DOE/PC/79938--T9

DOE/PC/79938--T9

DE92 040282

Fifth Quarterly Report

October, November, December 1988

Studies of Coupled Chemical and Catalytic Coal Conversion Methods

Contract 22-87PC79938
Department of Chemistry
The University of Chicago
Chicago, Illinois 60637

Leon M. Stock, Principal Investigator
Kuntal Chatterjee and Michael Ettinger
Research Staff

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Introduction

Liquefaction of coal by depolymerization in an organic solvent has been studied for several years. The liquefied coal extract which results from such a process is far more suitable for conversion into liquid fuel by hydrogenolysis than is the untreated coal. Investigations 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, irrespective of the 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 been investigating these reactions [5-8]. 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 were soluble upto 92% in solvents like 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, 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. Other 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 Argonne National Laboratory. The analytical values of both the samples are summarized in Table 1. 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. Alkyl iodides (Aldrich) such as iodomethane, iodobutane and iodooctane were dried by molecular sieve 5A. Iodohexadecane was kept properly sealed in the refrigerator. Pyridine and chloroform were purified by distillation. The other chemicals such as n-butyllithium (1.6 M solution in hexane), potassium tertiary butoxide, sodium amide, ammonium chloride, tetrabutyl ammonium hydroxide, potassium trimethylsilanolate, methanol and hexane were used as received from Aldrich.

Typical reaction procedure for coal alkylation

Both Illinois No.6 and Wyodak coals were 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 and Wyodak coals were used as starting materials for all the reactions described in the subsequent paragraphs.

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 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.

Reactions of the coal with sodium amide in liquid ammonia was conducted by a similar procedure as described previously [6]. A typical reaction was carried out as follows : Liquid ammonia (200 ml) was condensed in a flame dried three necked flask (500 ml) and sodium amide (45 mmoles) was added. The reaction mixture was stired, and after 15 minutes, coal sample (1.0 grams) was added and the reaction mixture was left for stirring at -75 °C for 6 hours. To this coal anion suspension, the alkyl halide (60 mmoles) in tetrahydrofuran (100 ml) was added dropwise for a period of 30 minutes and the temperature was gradually increased to room temperature by stopping the supply of dry ice to the ethanol bath. During this period, all the ammonia evaporated. Then additional tetrahydrofuran (100 ml) was added to the mixture. After 48 hours, the excess base was quenched by the addition of ammonium chloride followed by methanol. The reaction was conducted under a flow of dry nitrogen. After the reaction was complete, the solvent and the excess alkyl halide were evaporated by using a rotary evaporator and subsequently at 90 °C under vacuum for 12 hours. The product obtained was washed with aqueous methanol (methanol : water =1:3 volume /volume) thoroughly (about 20L). Later on it was also washed with hexane (about 4L). The washing procedures were carried out in nitrogen atmosphere. The product was carefully collected and dried to constant weight at 110 °C under vacuum for 48 hours. A part of the alkylated product was subjected to Soxhlet extraction with pyridine. Control experiments were conducted by quenching the coal anions with ammonium chloride followed by methanol.

Analysis of the Products :

Solution phase ^{13}C-NMR and ^{2}H-NMR spectra were measured 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

The analytical data in Table 1 shows that the low rank Illinois No.6 and Wyodak coals are rich in oxygen. The ether and ester linkages are presumably important in binding the coal structure. However, previous work on Illinois No.6 coal with potassium/ naphthalene systems, where several ether linkages are cleaved, hasn't enhanced the solubility of this coal significantly[11]. It may be that the highly crosslinked structure does not experience molecular weight reductions when the fragments are formed by ether cleavage.

Alkylation on phenolic oxygen atom increases the solubility of the coal as shown in Table 2. As the table shows, for Illinois No.6 coal, the O-methylation reaction increases the solubility from 27% to 34%. However, the nature and length of the alkylating agent does not alter the solubility appreciably. O-Methylation is more effective, relatively speaking, for Wyodak coal; this reaction enhances the solubility from 9% to 35%, a factor of 3.5. However, the size of the alkyl group is not an important factor. Hydrogen bonding through the hydroxyl functional groups has been proposed as an important intermolecular linkage in the coal structure[10]. Once the hydroxyl groups are alkylated, the hydrogen bonds are cleaved and the coal structure is disrupted. Apart from the hydrogen bonds, the strong covalent bonds are not affected by O-alkylation.

The results of C-alkylation reactions are presented in Table 3. Almost all C-alkylation reactions on these low rank coals were carried out on the O-methylated coals rather than the raw coal so that the consequences of the C-alkylation reactions could be defined. Miyake and Stock reported earlier the high solubility of the high rank coals through non-reductive C-alkylations. Two different bases were used- sodium amide (pKa=35)[12] and n-butyllithium (pKa=42)[12]. The effect of these two bases on alkylation and subsequently, on solubilization, are shown in Table 3. Sodium amide, the weaker base, can only remove the benzylic protons, but n-butyllithium can also abstract aromatic hydrogens. However, in low rank coals, the abundance of hydroaromatic structures obviate the abstraction of aromatic protons. As Table 3 shows, there is not much difference in the solubility of the products obtained with different bases. For Wyodak coal,the sodium amide system always gave more soluble products than the "super base" system for the same alkylating agent.

The most important aspects of alkylation and solubilization are displayed in Tables 4 and 5. The observations represented in Table 4 reveal that the solubility of O-methyl Illinois No.6 coal is not greatly enhanced by designed C-alkylation reactions using methyl, butyl, octyl and octadecyl iodides. The experiment with octadecyl iodide seems anomalous and wil be repeated.

The results for Wyodak coal in Table 5 are very encouraging. The n-butyllithium / potassium t-butoxide system changes the solubility appreciably, from 16% for the C-butylated O-methyl coal to 44% for the C-octadecylated O-methyl coal. The results for the sodium amide system are even more striking with a solubility of 87% being realized for the C-octadecylated O-methyl coal. The high yield of soluble product obtained in this instance prompted us to examine the sample carefully and the result, which is based on the residue weight, seems secure.

Table 1

Analytical data of coal samples

	Illinois No.6	Wyodak
Ultimate analysis(wt%)		
C	77.8	72.0
H	5.7	5.7
N	1.4	1.0
S	2.6	0.5
O (by difference)	9.1	20.5
Ash	16.2	9.2
Maceral analysis(wt%)		
Vitrinite	88.0	89.0
Inertinite	9.0	10.0
Liptinite	3.0	1.0

Table 2

Effect of O-alkylation and acylation on the solubility of low rank coals.

1. Illinois No.6 coal

	Alkylating agent	Base	Alkylated coal recovered (wt%)	Pyridine solubility (wt.%,daf)
1.	Nil	-	-	27
2.	CH_3I	TBAH*	-	34
3.	$C_8H_{17}I$	KOH		33
4.	$C_{16}H_{33}I$	KOH	192	36
5.	C_3H_7COCl	Me_3SiOK	102	38
6.	$C_7H_{15}COCl$	Me_3SiOK	-	36

2. Wyodak coal

1.	Nil	-	-	9
2.	CH_3I	TBAH*		35
3.	$C_8H_{17}I$	TBAH		37
4.	$C_{16}H_{33}I$	TBAH		39

* TBAH = tetra butyl ammonium hydroxide

Table 3

Influence of the base on C-octylation with n-octyl iodide.

1. Illinois No.6 coal

	Coal	Base	Temp. °C	Solvent	Pyridine solubility wt% (daf)
1.	raw	-	-	-	27
2.	raw	KOH	25	THF	33
3.	(OMe)	n-BuLi K^tBuO	98	heptane	43
4.	(OMe)	$NaNH_2$	-75	Liq. NH_3	32

2. Wyodak coal

1.	raw	-	-	-	9
2.	raw	TBAH	25	THF	37
3.	raw	n-BuLi/ K^tBuO	98	heptane	33
4.	(OMe)	n-BuLi/ K^tBuO	98	heptane	20
5.	raw	$NaNH_2$	-75	Liq. NH_3	40
6.	(OMe)	$NaNH_2$	-75	Liq.NH_3	43

Table 4

Influence of the alkyl group on solubilization of Illinois No.6 coal with n-Butyllithium / tert. butoxide as base

	Coal	Alkyl halide	Pyridine solubility wt% (daf)
1.	raw	-	27
2.	Ill. No.6(OMe)		34
3.	Ill. No.6(OMe)	NH_4Cl	40
4.	Ill. No.6(OMe)	CH_3I	46
5.	Ill. No.6(OMe)	C_4H_9I	39
6.	Ill.No.6(OMe)	$C_8H_{17}I$	43
7.	Ill.No.6(OMe)	$C_{16}H_{33}I$	22

Table 5

Influence of the alkyl groups on solubilization of Wyodak coal.

(A) With $NaNH_2$ as base

	Coal	Alkyl halide	Pyridine solubility, (wt %, daf)
1.	raw	-	9
2.	Wyodak(OMe)	-	34
3.	Wyodak(OMe)	NH_4Cl	25
4.	Wyodak(OMe)	$C_8H_{17}I$	43
5.	Wyodak(OMe)	$C_{16}H_{33}I$	87

(B) With n-BuLi / K^tBuO as base

1.	raw	-	9
2.	Wyodak(OMe)	-	35
3.	Wyodak(OMe)	NH_4Cl	23
4.	Wyodak(OMe)	C_4H_9I	16
5.	Wyodak(OMe)	$C_8H_{17}I$	20
6.	Wyodak(OMe)*	$C_8H_{17}I$	44

* 100 mmoles of base used instead of the usual 45 mmoles.

References

(1) H.W. Sternberg, C.L. Delle Donne, P. Pantages, E.C. Moroni and R.E. Markby Fuel, 1971, 50, 432.

(2) R.M. Davison, Coal Science, 1982,1, 84.

(3) L.M. Stock, Coal Science, 1982, 1, 161.

(4) B. Ignasiak, D. Carson and M. Gawlak, Fuel, 1979, 58, 833.

(5) M. Gawlak, B. Carson, B. Ignasiak, T. Ignasiak and O.P. Strausz, 1987, Int. Conf. Coal Sci. , Preprints, 1987, p.57.

(6) N. Mallya and L.M. Stock, ACS Fuel Chem. Div., 1985, 30(2), 291.

(7) L. Lazarov, S.P. Marinov, M. Stefanova and G. Angelova, 1987 Int. Conf. Coal Sci., Preprints, 1987, p.745.

(8) R.R. Chambers Jr., E.W. Hagaman and M.C. Woody, 1987, Int. Conf. Coal Sci., Preprints, 1987, p.741.

(9) M. Miyake and L.M. Stock, Energy and Fuels, 00, 000, 1988.

(10) R. Liotta, K. Rose and E. Hippo, J Org. Chem., 1981, 46, 277-283.

(11) L.B. Alemany, Ph.D Thesis, University of Chicago, 1980.

(12) D.J. Cram in "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, pp.8-20, 41.

(13) Reported in the previous reports.

END

DATE FILMED

10 / 27 / 92