

## SOLUBILIZATION OF HIGH RANK POCAHONTAS NO. 3 COAL

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### INTRODUCTION

Reductive and non-reductive alkylation reactions are efficient methods of coal solubilization (1). C-Alkylation reactions using the strongly basic mixture of *n*-butyllithium and potassium *tert*-butoxide (called Lochmann's base) were successful for the near quantitative solubilization of Lower Kittanning coal (2). This contribution concerns the use of this reagent to promote C-alkylation of a high rank coal, Pocahontas No. 3, from the Premium Sample Program of Argonne National Laboratory. Evidence will also be presented to show that, apart from promoting C-alkylation, the basic reagent can alter the coal macromolecular structure by forming smaller fragments through hydrocarbon  $\beta$ -elimination reactions.

### EXPERIMENTAL SECTION.

Materials. Pocahontas No. 3 coal, APCSP 5, was supplied by the Premium Sample Program of the Argonne National Laboratory (Anal. C, 91.1; H, 4.4;

N, 1.3; S, 0.5; O (by difference) 2.7; ash 4.7). The coal samples were dried at 110 °C under vacuum for 48 h prior to use.

*n*-Heptane (Aldrich) was shaken with concentrated sulfuric acid and subsequently distilled. The purified solvent was stored in the presence of molecular sieve 5A. Pyridine was purified by distillation over barium oxide. The alkyl iodides were obtained from Aldrich and were dried over molecular sieve 5A. The other chemicals such as *n*-butyllithium (1.6 M solution in hexane), potassium *tert*-butoxide, ammonium chloride and methanol were used as received from Aldrich Chemical Company.

Reaction Procedure for the Coal Sample. The C-alkylation reactions of the coal sample were carried out as reported earlier (2,3). *n*-Heptane (170 mL), potassium *tert*-butoxide (5.01g, 45 mmol) and *n*-butyllithium (30 mL, 1.6 M solution in hexane, 48 mmol) were added to a flame dried flask. The mixture was stirred at room temperature for 15 min, the coal sample (1g) was added, and the solution was refluxed for 6 h. The initial black solution turned brown when refluxing began. The alkyl iodide (55 to 60 mmol) was added dropwise to this coal anion suspension, after cooling the flask at 0 °C. The mixture was stirred for 48 h at room temperature to ensure complete alkylation of the coal anions. The residual base was quenched by adding ammonium-chloride and methanol. The solvents 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 (4L). The product was dried to constant weight at 110 °C under vacuum for 48 h. A portion of each of the product was subjected to Soxhlet extraction with pyridine.

In order to investigate bond cleavage reactions with bases, the coal anions were quenched with dilute acids instead of alkyl halides. The products thus obtained were washed and dried as usual and were subjected to pyridine extractions. In order to establish the optimum conditions for solubilization, the reaction conditions, the nature of base used, and the length of the alkyl group in the alkyl iodide were varied. The results are presented in the Tables.

## RESULTS

The C-alkylation reaction of Pocahontas No. 3 coal (APCSP 5) with sodium amide in liquid ammonia was studied first. Previous work in our laboratory using sodium amide in liquid ammonia with another high rank coal, Lower Kittanning coal, PSOC 1197, gave significantly soluble alkylated products (4). As shown in Table I, the solubility of the products increased with an increase in length of the alkyl group. With 45 mmol of the base per gram of coal, the octylated product was about 38% soluble in pyridine. It should be mentioned that the raw coal is only 5% soluble in pyridine.

The solubility of the products increased when the base concentration was increased. With 15 mmol of sodium amide, the butylated product was only 13% soluble whereas with 200 mmol of the base, the butylated product was 46% soluble.

When a stronger base was used to alkylate this coal, better results were obtained. The results of Lochmann's base promoted C-alkylations of Pocahontas No. 3 are summarized in Table II.

When the coal was treated with Lochmann's base in refluxing heptane for 6 h and quenched with methyl iodide, the product was 45% soluble in pyridine (compared to only 12% with sodium amide). However, when the coal was butylated with *n*-butyl iodide, the solubility of the product remained at 45%. In addition, when the coal was refluxed with the base for 18 h instead of 6 h, a 10% increase in solubility was observed. Once again both the butylated and octylated products gave the same solubility (55%).

We next probed for the occurrence of carbon-carbon bond cleavage reactions with very strong bases. The results are shown in Table III. Use of sodium amide in liquid ammonia at -75 °C, *n*-butyllithium at 98 °C, potassium *tert*-butoxide at 98 °C and Lochmann's base at 98 °C show that only Lochmann's base provides any evidence for C-C bond cleavage.

#### DISCUSSION

Non-reductive C-alkylation reactions of Pocahontas No. 3 coal with sodium amide in liquid ammonia convert the 5% soluble coal to a material which is 46% soluble. The increase in solubility with the increase in the size of alkyl group is in agreement with our previous results (4). The larger groups can disrupt the intermolecular polarization forces thereby enhancing solubility. However, the fact that a higher concentration of the base enhances the solubility to a greater extent suggested that other factors are also important.

Lochmann's base appears to be a superior reagent for the conversion of the coal into soluble materials. The extent of solubilization is

virtually independent of the size of the alkyl group, and the methylated and butylated products are equally soluble. When the coal was treated with the base for 18 rather than 6 hours, there was a modest enhancement in the solubility of the product.

The results in Table III suggested that a prominent reason for the high solubility of the products obtained after Lochmann's base are due to carbon-carbon bond cleavage. When the coal sample was treated with Lochmann's base in refluxing heptane and quenched with dilute acid, the solubility of the coal increased from 5% to about 35% depending on the time of reaction. Thus base treatment alone can convert the coal to soluble materials. We infer that the strong base forms carbanions that can fragment via  $\beta$ -elimination as previously proposed (1(B), 5).

#### CONCLUSION

The Lochmann's base system is more effective than any other base system for the C-alkylation and solubilization of high rank Pocahontas No. 3 coal. Our results suggest that coal carbanions undergo fragmentation to reduce the molecular dimensions. The solubility realized by these fragmentation reactions is enhanced by C-alkylation reactions.

#### ACKNOWLEDGEMENT

We acknowledge the support of this work from the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy.

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Table I. The C-alkylation of Pocahontas No. 3 coal with sodium amide in liquid ammonia.

reaction conditions: base, solvent, temperature, time	electrophile	solubility, wt% in pyridine
raw coal	-	5
coal ; NaNH <sub>2</sub> (45 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h	CH <sub>3</sub> I	12
coal ; NaNH <sub>2</sub> (45 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	21
coal ; NaNH <sub>2</sub> (45 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h	<i>n</i> -C <sub>8</sub> H <sub>17</sub> I	38
coal ; NaNH <sub>2</sub> (15 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	13
coal ; NaNH <sub>2</sub> (100 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	31
coal ; NaNH <sub>2</sub> (200 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	46

Table II. The C-alkylation of Pocahontas No. 3 coal with Lochmann's base.

reaction conditions: base, solvent, temperature, time	electrophile	solubility, wt% in pyridine
raw coal	-	5
coal; <i>n</i> -BuLi + <i>Kr</i> -OBu (1:1), heptane, 98 °C, 6 h	CH <sub>3</sub> I	45
coal; <i>n</i> -BuLi + <i>Kr</i> -OBu (1:1), heptane, 98 °C, 6 h	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	45
coal; <i>n</i> -BuLi + <i>Kr</i> -OBu (1:1), heptane, 98 °C, 18 h	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	55
coal; <i>n</i> -BuLi + <i>Kr</i> -OBu (1:1), heptane, 98 °C, 18 h	<i>n</i> -C <sub>8</sub> H <sub>17</sub> I	55

Table III. Base promoted solubilization reactions of Pocahontas No. 3 coal.

reaction conditions	product recovered, %	solubility, wt% in pyridine
raw coal	-	5
coal ; NaNH <sub>2</sub> (45 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h, protonation	92	5
coal ; NaNH <sub>2</sub> (100 mmol / g), NH <sub>3</sub> (l), -75 °C, 6 h, protonation	99	9
coal ; <i>n</i> -BuLi (45 mmol / g), heptane, 98 °C, 6 h, protonation	89	8
coal ; <i>Kt</i> -OBu (45 mmol / g), heptane, 98 °C, 6 h, protonation	91	10
coal ; Lochmann's base (45 mmol / g), heptane, 98 °C, 6 h, protonation	88	32
coal; Lochmann's base (45 mmol /g) heptane, 98 °C, 18 h, protonation	105	39