

The Solvent Swelling Behavior of AlCl_3 -Treated Coal Molecules

T. K. Green, G. T. Ransdell, and J. S. Flynn

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101

INTRODUCTION

Coals are known to be largely insoluble in most common solvents at their boiling points. A good solvent such as pyridine dissolves at best only 10-30 weight percent of the solid. However, the insoluble portion of coals is known to swell up to two to three times its own volume in good solvents, and this lends support to the idea that the insoluble portion is best viewed as a three-dimensionally crosslinked macromolecular solid (1). A minor amount of smaller molecules are thought to be trapped within this three-dimensional network and can be released by good swelling solvents such as pyridine. This paper is concerned with the relationship of the three-dimensionally crosslinked macromolecules that constitute the insoluble portion of coals and the smaller, potentially-extractable molecules.

The relationship between the macromolecular portion of coal and the smaller molecules has been of considerable interest to coal chemists for some time. A fundamental question concerning this relationship is whether the smaller molecules represent much the same stuff as the crosslinked macromolecules. This question has been addressed by Given in a recent review (2). Van Krevelen, in his proposed model of the coalification process, regarded the smaller molecules as the unreacted fragments of a condensation polymerization reaction (3). The insoluble macromolecular network was regarded as the product of this condensation polymerization. Thus the soluble, smaller molecules and the insoluble macromolecules were regarded by van Krevelen as much the same stuff. Given has rejected this view as not in accord with the facts (2). The details of his arguments are not presented here. Larsen and co-workers, in a study of the molecular weight distributions of pyridine extracts, have shown that coalification is not a simple condensation polymerization as proposed earlier by van Krevelen (4).

In spite of the evidence arguing against van Krevelen's view of the coalification process, we were intrigued by the possibility of modeling the insoluble macromolecules in coal by somehow "polymerizing" or crosslinking the soluble, smaller molecules into an insoluble network. If this could be accomplished, the various properties of the two materials (e.g. swelling behavior) could be directly compared. A study of this nature might lend insight into the relationship between the macromolecular network and the smaller molecules in coals.

APPROACH

Winans and co-workers have shown that lignin can be transformed into an insoluble material resembling low rank coals in the presence of montmorillonite at 150°C (5). In addition, aluminum bromide (AlBr_3) was shown to transform lignin to a coal-like material in a very short time (24 hr at 120°C). This fascinating result suggested to us that Lewis acids might promote crosslinking reactions between soluble coal molecules, leading to an insoluble three-dimensionally crosslinked material capable of swelling in organic solvents. Thus we chose to treat soluble coal molecules with AlCl_3 to see if an insoluble material might be produced.

The choice of AlCl_3 as a reactant imposed a significant constraint on our experimental approach. Most coals are largely insoluble in solvents that would be compatible with Lewis acids. For example, hydrocarbon solvents such as toluene will not strongly coordinate with Lewis acids in Friedel-Crafts alkylation reactions (6), but these solvents dissolve only a small fraction of most coals. On the other hand, pyridine and other donor solvents are effective extraction solvents for coals, but strongly coordinate to Lewis acids, rendering them ineffective as alkylation

catalysts (6). Thus pyridine would be a poor choice as a reaction solvent in the presence of AlCl_3 .

An alternative approach is to make the coal more soluble in solvents compatible with Lewis acids. One way of doing this is by O-methylation of the hydroxyl groups in coal. Liotta has shown that the extractability of an Illinois No. 6 coal in chloroform (CHCl_3) is increased from 3.2% to 21.7% upon O-methylation (7). The reaction is thought to render the coal free of its secondary structure by disrupting coal-coal hydrogen bonds. The primary covalent framework of the coal is left intact. The CHCl_3 -soluble fraction of the O-methylated Illinois No. 6 coal was found by us to be completely soluble in α -dichlorobenzene, a nonreactive solvent compatible with Lewis acids. Thus α -dichlorobenzene was chosen as the reaction solvent for the treatment of the coal extract with AlCl_3 .

EXPERIMENTAL

O-methylation

O-methylation of the Illinois No. 6 coal was carried out according to Liotta's method (7). Elemental analyses of both the native and O-methylated coals are given in Table 1.

Table 1
Elemental Analyses of Illinois No. 6 Coal^a

	C	H	N	S	O ^b	MM ^c
Illinois No. 6	78.3	5.4	1.3	4.5	10.5	13.3
O-methylated	76.5	6.0	1.7	2.9	12.8	9.6

^a dmmf basis

^b by difference

^c mineral matter, calculated according to MM=1.08 Ash +.55S

The Soxhlet extractability of the O-methylated Illinois No. 6 coal in chloroform was found to be 19.3%, (dmmf), in good agreement with Liotta's findings (7).

Treatment of CHCl_3 extract with AlCl_3

5 mL of nitromethane was placed in a 100 mL round bottom flask. Approximately 2 g of anhydrous AlCl_3 was dissolved in the nitromethane. 30 mL of α -dichlorobenzene and 1.75 g of coal extract were then added. The flask was flushed with N_2 , stoppered and allowed to stir at room temperature for three days.

A separate reaction identical to the above reaction was conducted, except that no nitromethane was added to the flask.

After three days, the contents of the flask was suction filtered. The residue was washed with α -dichlorobenzene, acetone, and then water. The residue was then placed in a thimble and Soxhlet extracted overnight with water, which was sufficient to give a negative silver nitrate test for chloride ion. The residue was then dried under vacuum at 105°C overnight.

Swelling Procedure

The residue from the AlCl_3 -treated coal extract was swollen in series of solvents using an established procedure (8).

RESULTS

The yield of *m*-dichlorobenzene insoluble material was 30% (based on the starting weight of extract) when nitromethane was used as a co-solvent. In contrast, the yield of insoluble material was only 5% when nitromethane was omitted from the reaction.

The insoluble material obtained from the AlCl_3 -treatment was swollen in series of solvents according to an established technique³(8). The volumetric swelling ratio, *Q*, is a measure of the volume of solvent absorbed by a unit volume of coal, and is defined as

$$Q = \frac{\text{Volume of Swollen Coal}}{\text{Volume of Unswollen Coal}} \quad 1)$$

When *Q* is 1.0, the coal has absorbed no solvent. The results of these measurements are presented in Table 2. The *Q* values for the native, *O*-methylated, and CHCl_3 -extracted *O*-methylated Illinois No. 6 coals are also presented.

The hydrogen to carbon ratios of the coals and the insoluble material from the AlCl_3 treatment are also shown in Table 2.

Table 2
Solvent Swelling Ratios (*Q*) and H/C ratios for Illinois No. 6 Coals
and AlCl_3 -treated Coal Extract^a

Coal	H/C	Q				
		Cyclohexane	Ether	Benzene	THF ^b	Pyridine
Illinois No. 6	0.83	1.0	1.2	1.1	1.9	2.6
<i>O</i> -methylated	0.94	1.1	1.4	1.7	1.9	2.2
<i>O</i> -methylated, CHCl_3 -insoluble	0.89	1.1	1.5	1.8	1.9	2.5
<i>O</i> -methylated, CHCl_3 -soluble	1.1	N/A	N/A	N/A	N/A	N/A
AlCl_3 - <i>NO</i> ₂ - <i>Me</i> -treated, CHCl_3 -extract ^c	0.90	1.1	1.4	1.8	1.9	2.3
AlCl_3 -treated, CHCl_3 -extract ^c	--	--	--	1.5	1.7	--

^a Extract was obtained from CHCl_3 -extraction of *O*-methylated coal.

^b Tetrahydrofuran.

^c Insoluble fraction only.

DISCUSSION

The yield of insoluble material from the AlCl_3 -treatment of the CHCl_3 -extract was found to increase from 5 to 30% when nitromethane was added as co-solvent.

Nitromethane is known to be an effective solvent for $AlCl_3$ (9), and the $AlCl_3$ -nitromethane complex that forms is known to be catalytically active in alkylation reactions (10). In contrast, $AlCl_3$ is only slightly soluble in *o*-dichlorobenzene at room temperature. We can speculate that the role of nitromethane as a co-solvent is to provide a homogeneous solution of $AlCl_3$, which somehow promotes condensation of the soluble coal molecules. Polish workers have found nitromethane to be an effective solvent for alkylation of coals with alkyl chlorides in the presence of $AlCl_3$ (11).

The swelling ratios of the coals and the insoluble material produced from the extract are presented in Table 2. The O-methylated coal is observed to swell substantially more in benzene than the native Illinois No. 6 coal. This effect has been previously described (12), and is attributed to the disruption of the hydrogen bond crosslinks in the native coal upon O-methylation. The O-methylated coal has a lower effective crosslink density than the native coal and swells more in good nonpolar solvents such as benzene. Pyridine, a good hydrogen bond acceptor, disrupts most of the hydrogen bond crosslinks and therefore swells both coals to nearly the same extent. The chloroform extraction is observed to have little effect on the swelling behavior of the O-methylated coals.

Remarkably, the swelling behavior of the insoluble material produced from $AlCl_3$ -treatment of the extract is virtually identical to that of the O-methylated Illinois No. 6 coals. The H/C ratio of this material also closely matches that of the $CHCl_3$ -insoluble, O-methylated coal. It is substantially lower than that found for the $CHCl_3$ -extract from which it was produced. This latter result is expected if a more highly-crosslinked material is being produced from the $CHCl_3$ -extract.

It is clear from these results that the insoluble material produced from the $AlCl_3$ -treatment of the coal extract has as apparent crosslink density identical to that of the $CHCl_3$ -insoluble, O-methylated Illinois No. 6 coal. The underlying reason(s) for this result is not known, but we do not believe the result is fortuitous. It clearly suggests a close structural relationship between the insoluble macromolecules and the $CHCl_3$ -extractable molecules of the Illinois No. 6 coal. It also suggests the possibility that the macromolecules are derived from the smaller molecules in coal, although we have no independent evidence to support this claim. Finally, the insoluble material produced from the coal extract is presumably insoluble because covalent bonds hold the molecules together. If so, a knowledge of the reactions leading to the formation of this material should provide a better understanding of the nature of the covalent crosslinks in coals.

ACKNOWLEDGEMENT

We wish to thank the Exxon Education Foundation for the support of this work.

REFERENCES

1. J. Larsen, T. Green, J. Kovac and D. Brenner, "The Macromolecular Structure of Coal," Coal Structure, R. A. Meyers, ed., Academic Press, N.Y., 1982, 199-280.
2. P. H. Given, "The Organic Geochemistry of Coal," in Coal Science, Vol III, M. L. Gorbaty, J. W. Larsen, and I. Wender, eds., Academic Press, N.Y., 1984, 65-252.
3. D. W. van Krevelen, Fuel, 1965, 44, 229-242.
4. J. W. Larsen, M. Mohammadi, I. Yiginsu, and J. Kovac, Cosmochem. Acta, 1984, 48, 135-42.
5. R. Hayatsu, R. L. McBeth, R. G. Scott, R. E. Botto and R. E. Winans, Org. Geochem., 1984, 6, 463-471.
6. G. A. Olah in Friedel-Crafts and Related Reactions, G. A. Olah, ed., Interscience Publishers, N.Y., 1963, 247.
7. R. Liotta, K. Rose, and E. Hippo, J. Org. Chem. 1981, 101, 1735.
8. T. K. Green, J. Kovac, and J. W. Larsen, Fuel, 1984, 63, 935.
9. See Reference (6), p. 300.
10. L. Schmerling, Ind. Eng. Chem., 1948, 40, 2072.
11. T. R. Wojtaszek, J. Biner, and A. Wielopolski, Koks. Smola. Gaz., 1980, 25(3), 59-63, C. A.; 93: 170727e.
12. J. W. Larsen, T. K. Green, and I. C. Chiri, Proc. 1983 Int. Conf. Coal Science, Pittsburgh, PA, 1983, 277-281.