

COAL SOLUBILIZATION THROUGH C-ALKYLATION

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INTRODUCTION

C-Alkylation is an attractive process for the disruption of the intermolecular polarization forces that contribute to the binding of coal molecules in the solid state (1,2). This contribution concerns the use of a powerfully basic reaction system that consists of a 1:1 mixture of *n*-butyllithium and potassium *t*-butoxide, super base, to promote the C-alkylation reaction of coal with an alkyl halide (3). This choice was prompted by the work of Bates and his coworkers who showed that dimethylphenol was readily converted to diethylanisole with *n*-butyllithium-potassium *t*-butoxide and methyl iodide (4).

EXPERIMENTAL SECTION

Coals. The coals that were used in this investigation included Wyodak (APC 2), Illinois No. 6 (APC 3), Pocahontas No. 3 (APC 5), and Lower Kittanning (PSOC 1197). The Wyodak and Illinois coals were *O*-methylated by the procedure of Liotta and coworkers (5).

Procedure. The C-alkylation reactions of the coal samples were carried out essentially as reported by Bates and his coworkers (4). *n*-Heptane (170 ml), potassium *t*-butoxide (5.04 g, 45 mmoles) and *n*-butyllithium (30 ml, 1.6 M solution in hexane, 45 mmoles) were added to a flame dried flask. The mixture was stirred at room temperature for 15 minutes, the coal sample (1 g) was added, and the solution was refluxed for 6 hours. The initial black solution turned brown when refluxing began. *n*-Butyl iodide (11.0 g, 60 mmoles) in *n*-heptane (70 ml) was added dropwise to this coal anion suspension, after cooling the flask at 0 C. The mixture was stirred for 48 hours at room temperature to ensure complete alkylation of the coal anions. The residual base was quenched by adding ammonium chloride and methanol. The solvents and the excess *n*-butyl iodide were removed by a rotary evaporator. The product was carefully collected and washed with an acidic solution of water and methanol (3:1 by volume), aqueous methanol (3:1, 20 L) and *n*-hexane (4 L). The product was dried to constant weight at 110 C under vacuum for 48 hours. A portion of each product was subjected to Soxhlet extraction with pyridine.

RESULTS

The Lower Kittanning coal, PSOC 1197, was studied first. This high rank coal is only 5% soluble in pyridine. Previous work established that the sodium amide promoted butylation yielded a product that was 50% soluble in pyridine (2). Previously, Chambers and his coworkers found that 1.8 methyl groups per

100 mol carbon were introduced into this coal by three successive treatments with a weaker alkyl lithium base and that the thrice methylated coal was merely 30% soluble in pyridine (6).

The results for the super base promoted C-alkylation reaction of PSOC 1197 are summarized in Table I.

In parallel experiments, we observed that the butylated products that were obtained through the reaction of n-butyllithium in tetrahydrofuran and through the reaction of sodium amide in ammonia were only 10 and 50% soluble in pyridine, respectively. In contrast, butylation with super base in heptane provided a 90% soluble product. There may be a direct relationship between the strength of base and the degree of solubility of the alkylated product of this coal. The information that is presented in Table I suggests that about 4 butyl groups per 100 mol carbon are introduced into the coal in the super base system.

Another relatively high ranking bituminous coal, Pocahontas No. 3, was also studied. The butylation and octylation of this coal converted it to a material that was 55% soluble in pyridine.

Further work on the C-octylation of Wyodak and Illinois No. 6 coal and the octylation of their O-methylated derivatives, Table II, implies that these materials can be converted to substances that are 30 to 40% soluble in pyridine.

DISCUSSION

Super base is an especially effective reagent for the C-alkylation and solubilization of the two higher ranking coals. Unreacted Pocahontas No. 3 and Lower Kittanning coals are merely 2 and 5% soluble in pyridine, respectively. C-Octylation with super base provides materials that, after acid hydrolysis, are 55 and 92% soluble in this solvent.

It is pertinent to note that treatment of the Lower Kittanning coal with super base followed by acid hydrolysis with ammonium chloride in methanol at ice temperatures provides unalkylated coal that is 39% soluble in pyridine. Clearly, treatment with the base alone must alter the structure in a significant way. We postulate that the carbanions formed by the base undergo fragmentation reactions to reduce the mass of the macromolecules in the coal and that this transformation increases the solubility (7). C-Octylation enhances the solubility to an even greater degree. Inasmuch as the degree of solubilization depends upon the dimensions of the electrophilic reagent, we postulate that the larger n-alkyl groups enhance solubility by the disruption of intermolecular polarization forces (2).

The lower ranking coals are much more difficult to solubilize through treatment with base and C-alkylation. The pyridine solubility of Wyodak is increased from 9% to 37% by exhaustion O-octylation. No significant improvement in solubility was realized by C-octylation of the O-methylated coal.

Similar results were obtained with the Illinois No. 6 coal. It is 27% soluble in pyridine. This solubility is increased to 33% by O-octylation and to 43% by C-octylation of the O-methylated coal. The results indicate that only modest increases in solubility are achieved through the C-alkylation of these coals.

Several factors can contribute to the striking difference between the impact of base promoted C-alkylation on the solubility of the high and low rank coals, but only two factors will be mentioned here. First, there may be major differences in the sizes of the coal macromolecules that are present in these coals. Our observations appear to be in accord with the observations of Ouchi and his coworkers who suggested that the higher rank coals have highly condensed aromatic rings but a modest degree of polymerization (2,8). In this situation, reaction chemistry that cleaves carbon-carbon bonds and simultaneously adds large alkyl groups to disrupt the intermolecular polarization forces between the constituents can have a large influence on solubility. Second, there may be appreciable differences in the opportunities for base-catalyzed elimination reactions in the hydrocarbon-like, structurally condensed high rank coals and the oxygen-atom rich, low rank coals with their smaller ring structures. No specific suggestions can be made at this time concerning the relative importance of these factors and of other factors that arise because of constitutional differences such as, dipole-dipole interactions between the oxygen containing structural elements of the alkylated low rank coal, and because of the intermolecular and intramolecular steric strains that arise between the condensed hydrocarbons of the high rank coals.

SUMMARY

The n-butyllithium-potassium t-butoxide reagent system is more effective than other reagent systems for the C-alkylation and solubilization of coals. The yields of soluble products, which range from 33 to 92%, appear to depend upon coal rank. Although only tentative explanations for the differences in the degree of solubilization can be advanced at this time, we suggest that super base cleaves carbon-carbon bonds in the high rank coals and that the C-alkyl groups diminish intermolecular polarization forces to render the materials soluble.

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Table I. The C-Alkylation of Lower Kittanning Coal, PSOC 1197.

reaction conditions: base, solvent, temperature, time	electrophile	alkyl groups per 100 mol C	solubility, wt % in pyridine ^a
n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours.	NH ₄ Cl	-	39
n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours.	n-C ₄ H ₉ I	4.2	90
n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours	n-C ₈ H ₁₇ I	2.8	92

^aApproximately 5 wt% of the original coal could be extracted into pyridine.

Table II. The C-Octylation of the Two Low Rank Coals.

coal	reaction conditions: base, solvent, temperature time.	octyl groups per 100 mol C	solubility, wt % in pyridine ^a
Illinois No. 6			
raw	KOH, THF, 25°C, 6 hours	3.4	33
(OMe)	n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours.	2.4	43
Wyodak			
raw	Bu ₄ NOH, THF, 25°C, 6 hours	3.2	37
raw	n-C ₄ H ₉ Li + t-C ₄ H ₉ OK (1:1), n-heptane, 98°C, 6 hours	2.2	33
(OMe)	n-C ₄ H ₉ Li + t-C ₄ H ₉ OK 9 (1:1), n-heptane, 98°C, 6 hours	2.5	20

^aApproximately 27 wt% of the original Illinois No. 6 coals and 9% of the original Wyodak coal could be extracted into pyridine.