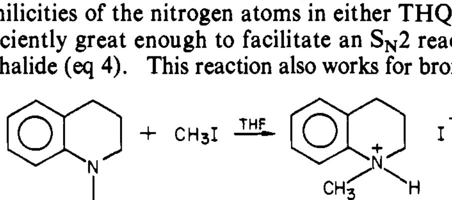
[9] For a more thorough treatment see ref 2, p 31.

concentration of the cyclohexanolate in the relative rate study, then the major product of the reaction would not have been anisole but instead cyclohexyl methyl ether. The intrinsic reactivity of the alcoholate is very much greater than that of the phenoxide. To demonstrate this, we performed another relative rate study. This time there was no unfavorable equilibrium which favored one reactant over the other. Equimolar amounts of phenol and cyclohexanol were dissolved in *p*-dioxane. Enough sodium metal was added to quantitatively produce the soidum salts of each compound. The excess sodium was removed. To this mixture was added iodomethane (eq 3). The sodium salt of cyclohexanol was quantitatively converted to cyclohexyl methyl ether, and after the reaction product mixture was acidified, there was a quantitative recovery of phenol. Thus, the intrinsically high relative reactivity of the alocholate over the phenate was demonstrated.



(3)

D. Alkylation of Tetrahydroquinoline and Tetrahydroisoquinoline. 1,2,3,4-Tetrahydroquinoline (THQ) and 1,2,3,4-tetrahydroisoquinoline (THIQ) can undergo alkylation without a base being present. During O-alkylation of phenols, the first step is a rapid proton abstraction to produce a phenate. This is followed by a nucleophilic displacement which is the rate-determining step. The mechanism of N-alkylation of an unactivated secondary amine (one which does not have a strong electron-withdrawing group(s) directly bonded to it) also involves two steps. The first step is the nucleophilic displacement which is rate determining. The second step is a fast proton abstraction. The nucleophilicities of the nitrogen atoms in either THQ or THIQ are sufficiently great enough to facilitate an S_N2 reaction with an alkyl halide (eq 4). This reaction also works for bromoethane, 1-bromobutane, and 1-bromoheptane, and it appears to be a general procedure. The proton associated with the *N*-alylated ammonium halide is extremely acidic, and in the presence of base it was rapidly removed[10] (eq 5). The final product is 1-methyl-1,2,3,4-tetrahydroquinoline.



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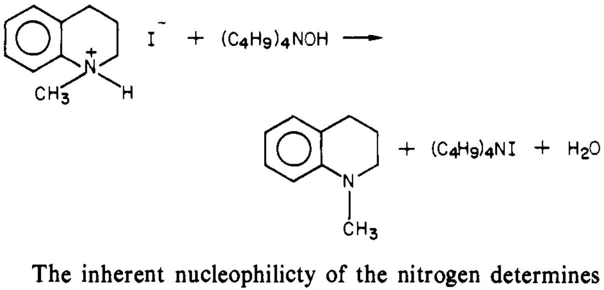
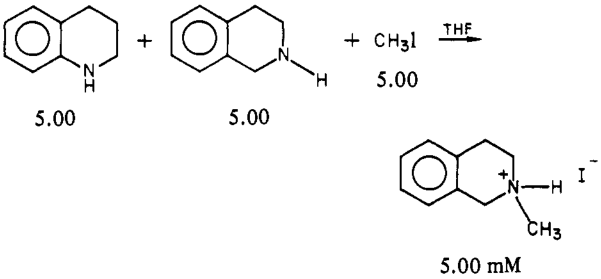


(5)

The inherent nucleophilicty of the nitrogen determines the relative reactivity of one secondary amine over another. This was demonstrated by the next experiment (eq 6). An equimolar mixture of THQ and THIQ was treated with only half an equivalent amount of iodomethane in THF. The THIQ reacted quantitatively while the concentration of THQ remained unchanged. The electron density about the nitrogen center of THQ was effectively delocalized into the aromatic ring reducing its nucleophilicity.

Aromatic amines such as pyridine rapidly react with iodomethane in THF solvent to produce *N*-methylpyridinium iodide (eq 7). This product is not thermally stable, and upon being heated, it will decompose and reform pyridine and iodomethane.



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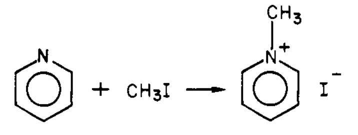

(7)

The N-alkylation reaction was important in the study of coal, especially the illinois no. 6 coal which has a 1.23 wt % nitrogen content. This will be discussed in section II.A.

II. Alkylation of Coal. A. Demonstration of Coal Chemistry. Under the reaction and workup coditions employed, the alkylation of both Illinois no. 6 and Rawhide coals was essentially an O-alkylation. This was demonstrated by using carbon-labeled iodomethane (99% ^{13}C enriched) as alkylating agent and then performing a solid-state ^{13}C NMR experiment. Figure 1A is the carbon spectrum of Illinois no. 6 coal before treatment. Two envelopes of peaks or bands are evident. The band on the right from 0 to 50 ppm is due to aliphatic carbon signals and the band on the left, from about 100 to 160 ppm, represents the aromatic carbon types.[11] Fortuitously, the chemical shift region from 50 to 100 ppm is unobscured by native coal signals. This is the region where the chemical shift of a methyl carbon bound to oxygen appears.[12] In Figure 1B, the ^{13}C NMR spectrum of O-methylated Illinois no. 6 coal is presented. The natural abundance of ^{13}C is only 1.08%, and the labeled carbon is 99% enriched. Although there are far more original coal carbons than added methyl carbons, because of the high enrichment of iodomethane, the added methyl group is about the only distinguishable feature. The insert above the aromatic region in Figure 1B is that region of the spectrum with a vertical scale 9 times greater than that of the full spectrum just below it, and it shows that aromatic carbons have been unaffected by the O-methylation reaction. It was important to note that the chemical shift of the added methyl was between 50 and 60 ppm, thus confirming O-alkylation had occurred. Parts A and B of Figure 2 are the spectra for Rawhide and methylated Rawhide coal, respectively. The interpretation of these spectra led to the same conclusion as before: almost exclusive O-methylation of the Rawhide coal occurred.

Parts A and B of Figure 3 are the ^{13}C NMR spectra of O-methylated Rawhide and Illinois no. 6 coals, respectively. These two spectra were run with resolution enhancement which resolved the major peak in each spectrum into separate peaks. It is now possible to see more clearly that in the case of the Rawhide coal that three distinct O-methyl derivatives are present. The smallest peak (49–52 ppm) represents methyl esters and the other two peaks represent various methyl ethers. In Figure 3B, the methyl ester signal is not significant enough to be resolved, and it appears as a shoulder on the major peak. A methyl group bonded to carbon, sulfur, or nitrogen would not have a chemical shift in the 50–60-ppm region of the ^{13}C NMR spectrum. Instead, methyl substituents bound to one of these three other elements have chemical shifts arising in the 14–48-ppm region. There is a

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[10] Only activated N-H groups deprotonate with quaternary ammonium hydroxide bases. See: Palecek, J.; Kutham, J. *Synthesis* **1976**, 550. Also Brehme, R. *Ibid.* **1976**, 113.

[11] Two reference ^{13}C NMR books appeared recently: Breitmaier, E.; Voelter, W. "^{13}C NMR Spectroscopy"; Verlag Chemie: Winheim, 1978. Shamma, M.; Hindenlang, D. M. "Carbon-13 NMR Shift assignments of Amines and Alkaloids"; Plenum Press: New York, 1979.

[12] Actually methyl esters arise in the 49–52-ppm region; sterically unhindered methyl aryl ethers, 54–56 ppm, sterically crowded methyl aryl ethers, 58–60 ppm, and methyl alkyl ethers, 54–60 ppm, range all relative to Me_4Si.

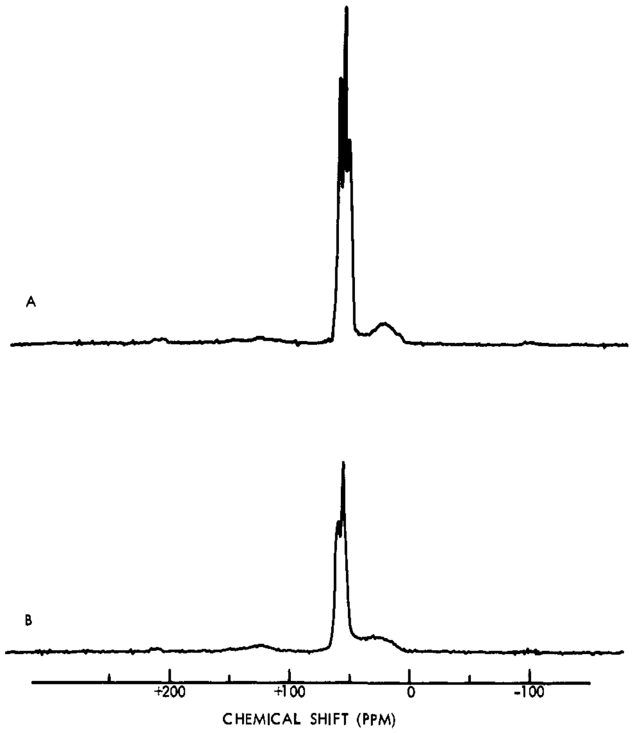

Figure 3. (A) The ^{13}C NMR spectrum of O-methylated Rawhide coal. (B) The ^{13}C NMR spectrum of O-methylated Illinois no. 6 coal. Both spectra were run with resolution enhancement.

perceptible increase in the aliphatic carbon signal in both O-methylated coal derivatives. But it is not very much compared to the enormous signal in the 50–60 ppm region. Closer examination of the aliphatic region in both coal derivatives revealed that the chemical shift of the added ^{13}C-enriched methyl appears in the 14–48-ppm region. Thus, there was some alkylation of mercaptans, acidic carbon centers, and nitrogen functional groups. The only form of sulfur which alkylates under the conditions employed here is S–H (mercaptan). Acidic carbon centers such as those found in indene and fluorene are all C-alkylatable under these conditions. The NMR evidence indicates that very few of these functional groups were methylated, so it is likely that there are very low levels of these functionalities actually present in the coals[13] studied.

The N-alkylation of coal is a different matter. As shown earlier, the N–H functional group is permanently derivatized upon treatment with iodomethane and base, because the trialkylamine product is stable to the workup conditions. The N–^{13}CH$_3$ moiety has a carbon chemical shift which occurs just upfield from the O–^{13}CH$_3$ moiety. The ^{13}C NMR spectra of both methylated coals (Figures 1B and 2B) do show a very slight increase in intensity in the *N*-methyl region, but it is not appreciable. The aromatic nitrogen in these coals likely reacted with the iodomethane. However, the product of such a reaction is thermally labile, as illustrated by *N*-methylpyridinium iodide which did not survive the workup procedure that was used in this study.

B. Intrinsic Coal Reactivity. It was instructive to run rate studies on the coals with various model compounds. For both coals, methyl ethers and esters are produced. This suggested the use of phenols, alcohols, and carboxylic acids as model compounds. The full extent of each coal's reactivity was determined by following the incorporation of alkyl groups as a function of time and comparing these results with those of the model systems.

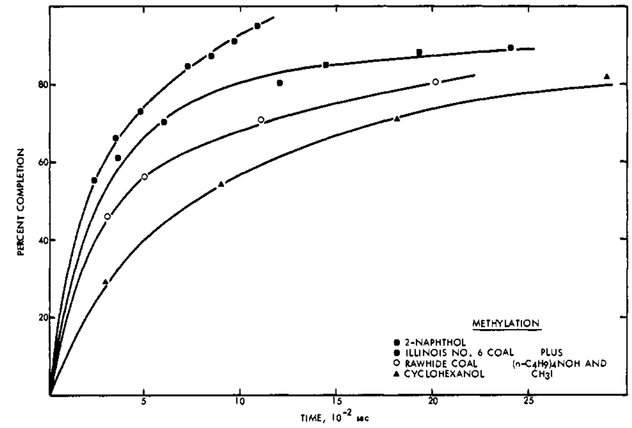

Figure 4. The comparison of the rate of O-methylation of two model compounds and two coals.

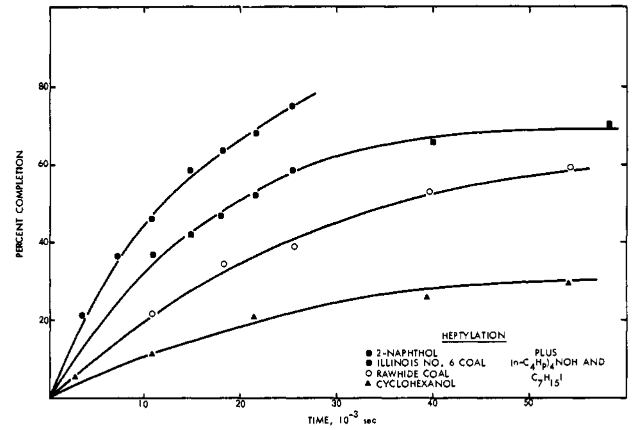

Figure 5. The comparison of the rate of O-heptylation of two model compounds and two coals.

The solvent employed in the O-alkylation of coal was aqueous THF (20 wt % water). This reaction medium provided a homogeneous solution for all reactants except for the coal. Thus, one might expect that there would be a mass transport limitation of the O-alkylation of coal which would not exist for this same reaction on the model compounds.

Four individual O-alkylation reactions were carried out under identical conditions. Two reactions were O-methylations of 2-naphthol and cyclohexanol in aqueous THF with 1 equiv of tetra-*n*-butylammonium hydroxide base and 2 equiv of iodomethane as the alkylating agent. The other two reactions were performed in the same manner on the two coals. In each case, the base and the material to be alkylated were mixed in THF for 30 min before the addition of the iodomethane. In the two experiments with coal, a labeled alkylating agent was used (iodomethane-d_3). The four reactions were performed on a large scale, and a small aliquot was removed periodically, quenched with acid and analyzed by gas chromatography. For the model compound reactions, internal standards were employed to quantify the amount of unreacted model compound and alkylating agent as well as the O-alkylated product. In these cases, the number of millimoles of product corresponded precisely to the number of millimoles of consumed reactants. However, in the case of the coal reactions, only the consumed alkylating agent was followed chromatographically relative to the internal standard. The percent completions of the four reactions were monitored with respect to time. The graph showing these results is presented in Figure 4. The 2-naphthol was O-methylated more quickly than cyclohexanol. Most surprisingly, the rates of O-methylation of the two coals were intermediate between the two model compounds. That is, the two coals actually alkylated slightly faster than cyclohexanol but also somewhat slower than 2-naphthol. The only possible explanation for this was that the mass transport of reagents in solution penetrating into the solid coal was not the rate-limiting step. The rate-determining step was the S_N2 reaction itself.

One reason why iodomethane seemed to have so little difficulty in penetrating the coal structure was perhaps its small size. An identical set of alkylations were run by using 1-iodoheptane. The

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(13) C-alkylation is a much slower chemical process than O-alkylation so there is a likelihood that more C-alkylatable sites existed but were not alkylated. This area of research is under investigation.

Table IV. The Relative Reactivity of Representative Weak Acids toward O-Methylation

2-naphthol (56) vs. Illinois no. 6 coal (44)
cyclohexanol (37) vs. Illinois no. 6 coal (63)
2-naphthoic acid (30) vs. Rawhide coal (70)
cyclohexanol (45) vs. Rawhide coal (55)

results of these reactions are presented in Figure 5. The order of reactivity for the heptylations was exactly the same as it was for the methylations, but the rate of heptylation for each case was about 50 times slower than the rate of methylation. This was expected since nucleophilic displacement on a bulkier molecular is a kinetically slower process. So, just as before, this alkylation step on base-treated coal was not hampered by mass transport limitations.

C. Relative Rate Measurements. (1) Model Compound vs. Coal. A series of competitive rate measurements were made under the same conditions as before to further explore this alkylation reaction. In the first set of experiments, 10 mmol of a model compound was mixed with the corresponding amount of coal (as before, a certain weight of a particular coal is known to contain 10 mmol of alkylatable sites). To this mixture was added 20 mmol of tetra-*n*-butylammonium hydroxide, and after 30 min of stirring, 10 mmol of iodomethane-d_3 was also added. The workup of the reaction product was facilitated by the removal of the organic reagents out of the coal by a Soxhlet extraction with methanol. Both Illinois no. 6 and Rawhide coals, as well as their O-alkylated derivatives, are almost totally insoluble in methanol. This effected a clean separation of the chemical reagents from the coal. Internal standards were added to the methanol. This fraction was analyzed by GC, and the number of millimoles of starting model compound and alkylated model compound were determined. The coal product was thoroughly dried, and the elemental analysis revealed the number of labeled methyl groups present. Thus, the relative reactivity of the model compound and the coal was established. These reuslts are shown in Table IV. 2-Naphthol was slightly more reactive than the Illinois coal (56/44). This is in agreement with the individual rate measurements presented in Figure 4. The rest of the data in Table IV are also consistent with absolute rate experiments. Both the Illinois no. 6 and Rawhide coals were more reactive than cyclohexanol. Since the Illinois coal's reactivity relative to cyclohexanol was 63/37 and the corresponding ratio for Rawhide and cyclohexanol was 55/45, Illinois no. 6 coal must be more reactive than Rawhide, as was shown earlier (Figures 4 and 5).

Although the model compounds were in true solution and the coal was merely a suspended solid, the alkylatable sites on the coal reacted without the limitation of mass transport.

(2) Effect of Alkylating Agent. The nature of the alkylating agent, of course, affects the rate of the reaction. One convenient way to explore this was to perform a number of competitive rate reactions employing equimolar amounts of two different alkylating agents and only 1 equiv of a material to be alkylated. The two coals (Illinois bituminous and Rawhide subbituminous) and two model compounds (2-naphthol and 2-naphthoic acid) were tested in exactly the same fashion as in part II.B. A one-to-one molar equivalent of tetra-*n*-butylammonium hydroxide and material to be alkylated were mixed in the aqueous THF for 30 min before additin of the pair of alkylating agents. This pair was added simultaneously and the reaction proceeded to completion. Internal standards were present in each model compound study. The quantification of the unreacted alkylating agents and the two O-alkylated products was achieved by use of gas chromatography. For the reactions involving the two coals, the chemical reagents were selectively removed from the coal with methanol (by Soxhlet extraction). Internal standards were added to this methanol solution and the amount of each unreacted alkylating agent was found. The coal was then thoroughly dried and its elemental composition determined. The change in the composition of the alkylated coal from the starting coal was completely consistent with the amounts of each alkylating agent consumed by the coal as determined by GC analysis. Furthermore, the weight of the alkylated coal product was as expected for the specific number of each alkyl group added. Thus, even for the competitive reactions of coal, a mass balance was achieved.

Table V. The Relative Reactivity of Equimolar Pairs of Alkylating Agents

	1-bromo-heptane/ 1-bromo-octadecane	1-iodo-butane/ isobutyl iodide	1-iodo-propane/ 2-iodo-propane	1-iodo-heptane/ 1-bromo-heptane
2-naphthol	62/38	70/30	65/35	56/44
2-naphthoic acid	60/40	70/30	68/32	50/50
Illinois no. 6 coal	60/40	71/29	60/40	54/46
Rawhide coal	57/43	68/32	69/31	53/47

Table VI. Relative Reactivity of Equimolar Pairs of Weak Acids with Four Different Bases and Iodomethane

	$(CH_3)_4$-NOH	$(C_2H_5)_4$-NOH	$(C_4H_9)_4$-NOH	$(C_6H_{13})_4$-NOH
phenol vs. *p*-cresol	45/55	45/55	44/56	45/55
phenol vs. benzoic acid	76/24	77/23	78/22	75/25
2-naphthol vs. Illinois no. 6 coal	56/44	57/43	56/44	55/45
2-naphthoic vs. Rawhide coal acid	30/70	30/70	30/70	29/71

These results are presented in Table V. The first striking feature of this data is that the relative reactivity of each alkyl halide pair was the same regardless of which material was alkylated. The first column of the table shows that n-heptylation was more favorable than n-octadecylation by about 60/40. This example is especially important for two reasons. First of all, there was a tremendous weight difference between the two alkyl bromides. As such, each would impart a drastically different composition to the treated coals. Unlike the other examples presented in Table V, which had pairs of alkyl halides with identical H/C ratios, the analysis of the coals which were competitively alkylated with heptyl and octadecyl bromides produced a coal derivative whose composition revealed not only the total number of groups added but the proportion of each. Second, this reaction demonstrates that octadecylation of coal proceeds without mass transport problems. Apparently, there was little difficulty for such a large molecule to penetrate the coal structure. Therefore, the rate of diffusion was faster than the rate of nucleophilic displacement.

The data in the second and third columns revealed that branching in the position α to the halogenated carbon slowed the rate of halide displacement more than a secondary leaving group did. 1-Iodobutane was more reactive than isobutyl iodide by about 70/30, whereas 1-iodopropane reacted faster than 2-iodopropane by a somewhat lower ratio.

The relative reactivities in the fourth column showed that iodides and bromides were similar in their ease of displacement. In a separate set of experiments, 1-chloroheptane was found to react very much slower than 1-bromoheptane. Thus, the order of reactivity of the halides in these S_N2 reactions was $I \approx Br \gg Cl$.

(3) Effect of Base. Earlier, it was discussed that the structure of quaternary ammonium cations played a role in governing the rate of reaction. For example, the rate of O-alkylation of phenoxide depends on the ionic radius of the cation: $(n\text{-}C_6H_{13})_4N^+ > (n\text{-}C_4H_9)_4N^+ > (C_2H_5)_4N^+ > (CH_3)_4N^+$.

In this series, tetramethylammonium phenoxide was the least reactive. This trend in reactivity was found to be the same regardless of the nature of the phenoxide. In fact, the trend held for all types of acidic hydroxyls and it did not matter if the substrate was in solution or merely a suspended solid as in the case of coal.

A set of competitive O-methylations was run by employing the four quaternary ammonium cations and equimolar pairs of weak acids. The results are shown in Table VI. These experiments demonstrated that the relative reactivity of the various alkylatable species are base independent.

In the field of phase-transfer catalysis, tetramethylammonium cations are not used because of their low solubility in organic media, but this is not a problem in aqueous THF. As a result, even the lowest molecular weight quaternary ammonium hydroxide effectively neutralizes solid coal in this medium. However, the rate of O-alkylation of the corresponding tetramethylammonium coal anions is slower than for the larger members of the series.

III. Phase-Transfer Catalysis. A. Absolute Second-Order Rate Constant. O-alkylation using only a small amount of quaternary ammonium cation was a slower process than the analogous one employing a stoichiometric equivalent of base. THF is not very miscible with 50% aqueous NaOH solution. The sodium hydroxide forms a concentrated, viscous aqueous layer which is much more dense than the aqueous THF. A 1.00 M aqueous solution of the bases used in this study (R_4NOH) produced a single phase when combined with THF; therefore, the O-alkylation utilizing the PTC method was much slower than the corresponding noncatalyzed method. The precise improvement in the rate was measured by determining the rate constant for the methylation of 2-naphthol with a catalytic amount of tetra-*n*-butylammonium iodide (2.5 mol % based on 2-naphthol) in THF with a tenfold excess of 50% aqueous sodium hydroxide. The second-order rate constant (25 °C) was 2.1×10^{-4} M^{-1} s^{-1}. This was about 45 times lower than the rate constant for the corresponding methylation which utilized a full equivalent of quaternary ammonium hydroxide instead of generating only a small amount in situ (see Table I). The only fundamental difference between these two reactions was their rates. The reaction run in the catalysis mode took nearly 9 h to go to completion, whereas the O-methylation of tetra-*n*-butylammonium 2-naphthoxide was complete in under 20 min.

B. Relative Rates. Illinois no. 6 coal and 2-naphthol (7.00 mmol of acidic protons in each) were combined with tetra-*n*-butylammonium iodide (0.35 mmol) in THF. Sodium hydroxide (50 wt % in water) was also present, and the mixture was vigorously stirred for 30 min before the addition of CD_3I (7.00 mmol). This reaction is analogous to the one presented in Table IV except now it is a phase-transfer-catalyzed (PTC) O-methylation. Previously, the 2-naphthol reacted 55% of the time and the Illinois no. 6 coal only 45%. The result of the PTC reaction was exactly the same. In fact, all of the reactions presented here could have been conducted in the catalysis mode of operation. The only drawback would have been the slower rate.

This relative rate study was repeated keeping all the parameters the same except tetra-*n*-butylphosphonium iodide was employed instead of the ammonium analogue. This substitution had no effect on the outcome.

Discussion

The first O-alkylation of coal was reported in 1947 by Yohe and Blodgett.[14] Dimethyl sulfate was the alkylating agent, and the authors conceded that this was likely a methylation of surface hydroxyl groups. Later diazomethane was used to O-methylate coal,[6] but this met with only moderate success. Acetylation with acetic anhydride, which is a somewhat related reaction, has been used consistently over the years to esterify coal.[6] The one feature that all these reactions have in common is that the rate of reagent transport into the solid coal governs the rate of reaction. It actually requires days for some of these reactions to go to completion compared to a reaction time of minutes or a few hours for the corresponding reaction of model compounds which are in solution.

Until now it was generally believed that an insoluble material like coal was doomed to slow reactivity. In order to cause a more rapid reaction, we had to employ severe conditions. This made selective transformation of a multifunctional substance impossible and has led to tremendous confusion in the interpretation of experimental observations. Often authors either were not aware of or underestimated the extent of side reactions. As a result, there is very little understanding of the true inherent reactivity of coal. Furthermore, there is a comparable level of ignorance regarding coal structure. Actually, the structure and reactivity of coal are two sides of the same coin. Using selective chemical reactions to derivatize coal probes its structure and reactivity simultaneously. The O-alkylation procedure is one chemical reaction which is well suited for this purpose.

This work raises two questions. (1) Why does the neutralization of coal by quaternary ammonium hydroxide bases occur so rapidly? (2) Why is there no mass transport hindering the rate of coal's O-alkylation?

In solution studies, neutralization reactions are invariably the kinetically fastest types of reaction. The rates of these reactions are diffusion controlled in solution. Alkali-metal hydroxides are not soluble in organic media, but, quaternary ammonium hydroxides are soluble in organic media. A solvent like THF penetrates coal and permeates its structure, taking with it the dissolved base. Perhaps the attractive interaction between tetraalkylammonium cations and aromatic molecules is a more important factor. Most of the carbons in both Illinois no. 6 and Rawhide coals (or any other coal for that matter) are aromatic. Hardy et al.[15] reported that there is a 1:1 crystalline adduct between aromatic compounds and tetraalkylammonium cations. This interaction is not as stable as the bond between a tetraalkylammonium cation and a phenol or carboxylic acid. The aromatic cation interaction may result first, and then the more stable phenates and carboxylates are produced. This may play a key role in explaining the speed with which these ammonium cations penetrate the coal.

Once the base reacts with an acidic hydroxyl a molecule of water is produced. This is the thermodynamic driving force of the reaction. The O-alkylation of coal is a reaction where the rate is a function of the intrinsic activation energy of each reactive site. Large alkylating agents such as 1-bromooctadecane or alkylating agents with secondary leaving groups such as isopropyl iodide are able to penetrate the coal structure with a diffusivity which is faster than the subsequent S_N2 reaction which produces the ether or ester.

Several speculative mechanisms can be postulated to explain this observation. Perhaps, the various alkylating agents are able to diffuse so rapidly through the coal structure because they do not have far to travel. That is, the active sites may be at or near the surface of the coal as opposed to being buried some distance below the surface. The action of the quaternary ammonium base is likely to cause a reorganization of the molecular network. The organic base reacts first with surface sites, producing a phenate or carboxylate. This exposes additional surface from beneath and further neutralization occurs. This process is diffusion controlled in accordance with Ficks' Law, but it is the fastest reaction of its kind ever reported for coal.[16] In this process the physical orientation of the coal molecules is drastically altered, and the secondary structure (intermolecular association) is also changed. Intermolecular distances have to be adjusted to accommodate the quaternary ammonium cations. Coal anions would tend to repel one another, further increasing the intermolecular distances. These coal anions are highly reactive, since large quaternary ammonium cations are only weakly coordinated to them. Therefore, the coal anions are likely solvated, which disperses the coal into fine particles.

So with this rationalization it might be said that coal anions actually diffuse up to the surface to react with the alkylating agent. Thus, regardless of the size of the alkylating agent, no mass transport limitation is observed during this coal reaction.

Conclusion

New insight has been gained concerning coal structure and its impact on chemical reactivity by functionalizing the indigenous hydroxyl and carboxyl groups. This was achieved by using a quaternary ammonium or phosphonium hydroxide base and an alkylating agent. This method is a unique chemical reaction of coal in that the kinetic rate is not limited by mass transport. The activation energy of the nucleophilic displacement determines the

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rate of O-alkylation. The ability to manipulate coal structure and alter its chemical composition rapidly at ambient conditions has profound importance in the field of coal chemistry and ultimately in coal conversion.

Experimental Section

General Data. Materials and Equipment. All of the chemical reagents were purchased commercially (vendors claimed a purity of 98–99.9%) and were used after their purity was verified.

Gas chromatographic separations were made on a Perkin-Elmer Sigma 1B and computed on a Sigma 10 data system. The chromatography columns were purchased from Supelco (Bellefonte, PA). Those used in this study were 10% SP-2250, 10% SP-2100, and 10% SP-1200/1% H_3PO_4, 3% Dexsil-300, and 3% SE-30. All the columns were stainless steel, 10 ft × 0.125 in., and their solid support mesh size was 100/120.

A Haake temperature controller was used to maintain 25 ± 0.3 °C in the water bath.

X-ray analyses were performed on a Phillips Energy Dispersive EDAX Model 711 to determine halogen content of coals.

All reaction mixtures (except those which contained coal) were subjected to mass spectral analysis in order to ensure peak assignments and structures. A Du Pont 491 mass spectrometer was used for this purpose.

The Illinois no. 6 and Rawhide coals were fresh consignments from the Illinois Monterey no. 1 and Wyoming mines, respectively. They were stored under water, ground to minus 80 U.S. mesh, and used under nitrogen.

Analyses. The amount of deuterium which was incorporated into various coal smaples were determined by Gollob Microanalytical Co. (Berkeley Heights, NJ). The elemental compositions of samples were all performed in accordance with ASTM procedures by the Analytical Division of Exxon Research and by Galbraith Laboratories (Knoxville, TN).

The solid-state ^{13}C NMR spectroscopy was performed on a JEOL QX-60 by the Analytical Division of Exxon Research.

The internal standard technique for quantification of solution components was employed. Th hot wire or thermal conductivity detector response factors of model compounds vs. the reference standards were found, and an average of three determinations was used.

Determination of the Second-Order Rate Constant. The O-alkylations of the various hydroxyl compounds and carboxylic acids were found to obey the second-order rate expression. These reactions were first order with respect to acidic hydroxyl compound and first order with respect to alkylating agent. The reduced form of the kinetic equation is

$$kt = \frac{1}{[\mathrm{RX}]_0 - [\mathrm{ROH}]_0} \ln \frac{[\mathrm{ROH}]_0[\mathrm{RX}]_t}{[\mathrm{RX}]_0[\mathrm{ROH}]_t}$$

where k is the rate constant, t is time in seconds, RX represents the alkylating agent, ROH is the weak organic acid, and the subscripts 0 and t indicate the concentration at the initial and measured times.

All the absolute second-order rate determinations were performed in the same fashion. The results are presented in Tables I and II. The O-methylation of 2-naphthol is shown here in detail as a representative procedure.

A 1-L round bottom flask equipped with an overhead stirrer was charged with the following: (1) 2-naphthol (10.7261 g, 74.38 mmol); (2) n-heptane (9.3393 g, 93.20 mmol); (3) tetrahydrofuran, THF (300 mL); freshly distilled from $LiAlH_4$ and maintained under nitrogen; (4) tetra-*n*-butylammonium hydroxide, 1.00 M aqueous solution (75.75 mmol). These four reagents mixed for 30 min at 25 °C under a static atmosphere of nitrogen. This inert atmosphere was maintained throughout the experiment. Iodomethane (21.5970 g, 152.16 mmol) was then added, and the timer was started. Aliquots were removed periodically. Each aliquot was 0.25 mL, and a total of 12 were removed and quenched. (The total actual volume of the reaction mixture was 394.61 mL. Thus, 3 mL out of nearly 400 mL is a negligible loss). Each aliquot was quenched at 0 °C in vial which contained 1.5 mL of 1 M HCl and 1.5 mL of ether. With the addition of the reaction aliquot, the vial was vigorously shaken for 15 s. The organic layer was analyzed by GC on a 10% SP-2100 column. The concentrations of iodomethane, 2-naphthol, and 2-methoxynaphthalene were monitored. The response factors were determined previously. The 12 sets of concentrations were used to calculate the value of k according to the second-order rate expression. The value was $9.4 \times 10^{-3}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1} \pm 3\%$.

Relative Reactivities of Representative Phenols Ten pairs of phenoxides were run in a competitive reaction in ten separate studies. One of these experiments is described here as a representative example.

A 100-mL round-bottom flask equipped with a stirring bar was charged with the following: (1) 2-*tert*-butyl-6-methylphenol (0.8222 g, 5.01 mmol); (2) phenol (0.4666 g, 4.96 mmol); (3) decane (0.4331 g, 3.04 mmol); (4) tetra-*n*-butylammonium hydroxide, 1.00 M aqueous (10.00 mol); (5) THF (40.0 mL) freshly distilled from $LiAlH_4$ and maintained under nitrogen. These five reagents were mixed for 30 min at ambient temperature under a static atmosphere of nitrogen. Then iodomethane (0.7097 g, 5.00 mmol) was added. The reaction was complete in less than 30 min. It was quenched with 20 mL of 2 M HCl at 0 °C. The acidified solution was warmed to room temperature. Then 15 mL of ether was added with continued stirring. After 5 min, the phases were separated and the organic layer was analyzed chromatographically. Good separation was achieved on a 10% SP-2100 column. The results of this and the other relative rate measurements of phenols are presented in Table III.

Competitive Heptylation and Octadecylation of Illinois No. 6 Coal. The composition of Illinois no. 6 coal was as follows: % moisture, 4.08 on a dry basis; % C, 67.85; % H, 4.78; % N, 1.23; % pyritic S, 1.42; % sulfate S, 0.06; % organic S, 2.96; % total oxygen (neutron activation), 14.84; % ash, 11.1, % mineral water, 13.2 (based on % MM ; 1.13 × ash + 0.47% pyritic S, a modified Parr formula), % organic O, 9.96. The empirical formula for the organic component of Illinois no. 6 coal normalized to 100 carbon atoms is $C_{100.0}H_{84.5}O_{11.0}N_{1.6}S_{1.6}$.

The titration of the Illinois coal with tetra-*n*-butylammonium hydroxide revealed that there was 2.85 mmol of acidic sites/g of dry coal. The percent of organic oxygen is 9.96, so that 1 g of dry coal has 0.0996 g or 6.23 mmol of oxygen. Since 2.85 mmol out of 6.23 mmol/g of dry coal of the oxygen is hydroxyl, then 5 out of 11 oxygen atoms, based on 100 carbon atoms, must also be bound as O–H. With this data in hand, the competitive O-alkylation of the coal was performed. Into a 200-mL round bottom flask Illinois no. 6 coal (4.08% moisture, 2.9899 g, 8.2 mmol of OH groups), THF (50 mL, freshly distilled from $LiAlH_4$), and tetra-*n*-butylammonium hydroxide (1.00 M aqueous, 8.25 mmol) were mixed under a static atmosphere of nitrogen for 30 min at ambient temperature. Then, 1-bromoheptane (1.5225 g, 8.50 mmol) and 1-bromooctadecane (2.7783 g, 8.33 mmol) were added simultaneously. The reaction mixture was allowed to stir for 1 week to ensure complete reaction. At this time 30 mL of 1 M HCl solution was added and agitation was maintained overnight. The entire reaction mixture was poured into a 1000-mL flask which contained 400 mL of methanol and was vigorously mixed for 10 min and then filtered. The O-alkylated coal derivative was virtually insoluble in methanol. However, all the reagents used in this reaction were soluble. The solid product was transferred to a Soxhlet thimble and washed for 48 h with hot methanol. The O-alkylated coal was then dried under vacuum (1 mmHg) at 110 °C overnight. The dried product weighed 3.5266 g. The compositional analysis revealed: % moisture, 0.05; % C, 72.88; % H, 7.67; % N, 0.90; % Br, 0.05 as determined by X-ray analysis and also a standard titration method ASM 270.02B). A complete reaction (that is, O-alkylation of all available acidic sites) would have incorporated five alkyl substituents per 100 carbons. The compositional analysis indicates that three *n*-heptyl and two *n*-octadecyl groups were added: $C_{100.0}H_{84.5}N_{1.6} + 3C_7H_{15} + 2C_{18}H_{37} - 5H = C_{157.0}H_{198.5}N_{1.6}$ which reduces to $C_{100.0}H_{126.4}N_{1.0}$. The experimentally derived empirical formula is $c_{100.0}H_{126.2}N_{1.0}$. This is in excellent agreement. Just for the sake of illustration: if 2.5 *n*-heptyl and 2.5 *n*-octadecyl groups had been added to the illinois coal, then the formula would have been $C_{100.0}H_{128.9}N_{1.0}$. On the other hand, if 3.5 n-heptyl and 1.5 *n*-octadecyl groups had been added to the coal instead, then the formula would be $C_{100.0}H_{123.8}N_{1.0}$. Thus, the H/C ratio is a sensitive probe, and it confirmed that 60% of the time the coal was heptylated and 40% of the time it was octadecylated. This result, along with the analogous reaction using Rawhide coal, is present in Table V.

Second Method for Determining Relative Reactivity of an Equimolar Pair of Alkylating Agents. All of the examples present in Table V were studied by gas chromatography. At the end of the O-alkylation the concentrations of the unconsumed alkylating agents were determined by the internal standard technique. In the case of the model compounds, the O-alkylated products were also quantified by GC analysis. A representative example is presented here. 2-Naphthol (0.7202 g, 5.00 mmol), THF (20 mL, freshly distilled), tetra-*n*-butylammonium hydroxide (1.00 M aqueous, 5.00 mmol) and decane (0.3830 g, 2.69 mmol) were mixed under nitrogen atmosphere at ambient temperature for 30 min. Then 1-iodopropane (0.7748 g, 4.56 mmol) and 2-iodopropane (0.8095 g, 4.76 mmol) were added simultaneously and the reaction proceeded overnight. The next day the round-bottom flask was cooled to 0 °C and 20 mL of 1 M HCl was added to the vessel with continued stirring for 2 h at room temperature. Ether (15 mL) was then added to effect a good phase separation. The organic layer was chromatographically analyzed on a 10% SP-2100 column. The results are shown in Table V.

Relative Reactivity Between Illinois No. 6 Coal and 2-Naphthol. When performing an alkylation of Illinois coal in competition with a model compound, it is important to remember that most (if not all) of the nitrogen in the coal will react with the alkylating agent. N-alkylation often is a much faster process than O-alkylation. The N-alkylation which occurs in coal is primarily unprotonated coal nitrogen going to form an *N*-alkylammonium halide by the coal's reaction with the corresponding alkyl halide. An example would be pyridine going to form *N*-methylpyridinium iodide when reacted with iodomethane. Illinois coal consumed 3.50 mmol of iodomethane/g of dry coal in the presence of a quaternary ammonium hydroxide. Only 2.85 mmol was hydroxyl and the remainder 0.65 mmol was N. Since Illinois no. 6 coal has 1.23% N, there are 0.88 mmol of nitrogen/g of coal. Apparently about three-fourths of them were alkylated. However, within the limits of the experimental error and given the rather small value of the nitrogen level in this coal, all of the nitrogen should be considered alkylatable.

During the routine drying procedure, the coal derivative is put into a vacuum oven and heated to 110 °C overnight. This treatment decomposes the *N*-methylammonium iodide salts which had formed during the methylation step. Only the O-methylated functionality survived this treatment (see Figures 1-3).

Procedure. In a 200-mL round-bottom flask the following were added: (1) 2-naphthol (0.6272 g, 4.35 mmol), (2) Illinois no. 6 coal (1.2947 g, 3.55 mmol of OH plus 1.09 mmol of nitrogen), (3) THF (50.0 mL, freshly distilled), and (4) tetra-*n*-butylammonium hydroxide (1.00 M aqueous, 10.00 mmol). After 30 min of mixing at ambient temperature under a static atmosphere of nitrogen, iodomethane-d_3 (0.7687 g, 5.31 mmol) was added. Two hours later, 20 mL of 1 M HCl was used to quench the reaction. The next day, the reaction mixture was filtered and the solid product was transferred to a Soxhlet thimble and exhaustively washed with methanol for 48 h. The methanol extract (50 mL) was combined with the original filtrate, and then ether (50 mL) was added to effect a phase separation. This solution was carefully concentrated by evaporating off most of the ether and some of the methanol at 30 °C under partial vacuum. At this point the internal standard 1-heptanol (0.3413 g, 2.94 mmol) was added, and the solution was analyzed by gas chromatography for 2-naphthol (1.82 mmol) and the methylated d_3 derivative (2.48 mmol).

The solid coal derivative was transferred from the Soxhlet thimble to the vacuum oven where it was dried at 110 °C overnight. The compositional analysis revealed the following: % moisture 0.05; % C, 66.96; % H, 4.44, % D, 0.80. The empirical formula of this partially alkylated coal is $C_{100.0}H_{79.6}D_{7.2}$. Since 7.2 D per 100 carbons were found, then 2.4 CD_3 must be present per 100 carbons. Thus, just less than half of the available O–H sites in the coal reacted while slighlty more than half of the 2-naphthol was O-methylated. These findings confirmed the GC results.

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Liquid-Phase Autoxidation of Organic Compounds at Elevated Temperatures. 2. Kinetics and Mechanisms of the Formation of Cleavage Products in *n*-Hexadecane Autoxidation

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Abstract: The cleavage products from the autoxidation of liquid *n*-hexadecane in a stirred flow reactor at 160 and 180 °C and 100–110 kPa of oxygen gas pressure have been determined. In the range of 0.1–2.3 mol % conversions the cleavage products are alkanoic acids, methyl ketones, 1-oxo- and/or 1-oxyalkanes, H_2O_2, CO_2, and CO. Measurable quantities of esters and γ-lactones first appear at higher conversions. These results together with those obtained from studies of the thermal decomposition of primary autoxidation products are consistent with two independent modes of cleavage product formation. The first process accounts for the formation of methyl ketones and 50–60 percent of the acids. It involves a first-order molecular decomposition of di- and trifunctional C_{16} autoxidation products which contain α,γ-hydroperoxy ketone structures. The rate constants for the decomposition (in s^{-1}) obey the Arrhenius equation in the temperature range of 120–180 °C with log A equal to 12.3 and $\Delta E^{\ddagger}$ equal to 30 kcal/mol. The second cleavage sequence accounts for the formation of the remaining acids and other cleavage products. This sequence involves reactions of alkoxy radicals formed from initiation reactions and from nonterminating decomposition of dialkyl tetroxide intermediates. Combining these results with those reported in earlier work, the reactivity ratios per hydrogen atom for intra- and intermolecular hydrogen atom transfer reactions of chain-carrying peroxy radicals have been determined for the *n*-hexadecane system at 120 to 180 °C. From these reactivity ratios and the number of hydrogen atoms available for each process, the relative contributions of α,γ-cleavage processes in the liquid-phase autoxidation of *n*-alkanes as a function of the number of methylene groups per molecule have been estimated.

Present knowledge of the kinetics and mechanism of cleavage product formation in the oxidation of *n*-alkanes is limited to the *n*-butane system. Mill et al.[1] showed that the cleavage products from the initiated oxidation of liquid and gaseous *n*-butane at 125 °C could be accounted for by the reactions of alkoxy radicals formed in nonterminating bimolecular reactions of chain-carrying peroxy radicals. However, in the extension of their studies to *n*-pentane and *n*-octane[2] product complexity and incomplete product recovery precluded kinetic analyses of cleavage processes.

This study reports the results of an investigation of the formation of cleavage products in *n*-hexadecane autoxidation by using the stirred flow reactor technique. The technique was previously used in the study of the formation of C_{16} primary oxidation products in *n*-hexadecane autoxidation.[3] This led to the discovery of

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† Deceased Feb 4, 1981.

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