Dideuterium was used to probe the role of dihydrogen in the reaction. Although the influence of the gas on the conversion and oil yields was modest, the spectroscopic data clearly establish that deuterium atoms were incorporated into the products. Weak absorptions near 2100 cm^{-1} were observed in the infrared spectra of most of the products. Our preliminary results suggest that more deuterium is incorporated in the oil than in the other fractions, and the representative ^{2}H NMR spectra, Figure 2, indicate that the deuterium is incorporated into aliphatic structural elements with resonances between 1 and 2 ppm. Lesser amounts of deuterium appear in benzylic and aromatic positions. We estimate that 0.1–0.2 mmol of dideuterium was incorporated per gram of the reaction mixture. The deuterium incorporation was somewhat higher in the reactions of the Wyodak coal than for the Illinois No. 6 coal. Research is currently underway to establish the degree of deuterium incorporation quantitatively. However, it is already evident that the gas plays an important role in the chemistry with a very high degree of incorporation in the highly aliphatic constituents of the asphaltenes and the oils as noted in previous work by Skowronski and his associates.[20]

Conclusion

The experimental results strongly suggest that coprocessing proceeds via a stepwise reaction sequence in which the coal macromolecules are degraded in stages, first forming large polar asphaltenes that are subsequently converted into smaller, less polar oils. Adduction reactions of the aliphatic resid molecules to the aromatic coal molecules proceed at all stages of this chemistry. Indeed some coal fragments appear in the oil at short reaction times. Hydrogen-transfer processes occur very rapidly among all the constituents, and dideuterium is added to the reaction products in the presence and absence of the molybdenum catalyst. The reactivity patterns for the four fossil materials suggest that their hydrogen-atom-transfer reactions have a significant influence on the course of the reaction. Our results suggest that the hydrogen donor properties of Illinois No. 6 coal may actually interfere with its conversion.

Rank Dependence of Associative Equilibria of Coal

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Associative equilibria of coal have not been fully recognized. Evidence for associative equilibria is presented. The dependence of associative equilibria on coal rank is also investigated. Associative equilibria are highly rank dependent. This results in remarkable differences in extraction rate, effect of preheating on extraction, and effect of solvent-soaking on extraction for coals of different regions: the A region (<87% C), the B region (87–90% C), and the C region (>90% C). This implies that relatively strong intra- and intermolecular interactions in coal is, largely, a function of coal rank. It has been reported that the so-called "stacking interactions" between polycyclic aromatic compounds play an important role in the structure of higher rank coals. Other relatively strong interactions are, however, important in high-volatile bituminous coals.

Introduction

Results of earlier studies[1,2] have shown that the solvent-induced associations of high-volatile bituminous coal and its pyridine extract occur after soaking in organic solvents. Heating in poor solvents and immersing in good solvents, followed by the removal of good solvents, caused a decrease in the pyridine extractability of the coal. As some portions of these associates could not be solvated with one of the best solvents, pyridine, the new intra- and intermolecular (secondary) interaction was thought to be relatively strong.

The solvent-induced association results from associative equilibria. Various factors such as temperature, solvent compositions, coal compositions, and coal concentration could change the position of equilibrium. Various physical parameters such as extractability, solvent swelling, and micelle sizes may also be changed. Hence, associative

Table I. Elemental Analyses of Coals Used

coal	analysis, wt % (dry)				
	C	H	N	S + O[a]	ash
Illinois No. 6	70.6	4.51	1.59	11.7	11.6
Pittsburgh No. 8	79.3	5.29	1.42	8.5	5.4
PSOC-1336	72.8	4.84	1.13	7.8	13.4
PSOC-721	76.9	5.28	1.58	3.1	13.1
PSOC-1300	78.1	4.69	1.32	2.4	13.5
PSOC-991	76.0	4.44	1.46	3.1	15.0
PSOC-688	73.4	3.87	1.15	1.4	20.2

[a] By difference.

equilibria affect all processes using coal in the presence of solvents.

Associative equilibria of coal have not been fully recognized. In this paper, evidence for associative equilibria

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(1) Nishioka, M.; Larsen, J. W. *Energy Fuels* 1990, *4*, 100–106.
(2) Nishioka, M.; Larsen, J. W. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 1990, *35*(2), 319–326.

is presented. A knowledge of relatively strong secondary interactions is required to better understand coal structure and reactivity. As coal rank appears to correlate to such interactions, the dependence of coal rank on associative equilibria which are caused by these interactions is also investigated.

Experimental Section

All chemicals were ACS and HPLC grades. The coal samples were obtained from Exxon Research and Engineering Co. and the Pennsylvania State University Coal Bank. Their elemental analyses are listed in Table I. Coal samples were ground and sifted under a nitrogen atmosphere, and –60-mesh particles were used in the experiments.

Approximately 5 g of each coal sample was placed in 100 mL of solvent in a 250-mL flask and magnetically stirred under nitrogen. The mixture was stirred at room temperature, heated, or mildly refluxed in an oil bath. The cooled mixture was dried using a rotary evaporator, mixed with methanol, and filtered, while being rinsed with methanol several times. The coal was dried to constant weight in the vacuum oven at 50 °C. When pyridine was used, the solvent was removed as follows. One series of cooled samples were dried in the same way as above. Another series of samples were filtered by using a Whatman (Hillsboro, OR) grade 1 filter, the wet residues were promptly Soxhlet-extracted, and these extracts were mixed and dried.

Coal samples (2–5 g) were extracted with 200 mL of pyridine for the necessary time by using a Soxhlet apparatus under a nitrogen atmosphere. The coal extracts were concentrated by using a rotary evaporator and dried to constant weight in a vacuum oven at 50 °C.
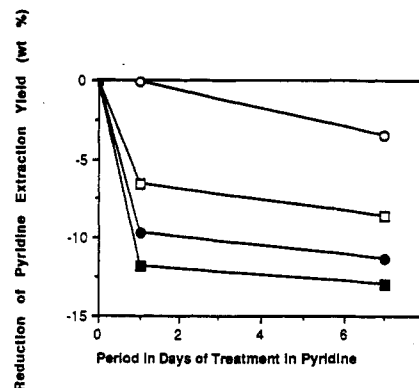
The pyridine extracts of PSOC-1336, Illinois No. 6, and Pittsburgh No. 8 coals were concentrated by using a rotary evaporator, and filtered by using the Whatman filter paper. The filtered extract solutions were put into Pyrex flasks under a nitrogen atmosphere, sealed, and stored at room temperature. At the desired time, the samples were again filtered as mentioned above, and the extracts and residues were dried and weighed.

Results and Discussion

Evidence for Associative Equilibria. Pyridine extractability of Pittsburgh No. 8 coal significantly decreased after soaking in pyridine at both room temperature and at its boiling point if the solvent was removed from the soaked coal, while the pyridine extractability did not change if the solvent was not removed.[1,2] This was attributed to the fact that pyridine strongly solvates the sites generating the strong secondary interactions.[2]

However, association was observed, even though pyridine was not removed, for coals of higher rank than the Pittsburgh No. 8 coal. Pyridine extraction yields of PSOC-1336 coal (84.1% C) after soaking in pyridine at room temperature and at reflux were compared with that of the starting coal. In one series of experiments, soaked coals were dried and Soxhlet-extracted. In another series of experiments, soaked coals were Soxhlet-extracted without removal of pyridine. Figure 1 shows the changes in pyridine extractability for such treated coals. The pyridine extractability of all samples decreased on soaking. The solvent-induced association occurred even in the wet state of pyridine at both room temperature and reflux.

Aggregation in a solution is seen in phase separation phenomena such as precipitation, gelation, and crystallization. The extent of equilibration is generally controlled by conditions such as concentration, pH, and temperature. Precipitation from a pyridine-soluble Soxhlet extract was studied by Dormans and van Krevelen.[3] Pyridine extracts from coals of less than 87% C did not form precipitates after 240 h, while those from coals with more than 87%

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(3) Dormans, H. N. M.; van Krevelen, D. W. *Fuel* **1960**, *39*, 273–292.

Figure 1. Change in pyridine extractability of PSOC-1336 coal immersed in room temperature (●, □) and boiling pyridine (○, ■), (●, ■: dried samples, ○, □: nondried samples).

C yielded precipitates amounting to between 10 and 30 wt % of extracts.

The pyridine extract of the PSOC-1336 coal was concentrated, filtered, and held at room temperature under nitrogen. The extract solution with concentration of 13.4 mg/cm³ precipitated 0.5 wt % of the extract after 5 days. Concentrated pyridine extracts of Illinois No. 6 (79.9% C) and Pittsburgh No. 8 (83.8% C) also formed precipitates if their concentrations were more than 100 mg/cm³. Possibility of cross-linkings by chemical reactions due to conditions such as light exposure and trace amount of oxygen cannot be completely ruled out. However, if chemical reactions significantly affect precipitation under the condition used, diluted samples should also precipitate to some degree, but this was not observed. Therefore, it seems that higher concentrations mainly affect the aggregation of pyridine solubles. The Dorman and van Krevelen's result suggests that high-temperature (Soxhlet extraction) extracts of higher rank coals easily associate at low (room) temperature. The present result shows that high-temperature extracts of lower rank coals do not associate at low temperature when their concentration is dilute.

The effect of temperature on association of coal extract was previously observed for a pyridine solution.[1] The molecular weight distribution of a room temperature nonextractable/Soxhlet-extractable fraction with pyridine of the Pittsburgh No. 8 coal was measured by gel permeation chromatography at room temperature and at 70 °C. A significant shift to lower molecular weight was observed at 70 °C for this particular sample.

The above results show the existence of associative equilibria of coal components in solvents and formation of intermolecular complexes under certain conditions. The associative equilibria depend upon coal rank, temperature, and coal concentration. Changes in extractability, precipitation, and molecular weight can be interpreted as a change in the position of equilibria.

Consideration of Extraction Rate on the Basis of Associative Equilibria. The presence of associative equilibria of coal components in solvents suggests that solvent extraction may be controlled by the equilibrium between extractable material and coal. In this section, the extraction rate is investigated based on associative equilibria.

Assume that a complex A·B equilibrates with each component A and B in a solvent.

$$A\text{·}B \underset{v_{-1}}{\overset{v_1}{\rightleftharpoons}} A + B \tag{1}$$

If the complex A·B is not extractable, components A and

Table II. Values of the Constant k_1 and Calculated Days Required for the Given Extractions

	Illinois No. 6	PSOC-1300	PSOC-688
% C (daf)	79.9	89.9	92.0
constant k_1 (day unit)	2.3	0.26	0.43
days required for 95% extraction	1.3	11.5	7.0
days required for 99% extraction	2.0	17.6	10.7

B are extractable with a solvent, and the velocity v_1 is much greater than the velocity v_{-1}, the extraction rate of each component is given by

$$dE/dt = k_1(E_\infty - E) \qquad (v_1 \gg v_{-1}) \qquad (2)$$

where E and E_∞ are concentrations (or extraction yields) given as follows

$$A \cdot B \overset{v_1}{\underset{v_{-1}}{\rightleftharpoons}} A + B \qquad (3)$$

E_∞	0	0 (at initial time)
$E_\infty - E$	E	E (at time t)

Therefore, an extraction yield at given time t is

$$E = E_\infty(1 - e^{-k_1 t}) \qquad (4)$$

where E_∞ and k_1 are regarded as an ultimate extraction yield and a constant concerning an extraction rate, respectively. Equation 4 is the same form as a first-order reaction rate equation. The constant k_1 is determined by extraction yields E_1 and E_2 at two different times t_1 and t_2

$$k_1 = \frac{\ln (E_\infty - E_1)/(E_\infty - E_2)}{t_2 - t_1} \qquad (5)$$

or by measurement of increment of extraction by half (τ)

$$k_1 = \ln 2/\tau \qquad (6)$$

A similar equation was derived by Oele et al.[4] for the extractive disintegration of bituminous coals at high temperatures (150–350 °C) in an anthracene oil and β-naphthol. They assumed a zero-order process for a forward disintegration at the initial step and additionally a first-order process for a backward integration when extraction proceeds.

Figure 2A shows calculated values using eq 4 and experimental data for extractability with pyridine versus extraction time. In the calculation of eq 4, the constant k_1 was calculated by using eq 5, and the observed value E_∞ was used. These values are given in Figure 2. Agreement between observed and calculated extraction yields is good except for the initial extraction of high-volatile bituminous coals by pyridine. If extracts are bound to coals or themselves by weak van der Waal's forces, their extractions could be mainly controlled by solubility of these material in solvents. Therefore, deviation at the initial extraction of high-volatile bituminous coal by pyridine is presumably attributed to the solubility of extractable material in solvents not due to equilibrium. It is seen that high-volatile bituminous coals are promptly extracted by pyridine, but medium- and low-volatile bituminous coals are very slowly extracted. Table II sum-
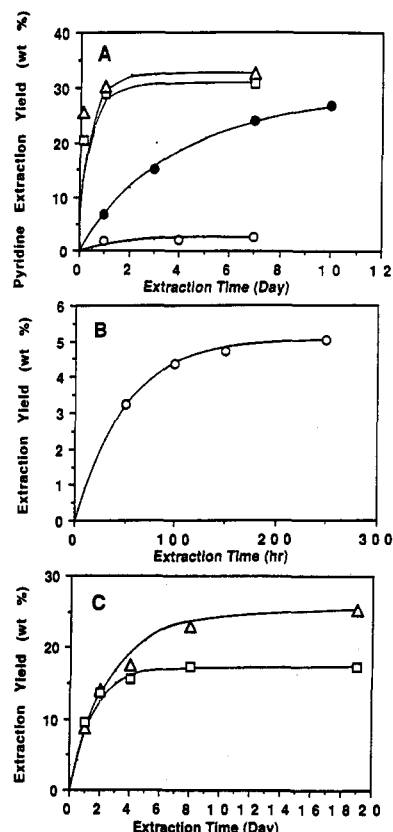
Figure 2. Solvent extractability versus extraction time. (A) Pyridine, (□) Illinois No. 6 (79.9% C) (E_∞ = 31.2, k_1 = 2.3), (△) PSOC-1336 (84.1% C) (E_∞ = 32.8, k_1 = 2.3), (●) PSOC-1300 (89.9% C) (E_∞ = 29.0, k_1 = 0.26), and (○) PSOC-688 (92.0% C) (E_∞ = 2.7, k_1 = 0.43). (B) Benzene/ethanol,[5] 81.4% C coal (E_∞ = 5.03, k_1 = 0.51). (C) Phenol,[6] 89.0% C coal, (△) β-fraction (E_∞ = 25.4, k_1 = 0.36) and (□) γ-fraction (E_∞ = 17.3, k_1 = 0.69). Solid line denotes calculated values (see text).

marizes the values of k_1 and the calculated times required to obtain 95 and 99 wt % extraction under the condition used. Approximately 1 day is sufficient to extract 95 wt % of the extractable materials from high-volatile bituminous coals, whereas more than 7 days are required to get the same 95 wt % extraction from medium- and low-volatile bituminous coals.

Figure 2, B and C, shows comparison of literature extraction data using other solvents.[5,6] When high-volatile bituminous coal is extracted with a relatively poorly solvating solvent, benzene/ethanol, extraction rate is slow.[5] Illingworth[6] extracted a medium-volatile bituminous coal with phenol at 180 °C and then fractionated the extract into the β and γ compounds. Again, agreement between observed and calculated extraction yields is good. Therefore, eq 4 is useful to predict extraction yields, particularly in the case of slow extraction rate.

For this reason, it is indicative that the dissociation of the coal–coal interactions is the rate-determining step in an extraction process. The slow rate of Soxhlet extraction is interpreted as the slow dissociation (small k_1) of aggregated material. The stronger the physical interactions are, the smaller will be the constants k_1. The poorer the solvents that are used for the extraction, the smaller the constants k_1 will be. In the case of very small rate constants, high temperature would be required to overcome the activation energy to allow dissociation of complexes.

(4) Oele, A. P.; Waterman, H. I.; Goedkoop, M. L.; van Krevelen, D. W. Fuel 1951, 30, 169–178.

(5) Spence, J. A.; Vahrman, M. Fuel 1970, 49, 395–408.
(6) Illingworth, S. R. Fuel 1922, 24, 213–219.

Table III. Differences in Behaviors in Extraction, Soaking, and Sitting of an Extract Solution for Coal from Each Region

%C (daf)	A <87% C	B 87–90% C	C[a] >90% C
pyridine extraction rate	fast	slow	
temperature (115 and 180 °C) effect on pyridine extraction	small	large	
preheating (200–400 °C) effect on pyridine extraction	small	large	
immersion in pyridine and removal of the solvent before pyridine extraction	decrease in extractability	increase in extractability	
soaking in hot toluene or chlorobenzene before pyridine extraction	decrease in extractability	increase in extractability	
precipitation of Soxhlet pyridine extracts at room temperature	no precipitation[b]	precipitation	

[a] Differences are very small because of very small ultimate extractability. [b] Precipitation occurs only at high concentration.

In fact, the effect of temperature on extractability becomes predominant upon increasing in coal rank as discussed in the next section, because the k_1 value becomes smaller upon increasing in coal rank.

If dissociation of coal associates is the rate-controlling step in solvent extraction, solvent-soaked coals should be extracted more quickly than native coals because opportunity for some dissociation is provided by soaking. The PSOC-1300 coal (89.9% C) was very slowly extracted with pyridine as shown above, and it took about 3 weeks to attain to the ultimate value (E_∞) of 29 wt %. This coal was refluxed in pyridine for 7 days, and filtered, and the wet residue was Soxhlet-extracted for just 1 day. The total extraction yield was 28.2 wt %. This result supports the concept that disruption of secondary interactions is the rate-determining step in an extraction procedure and that rinsing coal with fresh solvents is not a critical factor, particularly for a system with a small k_1 value.

The extraction process of coal is complicated and the details are not well known. However, it is suggested that solvent extraction may be primarily controlled by the equilibrium between extractable material and coal as discussed above. Equation 4 derived from the concept of associative equilibria is useful as a semiempirical equation. The nature of the constant k_1 in eq 4 is also complex, but it is seen that the value is highly rank dependent. This rank dependence is discussed in the following section.

Rank Dependence of Associative Equilibria. Coal extractability is dependent upon the duration and the temperature of extraction, and preheating before extraction. Although the dependence of these effects on coal rank has not been systematically studied, existing data suggest that these are strongly rank dependent. The following is the brief summary of the rank dependence of these factors on coal extractability.

Pyridine extractability varies with coal rank as shown in Figure 3.[3] Extractability rectilinearly increases up to 86–88 wt % C coal (named as A region here), then decreases sharply with rank (B region). At still higher rank (C region), only a few percent are extracted.

The A-region coals are promptly extracted with pyridine within 1 or 2 days, whereas the B-region coals are very slowly extracted under the same condition as shown in the previous section. The C-region coals yield extract slowly, and the ultimate extractability is very small.

Increasing extraction temperature normally increases the extraction yield. Pyridine extractability of high-volatile B and A bituminous coals (the A region) was greater at boiling point (115 °C) than at room temperature.[1] However, extraction yields at 115 and at 180 °C were similar.[3,6] A high-volatile C bituminous coal (the A region) showed little temperature dependence, and extraction yields with pyridine at room temperature and when a Soxhlet extractor was used were similar.[1] Pyridine extractability of the B-region coals are highly temperature dependent, the extraction yields at 180 °C being much greater than those at 115 °C.[6] Coals in the A and B regions distinctively differ
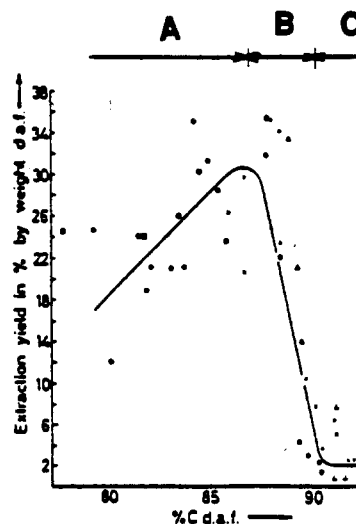
Figure 3. Pyridine extractability versus coal rank,[3] and the A-, B-, and C-region coals defined in this paper.

in the effect of temperature on pyridine extractability.

Since it was first reported by Harger and Illingworth[7,8] that coals preheated at 200–400 °C in an inert atmosphere gave much higher yields of extract than unheated coals, preheating effects have been investigated by several groups and reviewed.[9,10] The pyridine and chloroform extraction yields of the A-region coals are only slightly increased by preheating to 300 °C, whereas the B-region coals are much more extractable after preheating.[3] The dependence of preheating effect on coal rank was systematically studied by preheating to 250 °C for 24 h,[9] and it was confirmed that the effect was strongly rank dependent. Tetrahydrofuran extraction yields of higher rank coals increased after preheating, whereas those of lower rank coal decreased.

Heating the A-region coals at 115 °C in chlorobenzene for 7 days caused a decrease in pyridine extractability.[1,2] The same solvent treatment was given to the B-region coal, PSOC-1300, in this study. The pyridine extraction yield (24 h) of this treated coal increased to 18 wt % from 7 wt %. Various A- and B-region coals were soaked in pyridine. Figure 4 shows the change in pyridine extraction yields caused by this soaking at the boiling point for 7 days. The pyridine extractability of coals dried after soaking in pyridine at room temperature for 1 day is also included in this figure. Pyridine extractability of the B-region coals significantly increased after soaking in pyridine at the boiling point for 7 days. Pyridine extractability of the dried coals, after soaking in pyridine at room temperature, decreased for the A-region coals, while pyridine extracta-

(7) Harger, *J. J. Soc. Chem. Ind.* **1914**, *33*, 389–392.
(8) Illingworth, S. R. *J. Soc. Chem. Ind.* **1920**, *39*, 111–118.
(9) Nishioka, M.; Larsen, J. W. *Energy Fuels* **1988**, *2*, 351–355.
(10) Wynne-Jones, W. F. K.; Blayden, H. E.; Shaw, F. *Brennstoff-Chem.* **1952**, *33*, 201–206.
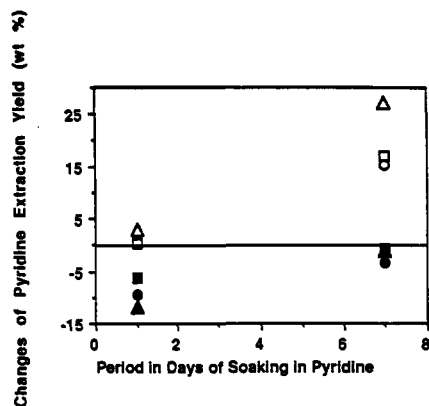
Figure 4. Changes in pyridine extractabilities of the A- and B-region coals immersed in pyridine at the boiling point for 7 days and their dried coals after immersing in pyridine at room temperature for 1 day: (△) PSOC-991 (89.4% C), (□) PSOC-1300 (89.9% C), (○) PSOC-721 (88.5% C), (■) Illinois No. 6 (79.9% C), (●) PSOC-1336 (84.1% C), and (▲) Pittsburgh No. 8 (83.8% C).

bility did not change or slightly increased for the B-region coals. These data show that the pyridine extractabilities of the A- and B-region coals, after treatment with pyridine and chlorobenzene, exhibit opposite trends.

The study of precipitation by Dormans and Krevelen[3] was discussed before. According to their result, pyridine extracts from the A-region coal did not form precipitate after 240 h, while those from the B-region coal yielded precipitates.

Concluding Remarks. Associative equilibria which are caused by the relatively strong intra- and intermolecular interactions exist for the system of coal and solvent and are highly rank dependent. Table III summarizes the rank dependences as discussed above. As the diversity in coals from different regions is noted, relatively strong intra- and intermolecular interactions is, largely, a function of coal rank.

As reported,[1,11] van der Waals' forces relating to π-electrons in polycyclic aromatics, so-called stacking or π–π interactions, are considerable for the B- and C-region coals. While, other relatively strong intra- and intermolecular interactions may be abundant for the A-region coal because of the suggested rank dependence of relatively strong intra- and intermolecular interactions. A very important interaction in the A-region coal is a charge-transfer interaction which was investigated in another paper.[12] A better understanding of these relatively strong intra- and intermolecular interactions is essential to the study of coal structure and reactivity.

(11) Quinga, E. M. Y.; Larsen, J. W. *Energy Fuels* **1988**, *2*, 300–304.
(12) Nishioka, M.; Gebhard, L. A.; Silbernagel, B. G. *Fuel*, in press.

31P NMR Spectroscopy for Labile Hydrogen Group Analysis: Toward Quantitation of Phenols in a Coal Condensate

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The chlorophospholanes $ClPOC(CH_3)_2C(CH_3)_2O$ (1) and $ClPSCH_2CH_2S$ (2) are utilized and compared as 31P NMR tagging agents for quantifying labile hydrogen functional groups known to be present in coal materials. The evaluation of these reagents was carried out with the use of model mixtures of phenols. After development of optimum NMR conditions with the model mixtures, quantitative analyses of an Illinois No. 6 low-temperature pyrolysis condensate were obtained with 1 and 2. The better analytical results with reagent 2 compared with 1 are tentatively attributed to greater 31P chemical shift sensitivity as a result of decreased ring strain and increased hybridizational flexibility in 2.

Introduction

In previous publications[1–5] we have addressed the utility of nonsubstituted and variously methyl-substituted chlorophospholanes as NMR spectroscopic tagging agents for the identification of labile hydrogen functional groups known to be present in coal materials (e.g., phenols and carboxylic acids). From those studies, 1[2,3] and 2[4,5] emerged as the two best candidates for further investigation. In this report, we compare the applicability of these reagents to the quantitative analysis of a model mixture of phenols

and to a low-temperature pyrolysis condensate of an Illinois No. 6 coal sample.
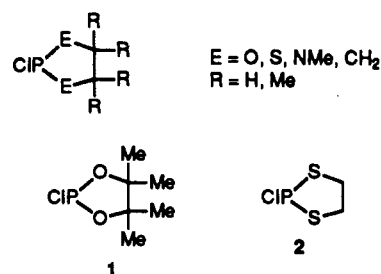
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