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Studies of Coupled Chemical and Catalytic Coal Conversion Methods

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Abstract

C-Alkylation has been utilized in the solubilization of various coals. Low rank, high oxygen Illinois No.6 coal was alkylated with different alkylating agents under different conditions to determine the most suitable reaction conditions. A new method of alkylating coal with n-butyl lithium and potassium tertiary butoxide in refluxing heptane has been studied. The influence of the solvent for alkylation on the pyridine solubility of the product was studied. The pyridine solubility of the products obtained with n-butyl iodide ranged from 39% for the reaction in heptane to 51% for the reaction in tetrahydropyran. Tetrahydrofuran, in contrast, produced only 33% pyridine soluble product. The reactivity pattern for alkylation was determined by deuterium and carbon NMR spectroscopy of the products that were obtained with deuterium and carbon-13 labelled alkylating agents.

Introduction

The objective of our work is liquefaction of coal by depolymerization under mild conditions. Investigations of this kind on the chemical structure and the reactive sites of coal can help to select useful reactions for the production of liqiuds from coal. Sternberg et al. demonstrated that the reductive alkylation method transforms bituminous coal into an enormously soluble substance under very mild reaction conditions. [1] The effectiveness of newly introduced alkyl groups for the disruption of intermolecular hydrogen bonds and pi-pi interactions between the aromatic sheets in coal macromolecules has been recognized.[1-3]

It has been reported by Ignasiak et al. that a C-alkylation reaction using sodium or potassium amide in liquid ammonia can be used to introduce alkyl groups at acidic carbon sites. [4] Several other research groups have investigated these reactions,[5-8] and a method has been developed recently in this laboratory for the solubilization of high rank coals.[9] In the previous reports it was shown that n-butyl lithium and potassium t-butoxide in refluxing heptane produced coal anions which could be alkylated with different alkyl halides. Such alkylated coals (high ranking) were 92% soluble in pyridine. Though the solubilization of coal depended very much on the length of the alkyl group, it also depended very much on the nature of the base used. Strong bases like n-butyl lithium (pKa=42) can cause proton abstraction from aromatic structures, if the more acidic benzylic protons are absent. The utility of this procedure, which was initially developed and used by Miyake and Stock, has now been tested with the high oxygen containing, low rank Illinois No.6 and Wyodak coals. Both Illinois No.6 and Wyodak coal contain substantial amount of phenolic hydroxyl groups. These phenolic groups were exhaustively methylated with tetrabutylammonium hydroxide and methyl iodide, so that the influence of C-alkylation could be uniquely evaluated. Some reactions were carried out with the raw coals instead of the O-methylated coal. Recent results on the low rank coals are discussed in this report.

Experimental

Materials :

Coal samples used in this part of the project were Illinois No.6 hvc bituminous and Wyodak subbituminous, both supplied by the Premium Sample Program of Argonne National Laboratory.

The coal samples were dried at 110 °C (refluxing toluene) under vacuum for 48 hours prior to use. The solubility of the original coals in pyridine were 27 and 9% (daf) for Illinois No.6 and Wyodak coals, respectively.

Heptane (Aldrich) was purified by shaking with concentrated sulphuric acid followed by distillation and then stored in presence of Molecular sieve 5A. Other solvents used in the course of this study like tetrahydropyran, 2,2,5,5-tetramethyltetrahydrofuran, pentane, etc. were purchased and stored over molecular sieve 5A. Alkyl iodides (Aldrich) such as iodomethane, iodobutane and iodooctane were dried by molecular sieve 5A. Deuterium oxide 99.8% D (Aldrich) was used as obtained. Iodomethane-*13C* with 99.3 atom % *13C* (Isotec Inc.) was also used as obtained. Pyridine was purified by distillation and stored over potassium hydroxide pellets. The other chemicals such as n-butyllithium (1.6 M solution in hexane), potassium tertiary butoxide, ammonium chloride, methanol and hexane were used as received from Aldrich.

Typical reaction procedure for coal alkylation

Illinois No.6 was methylated with tetrabutylammonium hydroxide and methyl iodide by the method of Liotta.[10] About 25 grams of coal was suspended in dry tetrahydrofuran (150 ml) and stirred for 30 minutes. Tetrabutylammonium hydroxide (80 ml, 91 mmoles) was added and the mixture was stirred overnight. Then methyl iodide (25.4 grams, 179 mmoles) was added to the reaction mixture and stirred for 48 hours. The reaction mixture was then acidified with 1N hydrochloric acid to pH = 2. The flask was then placed on a rotary evaporator to remove tetrahydrofuran and the product was filtered and washed with 50% aqueous methanol (about 2L). This process was repeated one more time to ensure that all the phenolic hydroxyl groups were methylated. After thorough washing, the products were dried at 110 °C under vacuum for 48 hours. The infrared spectra of the products show substantial decrease in the hydroxyl stretching frequency around 3300 cm^{-1}. These O-methylated Illinois No.6 coals were used as starting materials for some of the subsequent reactions.

The C-alkylation reaction of the coal samples were carried out in the same manner as reported in the previous reports. In a flame dried three necked round-bottom flask (500 ml), n-heptane (170 ml), potassium t-butoxide (45 mmoles) and n-butyllithium (45 mmoles) were added. After the mixture was stirred for 30 minutes at room temperature, the coal sample (1.0

gram) was added and the solution was refluxed for 6 hours. The initial black solution turned brown when refluxing began. To this coal anion, the alkyl halide (60 mmoles) in n-heptane (50 ml) was added dropwise, after cooling the flask to 0 °C. The mixture was stirred for 48 hours at room temperature. After the reaction, the remaining base was quenched with ammonium chloride followed by methanol. Then the solvent and the excess alkyl halide were evaporated with a rotary evaporator and then subsequently at 100 °C under vacuum for 12 hours. The product was washed with acidified water-methanol mixture (3:1 volume ratio), aqueous methanol (3:1) (about 20 L) and finally with n-hexane (about 4L). The product was collected and dried to constant weight at 110 °C under high vacuum for 48 hours. A part of the dry product was subjected to Soxhlet extraction with pyridine. The number of alkyl groups introduced per 100 mol carbon were estimated from the increase in weight of the recovered product relative to the coal sample taken initially for reaction. Control experiments were conducted by the addition of ammonium chloride followed by methanol, in place of alkyl halide, after 6 hours of coal anionisation.

Solvents other than heptane were tried in some of the experiments described later, but the reaction conditions remained the same. In one reaction, the coal sample was treated with the "super base", at room temperature. Another reaction was carried out in which, instead of the addition of alkyl halide to the coal anion, the coal anion-base mixture was added to the alkyl halide all at once. These variations in the reaction conditions were performed to achieve optimum C-alkylation and solubilization.

Analysis of the Products :

Solution phase ^{13}C-NMR and ^{2}H-NMR spectra were recorded using a Varian XL-400 spectrometer. FT-IR of the products were taken using a Nicolet Model 20SX spectrometer. Potassium bromide pellets of the coal products (2-4 wt.%) were dried at 90 °C for 24 hours before recording a spectra.

Results and Discussion

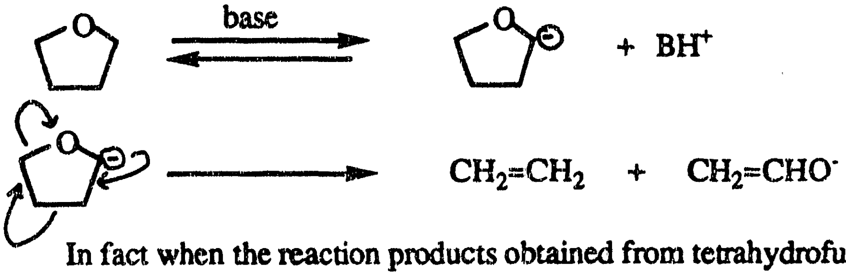
Only Illinois No.6 coal and its derivatives were studied in this phase of the work. In the previous report,[11] the dependence of the solubility on the nature of base used for alkylation was studied. There was not much difference in the solubility of the products when sodium amide was used instead of n-butyllithium/potassium tertiary butoxide. Also it was shown that the solubility of Illinois No.6 coal did not depend on the dimentions of the alkyl halide used for alkylation.[11]

Recently, investigations were carried out on the nature of the coal anions produced, the position of the carbon atoms in coal being alkylated and the effect of solvent on the pyridine extractibility of the coal. The O-methyl coal was treated with super base, as has been described before, and the "coal anion" was quenched with deuterium oxide. This reaction was used to prepare a "blank coal" sample, in which the acidic hydrogen atoms in coal (which were abstracted by the base) would be replaced by deuterium atoms. The positions of deuteriums could be determined by the ^{2}H-NMR of the pyridine extract of the product. The ^{2}H-NMR spectrum of the pyridine extract is shown in Figure 1.

Next the O-methyl coal sample, after the treatment with super base, was quenched with iodomethane-*C13*. This was done to locate the positions in coal being alkylated. The *C13*-NMR spectrum of the pyridine extract of the product is shown in Figure 2. The signals in the spectra indicate that substantial C-alkylation takes place together with O-alkylation. The nature and positions of the frequencies in the region around 15-30 ppm are consistent with the idea that benzylic or flourenic positions in coal are being alkylated. The O-methyl products may arise because certain ethers or hetrerocycles in the coal undergo cleavage during the reaction sequence. Attempts are being made to achieve better spectroscopic resolution so that more definite conclusions can be drawn. The same reaction (i.e. treatment with super base followed by iodomethane-*C13*) was also carried out with the pristine Illinois No.6 coal sample. The *C13* spectra of the pyridine soluble part of the product is shown in Figure 3. There is not much difference in the spectrum of this product when compared to Figure 2. Extensive C-alkylation takes place together with the expected degree of O-alkylation in this raw coal .

To be sure that the broad signals that appear in the Figures 2 and 3 are due to the *C13* label introduced into the coal and not due to the carbons present in coal itself, a *C-13* spectrum of the pyridine soluble part of the blank O-methyl coal was obtained (Figure 4). The blank sample was prepared by the reaction of O-methyl Illinois No.6 coal with super base followed by the addition of ammonium chloride/methanol. As is evident from the Figure 4, none of the carbon atoms present in coal are observed in the C-NMR spectra. The only signals that appear are due to pyridine-d_5 (solvent) in the low field and the signal near 80 ppm is due to chloroform-d (standard). Thus it becomes evident that the major signals in Figures 2 and 3 are entirely due to the labeled methyl groups and not due to carbon atoms from the coal.

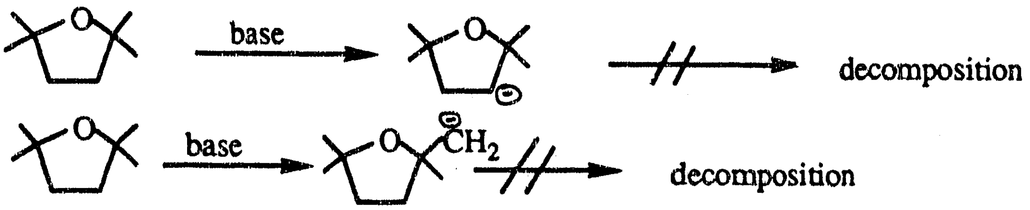
In subsequent reactions using the super base system, the role of the solvent was studied. Bates, who had used this procedure to trialkylate dimethylphenols, suggested that heptane was the solvent of choice .[12] Heptane, being a non-polar solvent, is certainly not the best solvent for ionic reactions. Also it does not swell the coal as well as certain other solvents . Thus, much of the coal structure, except for the surface, may remain inert to the reaction. Hence the efficiency of the reaction may be reduced. The most obvious solvent for the alkylation reaction would be tetrahydrofuran. It is also a very good solvent for coal swelling. But the use of tetrahydrofuran as the solvent failed. The pyridine solubility of the alkylated products decreased from 39% (in heptane) to 33 % (in tetrahydrofuran). The main reason is probably due to the decomposition of the solvent (tetrahydrofuran) in strongly basic medium. The solvent undergoes deprotonation in presence of the strong base and forms the tetrahydrofuranyl anion. This anion is the potential structure for the formation of stable acetaldehyde anion and ethene. Most likely, the tetrahydrofuranyl anion undergoes irreversible decomposition to ethene and acetaldehyde anion ;[13] the latter then undergoes base catalyzed polymerization.



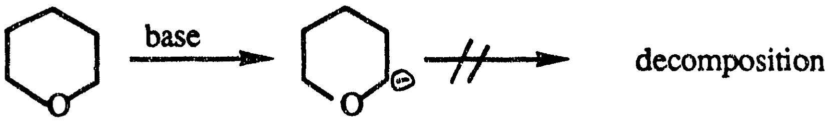
In fact when the reaction products obtained from tetrahydrofuran were washed and filtered, a deep red colored solution was obtained (it was not obtained when any other solvent was used). It is assumed that this coloration is due to the polymer formation, but this point was not tested.

Thinking that the high temperature of the reaction (67 °C) might be responsible for the decomposition of tetrahydrofuran, one reaction was carried out at -46 °C, without changing any other parameter. But once again the color of the wash solution was red and the pyridine solubility of the product was even worse (Table IIa).

Thus we needed a solvent which could play the same role as tetrahydrofuran. The use of 2,2,5,5-tetramethyltetrahydrofuran and tetrahydropyran gave very encouraging results. The probable reason is that both these solvents are stable in basic medium. The former solvent has no protons that can be abstracted by the base which eliminate the path to acetaldehyde anion.



So, at least theoritically, tetramethyltetrahydrofuran should react like tetrahydrofuran, though it is bulkier. The other solvent, tetrahydropyran, does not decompose either in strong base to form any stable anion. The pentamethylene bridge makes tetrahydropyran more stable than tetrahydrofuran in strongly basic medium.



Hence we expected better results with these two solvents because they can penetrate the coal structure and transport the other reagents. As shown as in Table II b, the extent of carbon alkylation does not differ very much but the pyridine extractability of the products differ considerably (Figure 2). The pyridine solubility of the products increase from 33% in tetrahydrofuran to 45% in tetramethyltetrahydrofuran to 51% in tetrahydropyran. Silmilar results were also obtained for a different set of experiments when the alkyl halide was changed from n-butyl iodide to n-octyl iodide. The results are presented in Table II c. Hence we can conclude that C-alkylation reactions with "super bases" are more successful in tetrahydropyran than in heptane.

The use of pentane as a solvent at room temperature did not increase the solubility. The results are shown in Table III. Various procedures were tried to get an optimum condition for alkylation. In one particular reaction, after the coal was refluxed with base, the mixture was poured into the alkyl halide so that the concentration of the alkyl halide remained in excess. Both the extent of alkylation and solubility did not change very much. In yet another reaction, after the addition of alkyl halide to the coal anion, the reaction mixture was quenched with ammonium chloride - methanol after one hour (normal reaction time is 48 hours). As shown in the results in Table III, the pyridine solubility of the product was low. The extent of reaction probably was not sufficient enough to give a more soluble product.

Calculations :

In the reaction where the O-methylated Illinois No.6 coal was treated with super base, and quenched with deuterium oxide, the number of anions formed per gram of coal was calculated from the number of deuterium atoms incorporated.

Reaction :

$$\text{Ill. No.6 (OMe)} \xrightarrow[\text{heptane, reflux}]{\text{super base}} \{\text{ Ill. No.6 (OMe) }\}^{-n} + n\ \text{BuH}$$

$$\{\text{ Ill. No.6 (OMe) }\}^{-n} \xrightarrow{D_2O} \{\text{ Ill. No.6 (OMe)-}d_n\ \} + OD^-$$

The 2H- NMR of the pyridine extract of the product is shown in Figure 1.

CD_2Cl_2 (99.6% ; Aldrich) was added as the internal standard.

Volume of CD_2Cl_2 added = 0.5 µl

Weight of CD_2Cl_2 added = 0.681×10^{-3} grams

and 0.681×10^{-3} grams of CD_2Cl_2 (99.6%) = 93.914×10^{17} atoms of of D

Integration ratio (from Figure 1) = 4.61

$$\text{ie- } \frac{\text{atoms of 'D' in } CD_2Cl_2}{\text{atoms of 'D' in coal}} = 4.61$$

atoms of 'D' in coal = $93.914 \times 10^{17} / 4.61$ = 20.372×10^{17}

Amount of coal sample taken for the NMR = 0.005 grams.

Thus, in 0.005 grams of the coal, deuterium atoms present = 20.372×10^{17}

Therefore, in 1.0 gram of the coal, deuterium atoms present = 4.0744×10^{20}

Thus in the pyridine soluble part of the product, deuterium atoms present = 4.0744×10^{20} atoms per gram of coal.

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Table I.

Pyridine solubility of the O-methylated Illinois No.6 coal treated with "super base" and quenched with various electrophiles.

Coal type	Nature of the electrophile	Pyridine solubility (wt%)
Ill. #6 (OMe)	NH_4Cl / MeOH	40
"	D_2O	42
"	$^{13}CH_3I$	46
Raw Ill #6	$^{13}CH_3I$	35

Table II a :

Influence of the temperature of reaction on the pyridine solubility of the product in tetrahydrofuran.

Ill. #6 (OMe) $\xrightarrow[\text{reflux}]{\text{super base}}$ $\xrightarrow{\text{n-butyl iodide}}$ Product.

Coal used	solvent of alkylation	Reaction temperature (°C)	Number of alkyls per 100 carbons[a]	Pyridine solubility (wt%)
Ill. #6 (OMe)	THF	-46	4.1	30
Ill. #6 (OMe)	THF	+67	4.2	33

Table II b :

Influence of the solvent of alkylation, on the pyridine solubility of the product.

Ill. #6 (OMe) $\xrightarrow[\text{reflux}]{\text{super base}}$ $\xrightarrow{\text{n-butyl iodide}}$ Product.

Coal used	solvent of alkylation	Reaction temperature (°C)	Number of alkyls per 100 carbons[a]	Pyridine solubility (wt%)
Ill. #6 (OMe)	heptane	98	4.5	39
Ill. #6 (OMe)	THF	67	4.2	33
Ill. #6 (OMe)	tetramethyl-tetrahydrofuran	112	3.2	45
Ill. #6 (OMe)	tetrahydropyran	88	3.9	51

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[a] The degree of alkylation was estimated from the increase in weight after the reaction.

Table II c :

Influence of the solvent of alkylation, on the pyridine solubility of the product.

$$\text{Ill. \#6 (OMe)} \xrightarrow[\text{reflux}]{\text{super base}} \xrightarrow{\text{n-octyl iodide}} \text{Product.}$$

Coal used	solvent of alkylation	Reaction temperature (°C)	Number of alkyls per 100 carbons[a]	Pyridine solubility (wt%)
Ill. #6 (OMe)	heptane	98	2.4	43
Ill. #6 (OMe)	tetrahydro-pyran	88	3.4	51

[a] The degree of alkylation was estimated from the increase in weight after the reaction.

Table III :

Effect of changes made in the reaction conditions of alkylation on the pyridine solubility of the products.

Ill. #6 (OMe) $\xrightarrow[\text{reflux}]{\text{super base}}$ $\xrightarrow{\text{n-butyl iodide}}$ Product.

Coal used	solvent of alkylation	Reaction temperature (°C)	Nature of change in the reaction condition	Pyridine solubility(wt%)
Ill. #6 (OMe)	heptane	98	alkyl halide added to the coal anion (normal way)	39
Ill. #6 (OMe)	pentane	25	"	41
Ill. #6 (OMe)	heptane	98	coal anion added to the alkyl halide solution (inverse addition)	32
Ill. #6 (OMe)	heptane	98	alkyl halide added to the coal anion as usual, but the reaction mixture was quenched after 1 hour, instead of the usual 48 hours	33

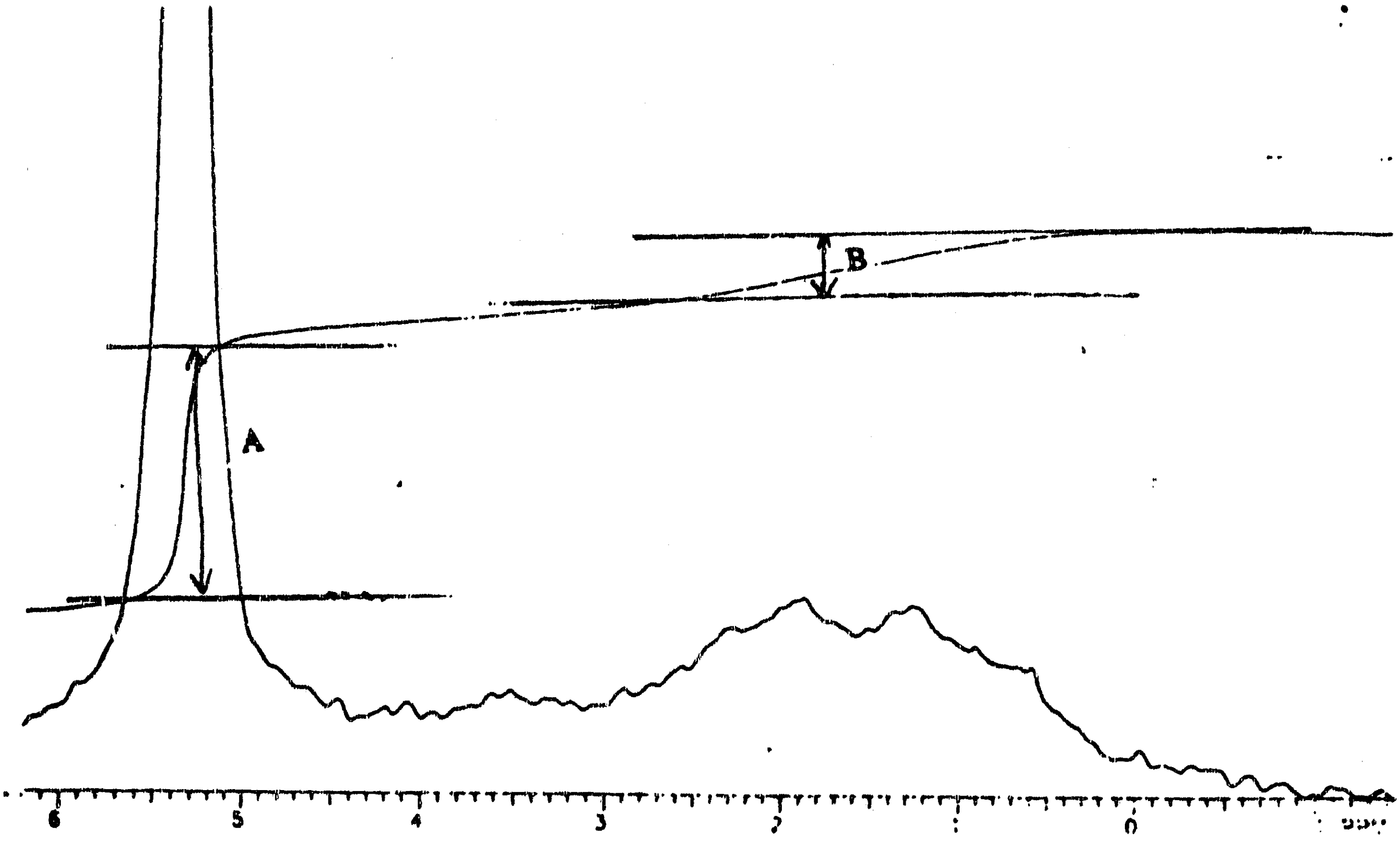

Figure 1. 2H-NMR spectra of Illinois No.6 (OMe) coal treated with "super base" and quenched with deuterium oxide (pyridine soluble part).
The ratio A / B = 4.61

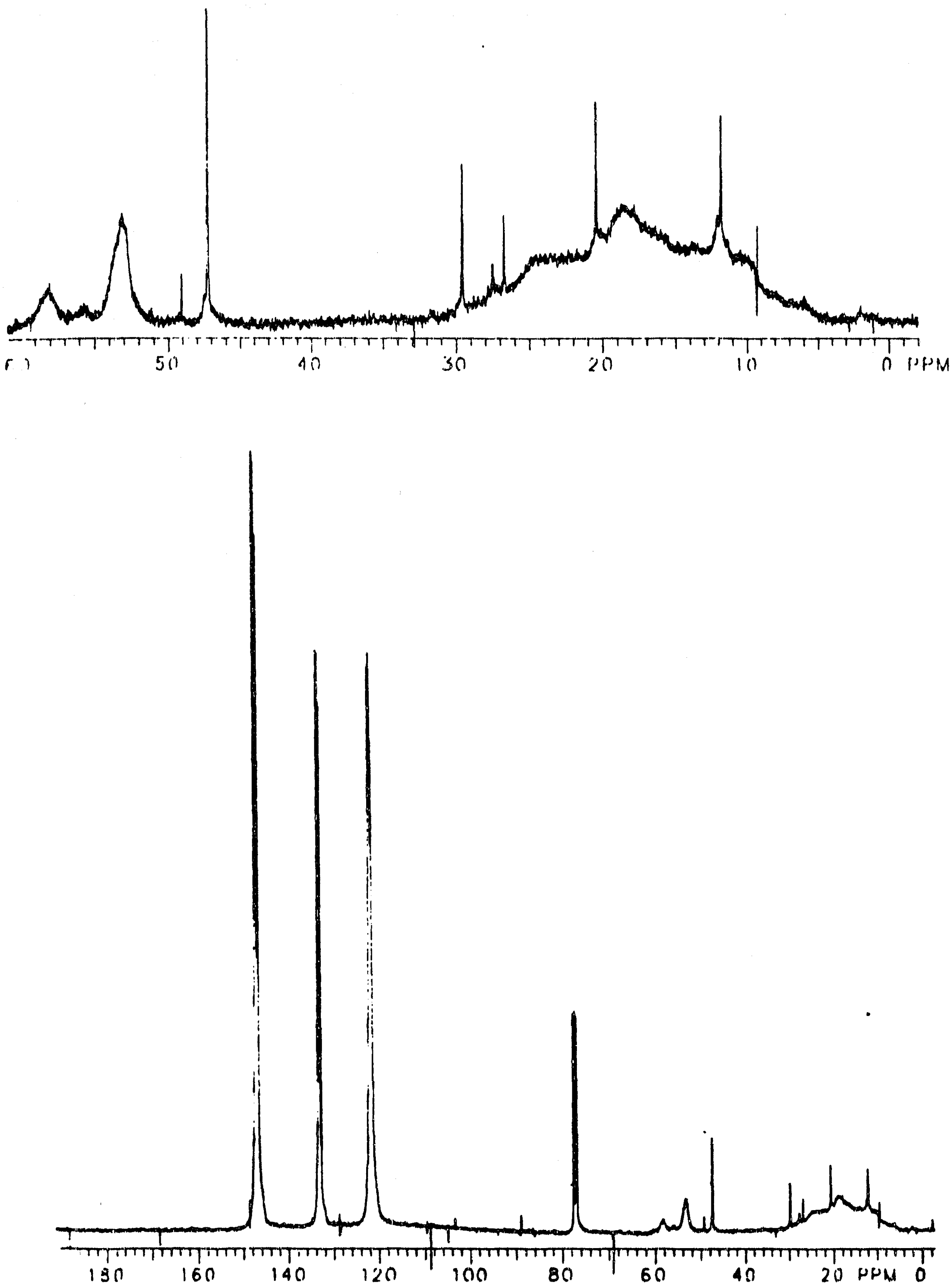

Figure 2. 13C- NMR spectra of the product (pyridine soluble part) of the reaction of Ill #6 (OMe) coal with super base and 13C- iodomethane. The region of interest is between 10 to 65 ppm.

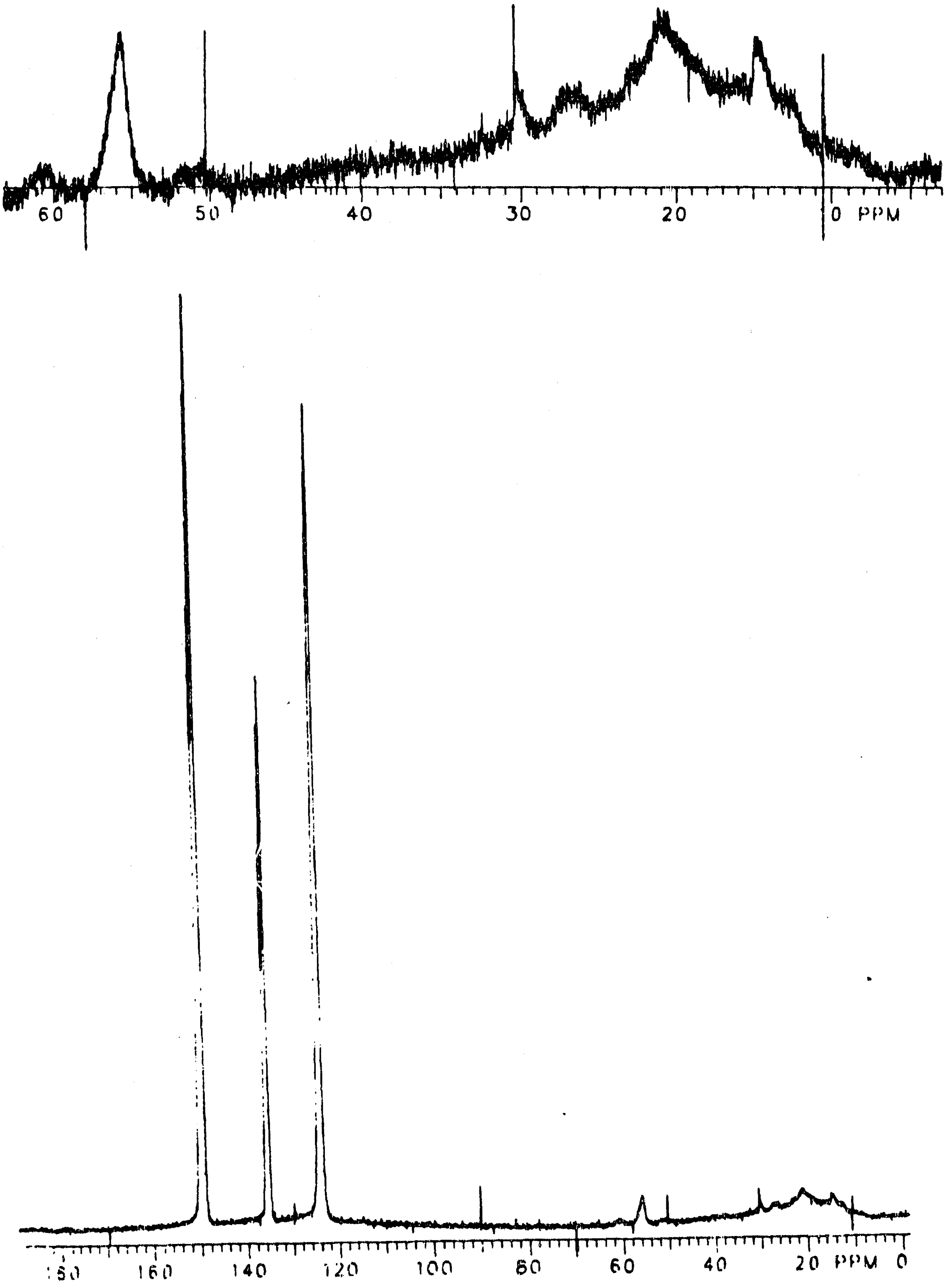

Figure 3. 13C- NMR spectra of the product (pyridine soluble part) of the reaction of raw Ill #6 coal with super base and 13C- iodomethane. The region of interest is between 10 to 65 ppm.

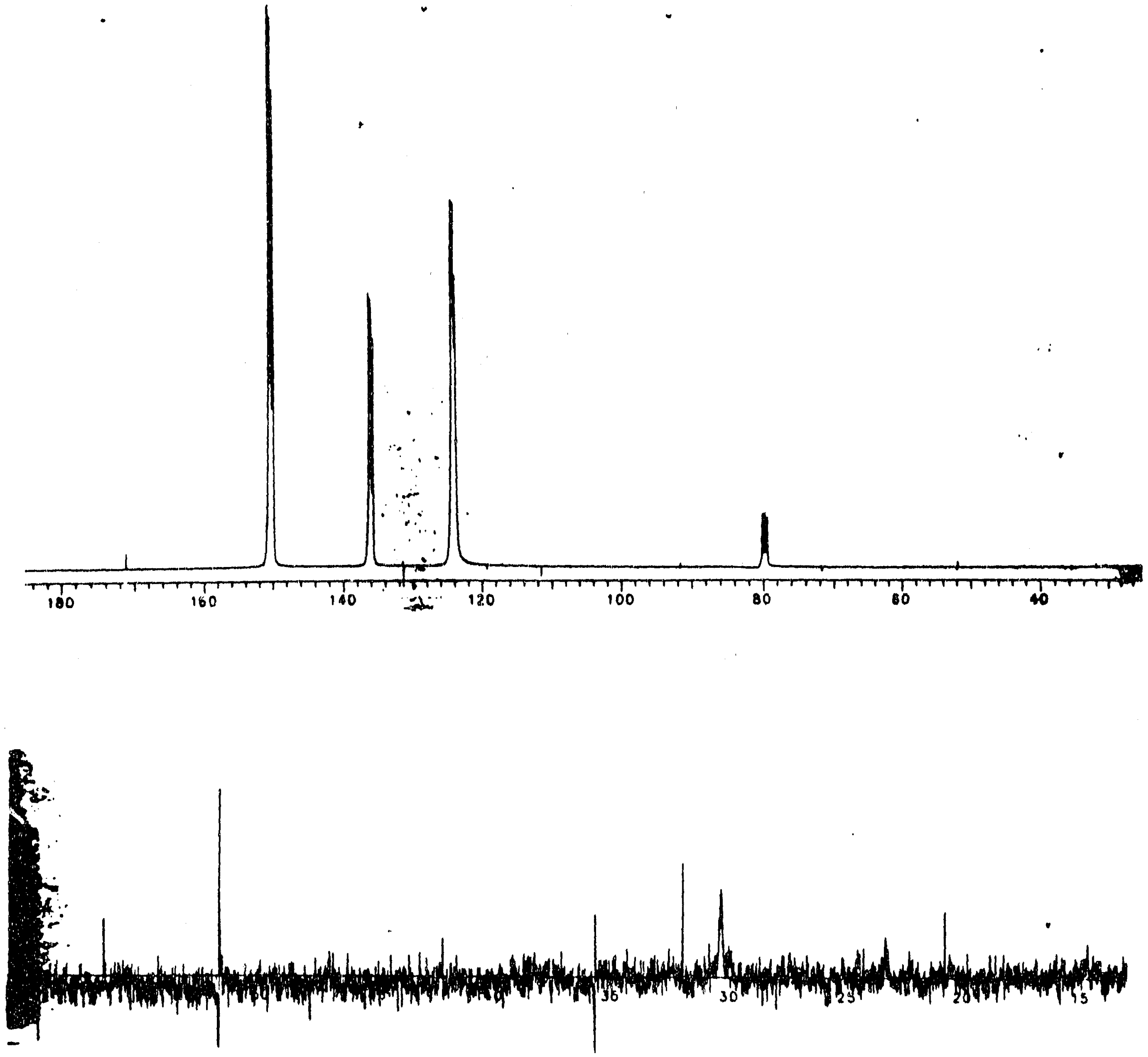

Figure 4. 13C- NMR spectra of the product (pyridine soluble part) of the reaction of Ill #6 (OMe) coal with super base and ammonium chloride / methanol.

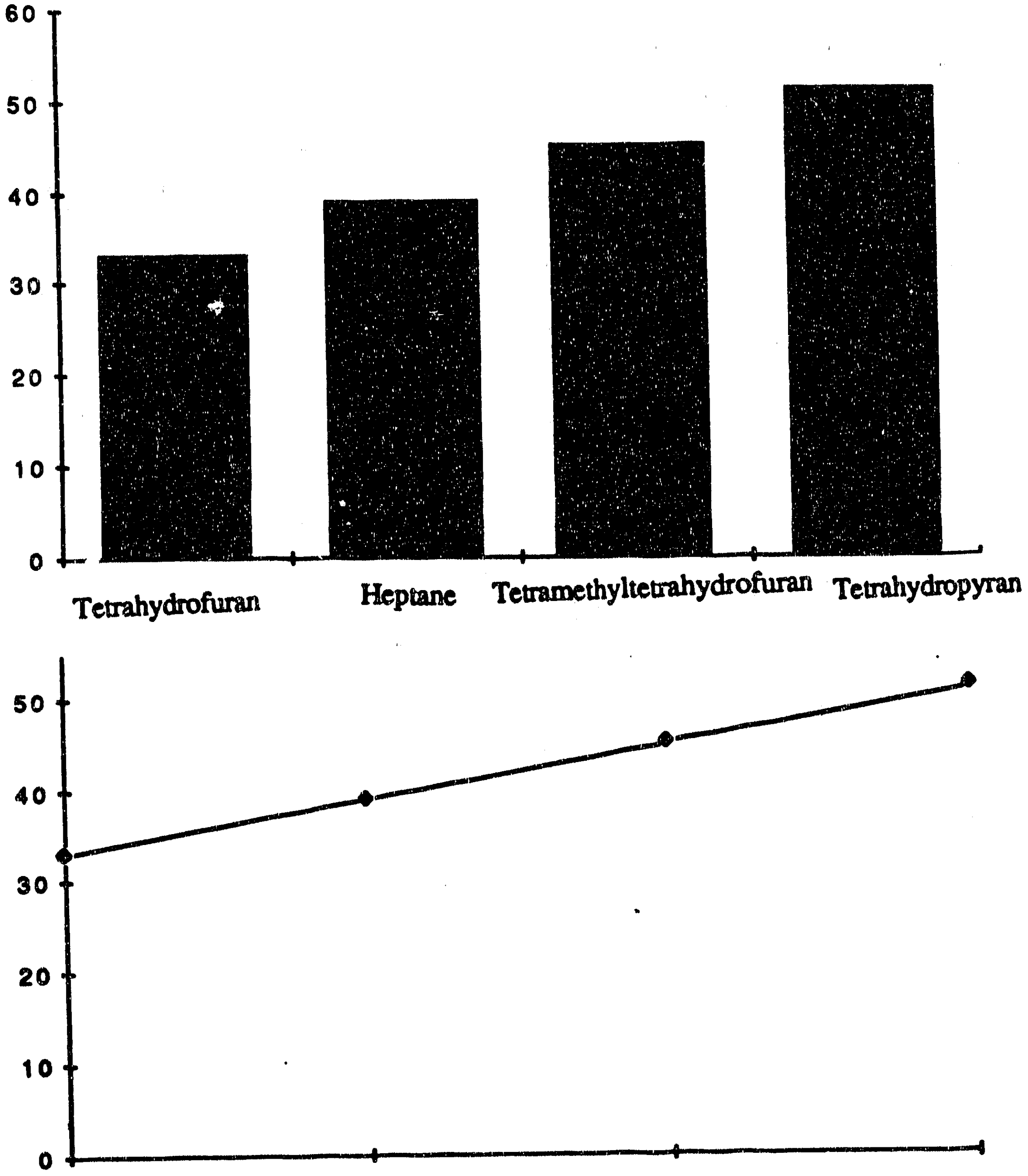

Figure 5. The influence of the solvent of alkylation on the pyridine solubility of the products.

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