

rise to a pulse of a voltage determined by the time at which the termination occurred. The pulses emerging from the TAC were then stored in a multichannel analyzer (Hewlett-Packard) in which the pulses were distributed according to time elapsed from initiation of ramp. From 20 000 to 25 000 counts were accumulated in each measurement, using an appropriately low ratio between count rate and the exciting pulse rate. Data were transferred to paper tape and then to cards via the CDC 6600 computer of Tel-Aviv University. Data from the channels of the pulse height analyzer were fitted to single exponential decay curve by a least-squares program. It should be explicitly noted that a single exponential decay is observed even in intermediate solvent polarities because the $S_{1,np}$ and $S_{1,ct}$ states are in equilibrium.⁸

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Friedel–Crafts Isopropylation of a Bituminous Coal under Remarkably Mild Conditions^{1a}

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Abstract: A bituminous coal, Illinois no. 6, has been treated under Friedel–Crafts alkylation conditions, some as mild as 0–5 °C and atmospheric pressure. The tools of mass spectroscopy and classical analytical techniques were employed to confirm unequivocally that the coal was alkylated. The alkylated product has both a higher hydrogen content and higher solubility in benzene and pyridine than the untreated coal. This work demonstrates that coal is very much more reactive than is conventionally believed.

"When I am asked what particular research on coal would be of most practical value to those who have to sell it, equally with those who wish to use it, I have no hesitation in saying: 'Research on the Composition of Coal'." R. V. Wheeler (1928).

Introduction

Coal is considered to be an organic rock. A major challenge for organic chemists today is to gain a better understanding of the organic structural types which exist in coal, so that, ultimately, more efficient conversion to clean fuels and/or chemicals can be achieved.

Coal is largely insoluble in most common organic solvents,² and therefore the characterization techniques available to the chemist, which require samples in solution, cannot be applied to more than the about 25% of the coal which is soluble in pyridine. In hydrocarbon solvents such as hexane, benzene, or toluene, the solubility is only 2% or less. Furthermore, it is not

possible to deduce all the structural types present in native coal from analysis of liquid products made during pyrolysis or liquefaction, because of the extensive bond making and bond breaking occurring under these high-severity conditions.

We have been investigating a mild chemical method to render large amounts of the coal soluble in organic solvents, i.e., Friedel–Crafts alkylation. While this reaction has been investigated earlier,^{3–5} we have been extensively characterizing the alkylation products obtained, and wish to describe our results here.

Results and Discussion

All alkylations were performed on coal from the Illinois no. 6 seam as described in the Experimental Section. Some results are listed in Table I.

The extent of alkylation is not very sensitive to marked increases in the severity of reaction conditions. Thus the H/C ratio of the product of alkylation at 0–5 °C and 1 atm (sample

Table I. Friedel–Crafts Isopropylation of Illinois no. 6 Coal

Sample	Coal size, μ	Catalyst	Reaction time, h	Reaction temp max, $^{\circ}\text{C}$	Reaction pressure max, atm	H/C Product
1	Raw Illinois no. 6					0.82
2	150	AlCl_3	0.17	0–5	1	0.94
3	80	$\text{ZnCl}_2/\text{AlCl}_3$	5.0	155–160	21	0.97
4	150	AlCl_3	4.0	150–155	22	0.98
5	300	AlCl_3	6.0	110–115	20	1.00

Table II. Extent of Alkylation vs. Time^a

Sample	Time, min	% C	% H	% moisture	H/C (dry)
A	1	68.22	5.26	1.24	0.90
B	3	68.56	5.20	0.78	0.89
C	5	68.99	5.42	1.09	0.92
D ^b	10	69.27	5.51	0.54	0.94
E	60	68.47	5.49	1.37	0.93
F	120	68.67	5.49	1.8	0.92

^a 15.0 g of Ill. no. 6 (<150 μ) (H/C = 0.82), 5 g of AlCl_3 , 15 g of 2-chloropropane at 0–5 $^{\circ}\text{C}$. ^b This is sample 2, Table I.

2) is not too different from that obtained at 22 atm and 150–155 $^{\circ}\text{C}$. Equations 1 and 2 try to quantify the extent of alkylation per typical unit of hydrocarbon in coal and show that the H/C ratio is a sensitive measure of reaction extent.

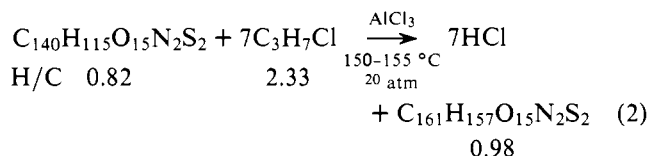
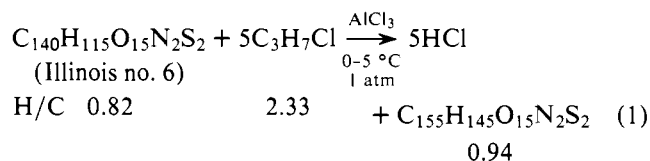
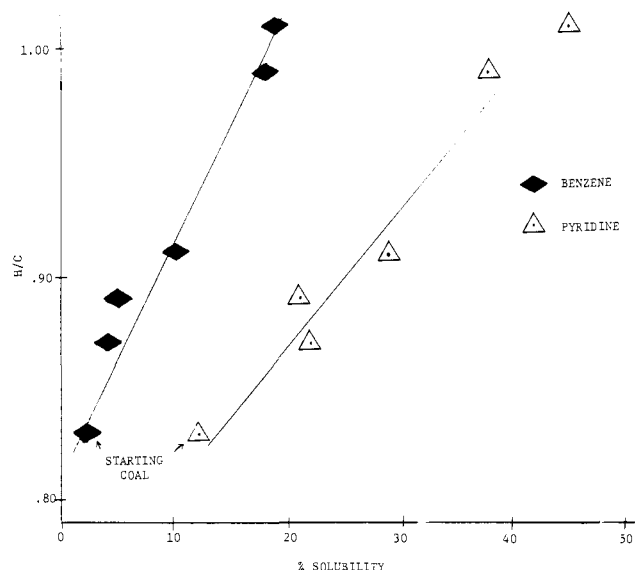


Table II shows that at 0–5 $^{\circ}\text{C}$ and 1 atm Illinois no. 6 is significantly alkylated at those sites where access of the alkyl halide Lewis acid complex is achieved within a few minutes. These are exceedingly mild conditions compared with other chemical reactions carried out on coal such as pyrolysis and liquefaction.

As the coal becomes richer in alkyl groups the solubility increases.^{3–5} The data shown in Table III and in Figure 1 reflect this phenomenon, both for benzene and pyridine.

Demonstration of Alkylation. It is not at all a straightforward task to determine if, indeed, the coal was alkylated. It is known that the weight of product after allowing coal to react with an alkylating agent increases. This product has a higher H/C atomic ratio than the starting material and is more soluble than the starting coal. These data can be accommodated by the hypothesis that the alkylating agent may be chemisorbed on the coal as well as by having been incorporated into the coal via the desired electrophilic aromatic substitution. The generation of HCl in the reaction can arise from the hydrolysis of the AlCl_3 with the ever-present water in the coal rather than by the desired reaction (eq 1). In addition, it is well known that under the more severe conditions a multitude of side reactions occur, chief among them being the direct reduction of the isopropyl chloride to propane.⁶

**Figure 1.** Solubility increases with H/C; Illinois no. 6 raw and alkylated to varying extents.**Table III.** Solubility of Alkylated Coals

Sample	% extracted ^a		Alkylating agent
	Benzene	Pyridine	
1	2	11	None
2	11	30	<i>i</i> -C ₃ H ₇ Cl/ AlCl_3
4	15	39	<i>i</i> -C ₃ H ₇ Cl/ AlCl_3

^a Entire reaction product extracted in solvent at 70–75 $^{\circ}\text{C}$ for 2 h; organic liquid phase separated by filtration and solvent removed in vacuo.

However, mass spectroscopic data coupled with wet chemical analyses allowed us to confirm the occurrence of alkylation. Comparative mass spectral data for extracts from raw and isopropylated Illinois no. 6 coal indicate that isopropyl groups were added to the coal matrix. For each series or class of compound in the coal liquid extracts (e.g., tetralin or naphthalene) data are presented in Table IV. Since coal liquids have significant peaks only for C₁, C₂, and C₃ homologues in a series, the relative abundances of 4-, 6-, 9-, and 12-carbon homologues are shown. This eliminates ambiguities in determining the origin of the C₃ peak. For the extracts from untreated coal, there is a monotonic decrease in these relative abundances as the number of carbon atoms in the homologous series increases above C₃. On the other hand, increased abundances were observed at mass/charge values representing di-, tri-, and tetraisopropylated aromatic systems in the spectra of the extracts of isopropylated coal. We believe that the increase in relative abundances of C₆-tetralin is indicative of diisopropylated tetralin, C₉-tetralin, triisopropylated tetralin, etc. None of the earlier reports in the area of alkylation^{3–5} presented similar confirming evidence for the occurrence of aromatic alkylation under Friedel–Crafts conditions.

Coal Extract Properties. Since the extracts are soluble in ordinary solvents, acquisition of rather complete characterization data is possible. Besides elemental analyses on the extracts, the following analytical determinations were made: infrared, ultraviolet, ¹H and ¹³C NMR spectra, and molecular weight by gel permeation chromatography and vapor pressure osmometry. These will be presented in a forthcoming paper. The extracts generally are dark brown, viscous oils. Table V lists some of the analyses obtained for the extracts described in Table III. The low sulfur and nitrogen levels in the extracts

Table IV. Mass Spectral Data for Coal Extracts

Series	C ₄	C ₆	C ₉	C ₁₂
Raw Coal Extract—Relative Abundances				
Tetralin	1	0.51	0.26	
Naphthalene	1	0.38	0.09	0.11
Biphenyl	1	0.73	0.17	0.09
Pyrene	1	0.33	0.17	0.03
Alkylated Coal Extract—Relative Abundances				
Tetralin	1	1.34	1.32	1.75
Naphthalene	1	5.81	6.53	3.27
Biphenyl	1	3.64	12.35	5.31
Pyrene	1	1.64	3.76	2.14

Table V. Comparison of Raw and Isopropylated Extract Properties

Sample	% H	% C	H/C	% S	% N
Illinois no. 6	5.4	77.7	0.82	4.8	1.4
1	8.4	84.0	1.19	<i>a</i>	<i>a</i>
4	7.7	76.3	1.21	0.71	0.69
5	10.4	86.5	1.43	0.3	<0.3

^a Analysis not obtained.

indicate that the heteroatoms are concentrated in the (nonextracted) residue. The elemental analyses do not add up to 100%; the difference is the oxygen and chlorine content.

Summary

By means of a very mild chemical reaction we have solubilized a considerable portion of the organic material in coal. In this study of the Friedel–Crafts alkylation of coal we have demonstrated unequivocally that alkylation has occurred, that the alkylation product is more soluble than the starting coal and the increased solubility can be correlated with increasing H/C. Because of the mild treatment and subsequent increased solubility of the coal this technique offers a potentially powerful tool for characterizing coal structure.

Experimental Section

Freshly comminuted Illinois no. 6 coal (−150 μ) was used. Precautions were taken that no air or oxygen contacted the coal.

Illinois no. 6 Ultimate Analyses			
	Dry ash free		Dry ash free
% C	77.66	% O (by diff.)	10.88
% H	5.36	% N	1.36
% S	4.75	H/C	0.82

Alkylation. A. Mild. A 500-mL, three-necked flask fitted with a mechanical stirrer, thermometer, and addition funnel was immersed in an ice bath. The reactor was charged with 15.0 g of dried (−150 μ) Illinois no. 6 coal and 5.0 g (0.038 mol) of aluminum chloride. With stirring, isopropyl chloride (15.0 g, 0.191 mol) was added over a 2-min period at a rate which allowed the temperature to remain below 5 °C. The reaction mixture was stirred at 0–5 °C and samples were removed after 1, 3, 5, 10, 30, 60, and 120 min. Each sample was water washed and vacuum oven dried prior to analysis.

B. High-Pressure Alkylation. A typical alkylation experiment was carried out as follows. Into a 125-mL Parr Hastelloy C autoclave was placed 10 g of −150 μ freshly comminuted and vacuum oven dried (>4 h, 105 °C) Illinois no. 6 coal and 10 g (0.13 mol) of 2-chloropropane. The resultant slurry was cooled in an ice bath. Aluminum chloride (3.0 g, 0.022 mol) was added to the stirred slurry, and the autoclave was sealed and heated to 150 °C for about 1 h ($P_{max} \sim 20$ atm), cooled, and vented. Upon opening the autoclave the system was quenched with water, the slurry filtered, and the solid vacuum oven dried (16 h, 105 °C) prior to any further treatment. Extractions were carried out as indicated. Mass spectra were obtained on an AEI MS 9 spectrometer.

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