

## COAL SOLUBILIZATION USING METAL ALKOXIDES IN REFLUXING ALCOHOLS

Kuntal Chatterjee, Sao Jiralerspong and Leon M. Stock  
Department of Chemistry, The University of Chicago  
5735 South Ellis Ave., Chicago, IL 60637

### INTRODUCTION

The inability to quantitatively solubilize coal in common organic solvents has been a detriment to the use and study of this vast fuel resource. Our efforts in the past few years have been directed toward its solubilization through O- and C-alkylation and base-promoted depolymerization.<sup>1</sup> O-Alkylation, which completely disrupts intermolecular hydrogen bonding, only increases the solubility of low rank coals such as Wyodak and Illinois No. 6 coals to the 35% level.<sup>1</sup> C-Alkylation, which can be extremely effective for the solubilization of high rank coals, is only moderately more effective for these coals than O-alkylation alone.<sup>2</sup> We were intrigued by the possibility that their solubilization could be improved by basic reagents without alkylation when we found that two high rank coals were rendered about 40% soluble merely by treatment with strong bases (most notably Lochmann's base).<sup>3</sup> We concluded that this procedure was effective because the carbanions generated by the strong bases underwent carbon-carbon bond cleavage and produced smaller, more soluble coal fragments.<sup>3</sup> Our prior work with basic reagents did not convert the two low rank coals to soluble products and we reasoned that the carbanions that are produced by very strong bases also undergo condensation reactions to retrogressively increase the size of the coal molecules. We, therefore, sought to eliminate this undesirable reaction by trapping the carbanions with a proton donor. The present study describes an approach to solubilize Illinois No. 6 coal (APCSP 3) by base treatment with metal alkoxides in refluxing proton donating alcohols.

### EXPERIMENTAL SECTION

*Materials.* The Illinois No. 6 coal (APCSP 3) was obtained from the Premium Sample Program at Argonne National Laboratory.<sup>4</sup> Elemental analysis (wt.%) of moisture-free coal: C, 65.7; H, 4.2; N, 1.2; S, 4.8; O (by difference) 9.8; Ash, 14.3. Pyridine was purified by distillation over barium oxide. Sodium, potassium, sodium methoxide, *n*-octanol, and benzyl alcohol were used as received from Aldrich Chemical Company. Methanol, *n*-butanol, and *tert*-butanol were used as received from J.T. Baker Inc.

*General Reaction Procedure.* In general, the alcohol (420 mmol) and solid potassium (80 mmol) were added to a flame-dried round-bottom flask and stirred under dinitrogen at room temperature for 30 to 45 minutes to form the metal alkoxide. The coal (2 g) was then added and the reaction mixture was stirred for 5 minutes before heating to reflux. Usually, a small pool of potassium was visible when the coal was added. The reaction mixture was refluxed for 24 hours. It was cooled in a 0 °C bath and any remaining base was diluted with *tert*-butanol followed by methanol and water. It was then acidified with dilute hydrochloric acid (2 M) until the pH was less than 1. This acidified mixture was stirred under dinitrogen for 48 hours and the solvents were removed from the reaction product either by rotary evaporation or by vacuum distillation, depending upon the boiling points of the solvents. The reaction product was then washed under dinitrogen on a Nucleopore polycarbonate membrane filter (pore size 0.8 mm) with dilute hydrochloric acid (2 M, 5 L), with methanol until the filtrate was colorless (8 L), and with aqueous methanol (50% by

volume) until the filtrate was free of halide ions (12 L). Finally, the reaction product was dried at 110°C under high vacuum for 48 hours. A sample was submitted for elemental analysis.

A portion of the product was subjected to pyridine extraction and unless otherwise mentioned, the solubility of the reaction product was determined from the weight of the insoluble portion.

*Analysis of Products.* Elemental analyses were performed by Commercial Testing and Engineering Company of South Holland, Illinois. Infrared spectroscopy was carried out on a Nicolet 20SXB FTIR spectrometer. <sup>2</sup>H NMR spectroscopy was carried out on a Varian XL-400 spectrometer.

## RESULTS AND DISCUSSION

Significant work has been done with alcohols as solvents and reagents for the liquefaction of coal. Use of low boiling alcohols under super critical conditions or in hydrogen donor solvents in the presence or absence of bases has been investigated by a number of workers.<sup>5-7</sup> Ross *et al.* have investigated potassium isopropoxide in isopropanol and potassium hydroxide in methanol at 400 °C.<sup>5</sup> More recently, Ouchi and his coworkers have reported the reactions of coals with ethanolic sodium hydroxide at temperatures ranging from 260 to 450 °C.<sup>6</sup> Similar reactions were also performed with ethylene glycol as solvent by Winans *et al.*<sup>7</sup> The yields of the liquified coals in these studies were high but the conditions were also severe. We sought milder conditions for the conversion so that the side reactions, if any, could be minimized. Also, some investigators have neglected the possibility that alcohols transform and adduct to coal molecules. Accordingly, we measured the conversion exclusively on the basis of the weight of the insoluble coal residue.

Potassium or sodium alkoxides, as described in the Experimental Section, were used in different alcohols at reflux for 24 hours and then the products were quenched with dilute acid. The results are presented in Table 1.

The reaction of Illinois no. 6 coal with sodium methoxide in refluxing methanol yielded a product which was only 33% soluble in pyridine. The pyridine solubility of the raw coal is 27%. Treatment with potassium *n*- and *tert*-butoxide in *n*- and *tert*-butanol with boiling points 118 and 83°C, respectively, increased the solubility of the coal to 42%. There was no significant difference between the effectiveness of the two isomeric butanols. Potassium *n*-octoxide in *n*-octanol (b.p. 196°C) gave an even more soluble product, 53%. Finally, potassium and sodium benzoxide in refluxing benzyl alcohol (b.p. 205°C) provided more than 70% soluble material.

We also briefly investigated the optimum conditions. There were differences in the yields at 6 and 24 hours, so we adopted the 24 hour reaction time for all our reactions. Selected other results are shown in Table 2. With sodium benzoxide, concentrations from 40 to 120 mmol per gram of coal gave good results and the product obtained was about 70% soluble in pyridine. However, higher concentrations of the base resulted in reaction products with masses much greater than those of the starting materials. Thus, it was evident that at higher base concentration, chemical addition reactions take place.

The results also show that the extent of solubilization does not depend on the basicity of the alkoxides. Rather, the differences in their effectiveness apparently arise as a consequence of the differences in their boiling points. There are two lines of evidence. First, the two higher-boiling alcohols, benzyl alcohol and *n*-octanol with boiling point near 200°C, gave more soluble products than the lower-boiling alcohols. Second, the use of sodium methoxide in refluxing benzyl alcohol was as effective as sodium benzoxide in the same solvent (Table 1). These results strongly suggest that there is a significant activation energy for the key conversion reaction.

We believe that there are two underlying reasons for the success of this strategy. First, hydrogen is probably transferred from the solvent to the coal. Previous work performed by the Argonne group demonstrated that the aromatic rings in coal underwent reduction in proton donor solvents with alkali hydroxides.<sup>7</sup> In this study, benzaldehyde was detected among the reaction products. The microanalytical data for the reaction products, however, indicate that the increase in

the hydrogen content is modest. Second, subtle base-catalyzed carbon-oxygen, carbon-sulfur and carbon-carbon bond cleavage reactions fragment the low rank coals. It has been shown previously that strong bases such as Lochmann's base, can cleave carbon-carbon bonds in hydrocarbons if the resulting carbanions are stable.<sup>1</sup> Also, it has been shown that sulfidic carbon-sulfur bonds undergo cleavage under basic conditions.<sup>8</sup> In presence of proton donor solvents, the anions formed in such bond scission processes are trapped and the possibility for their recombination to yield a condensation product is reduced.

A major point of interest was the large decrease in the total sulfur content of the products.<sup>8</sup> The reduction ranged from 16% for *tert*-butoxide in *tert*-butanol (4.1 wt% S) to 80% for benzoxide in benzyl alcohol (1.0 wt% S). This result implies that all the pyrite and at least 50% of the organic sulfur were removed. The extent of sulfur removal for the various alkoxides in the corresponding alcohols paralleled their ability to solubilize the coal.

### CONCLUSIONS

Treatment of Illinois No. 6 coal with alkoxides in refluxing alcohols yields products that are 40 to 70% soluble in pyridine, compared to 27% for the starting material. The extent of solubilization depends upon the boiling point of the alcohol and not upon the structures of the alkoxide and the alcohol. The best results were obtained with 40 mmol of sodium or potassium benzoxide per gram of coal in benzyl alcohol. Significant sulfur removal was achieved, an 80% reduction from 4.8 to 1.0 wt% S by using the benzoxide. Thus, base-catalyzed reactions at temperatures near 200 °C solubilize and desulfurize this Illinois No. 6 coal.

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TABLE 1.  
RESULTS FOR ALKOXIDE TREATMENT OF ILLINOIS NO. 6 COAL IN REFLUXING  
ALCOHOLS. DETERMINING THE OPTIMUM REACTANT-SOLVENT SYSTEM.

reaction conditions: base, solvent, time	reaction temperature, °C	coal recovered, wt%, db	pyridine solubility, wt%
raw coal	-	-	27
NaOMe (40 mmol/g), MeOH, 24 h, protonation	65	86	33
KO <i>n</i> -Bu (40 mmol/g), <i>n</i> -BuOH, 24 h, protonation	118	76	42
KO <i>r</i> -Bu (40 mmol/g), <i>t</i> -BuOH, 24 h, protonation	83	83	42
KO <i>n</i> -Oct (40 mmol/g), <i>n</i> -OcOH, 24 h, protonation	196	79	53
KOBz (40 mmol/g), BzOH, 24 h, protonation	205	43 <sup>a</sup>	82
NaOBz (40 mmol/g), BzOH, 24 h, protonation	205	51 <sup>a</sup>	74
KOBz (40 mmol/g), BzOH, 24 h, protonation	205	95	66
NaOMe (40 mmol/g), BzOH, 24 h, protonation	205	68 <sup>a</sup>	64

<sup>a</sup>The recovery of the products after the reaction was low since a significant portion of the coal was soluble in the alcohol, and this material was removed during washing and filtration.

TABLE 2.  
 RESULTS FOR SODIUM BENZOXIDE TREATMENT OF ILLINOIS NO. 6 COAL IN  
 REFLUXING BENZYL ALCOHOL AT 205 °C. EFFECT OF CHANGING THE BASE  
 CONCENTRATION.

concentration of sodium benzoxide (mmol/g coal)	coal recovered, wt%, db	pyridine solubility, wt%
raw coal	-	27
40	51 <sup>a</sup>	74
74	77 <sup>a</sup>	52
121	63 <sup>a</sup>	70
253	285	31
486	457	35

<sup>a</sup>The recovery of the products in these experiments was low since a significant portion of the coal was soluble in the alcohol and this material was discarded in these experiments.