

COAL PROCESSING IN NON-DISSOLVING MEDIA

Myron Kaufman, W. C. L. Jamison, S. Gandhi and Dennis Liotta

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Introduction

If coal is contacted with an organic reagent in a medium in which the reagent is marginally soluble, there may be a tendency for the reagent to transfer to the pores and surfaces of the coal, where it has maximum utility for reactions which cleave the coal macromolecular network. Thus, in such media it may be possible to employ lower concentrations of reagents than would be required in totally soluble systems. If, in addition, coal fragments are insoluble in the processing medium, the coal particles will be recovered intact after processing. The reagent can then be washed from the coal, and coal conversion assessed as solubility in a standard solvent. Since the reagent is not present when solubility is measured, conversion should be independent of the solvent properties of the reagent, and only dependent on its ability to break bonds during processing. In our work, we have focused on the reagent 1,2,3,4-tetrahydroquinoline (THQ), which has the unusual ability to disrupt coal macromolecules under mild conditions (200-250°C). A number of previous workers have commented on the efficacy of THQ as a coal solvent and have attributed it to either the basicity or the hydrogen-donating property of this molecule (1-3). Two types of non-dissolving media, perfluorocarbon liquids and water, have been employed in our studies.

Experimental

The perfluorocarbon liquids used in our experiments are typified by FC-70 (3M Corp.), a mixture of perfluorinated tertiary aliphatic amines, with a boiling point of 215°C. FC-70 has high solubility for gases such as H₂ and CO, but very low room temperature solubility for both polar and nonpolar organic molecules. Recently, we have performed some experiments in water, which is an interesting medium, since its solubility properties can be varied by adjusting pH.

Three very different coals, with the properties given in Table 1, are used in our experiments. Typically, 0.5g of coal, 0.1g of THQ and 7 ml of FC-70 or water are heated in a stainless tubing bomb under 8 MPa of H₂. Detailed procedures for carrying out the reactions and for removal of THQ before measuring the pyridine solubility of the coal have been given (4,5). Model compound studies were carried out in FC-70 with roughly equal weights of the model compound and THQ (or other reagent). The occurrence and nature of reaction was assessed by thin layer chromatography and 90 MHz proton NMR.

Table 1. Coal Properties

PSOC Designation	1104	247	1098
Moisture (%)	1.95	30.36	4.19
Ash (% on dry basis)	3.43	11.29	15.86
Volatile Matter (% MAF)	43.83	46.22	41.78
C (% MAF)	84.47	74.44	80.20
H (% MAF)	5.66	4.93	5.73
N (% MAF)	1.46	1.49	5.73
S (% MAF)	1.86	0.53	4.73
O (by difference)	6.48	18.61	7.89

1104 - HVA bituminous coal from Elkhorn #3 Seam

247 - North Dakota lignite A from Noonan Seam

1098 - Illinois #6 coal

Results

As previously reported, the pyridine solubilities of three very different coals were increased to 33-35% by long-term (18 hour) heating at 250°C with THQ in FC-70. For each coal, the kinetics were first-order with rate constant of ca. 0.6 hr⁻¹, and not mass-transport limited, as indicated by lack of dependence on particle size. A number of other reagents were evaluated concerning their ability to increase coal conversion under the mild conditions employed in these experiments. Quinoline, diethylamine, triethylamine, ethylenediamine and tetralin all produced less than 6% increase in the pyridine solubility of a bituminous coal heated at 250°C for 4 hours, while THQ produced almost a 20% increase under these conditions.

In order to determine the nature of the bonds in coal that were being cleaved by THQ under our mild conditions, a number of model compounds were heated with THQ in FC-70 under conditions identical to our coal experiments. These model compounds consisted of phenyl groups connected by various linkages that have been discussed as being of some importance in the coal macromolecular structure. The results of these studies are given in Table 2. For the two model compounds for which reaction was noted (diphenyldisulfide and phenyl benzoate), the reactions with tetralin and diethylamine were also investigated.

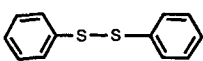
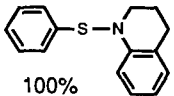

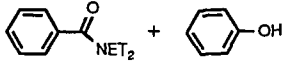
Two other media were employed to help understand the effectiveness with which small additions of THQ increase coal conversion in perfluorocarbon liquids. Dodecane has a similar boiling point to FC-70, but considerably greater solubility for THQ. It is probably only an effective extraction medium for free saturated hydrocarbons in coal. Water, on the other hand, while it has very low solubility for THQ, can dissolve strongly polar and highly acidic or basic components of coal. When bituminous coal was treated with THQ at 250°C for 4 hours in dodecane only 2% increase in coal pyridine solubility was obtained. With neutral pH water the results were very similar to what was obtained with FC-70. Very little of the coal dissolved in the water, as indicated by its light color. However, after washing out the THQ and water, the pyridine solubility of the coal was found to have increased by ca. 20%, a value very close to that achieved with THQ under similar conditions. Somewhat different results were obtained when a strongly basic (ca. 1M NaOH) solution was employed. In this case, the aqueous phase was very dark, but the remaining coal had only the pyridine solubility of unprocessed coal.

Discussion

Comparison of the results in FC-70, water and dodecane indicate that it is the marginal solubility of THQ in the first two of these media that permits low concentrations of this reagent to produce substantial increases in coal solubility. We envision that in FC-70 and water, THQ selectively transfers into the pores and onto the surfaces of the coal, while in dodecane it maintains a more uniform and low concentration throughout the system.

Although the model compound studies have not probed all possible bonds in coal macromolecules, our results suggest that only ester and disulfide bonds are susceptible to attack by THQ under the mild conditions of our experiments. In both cases the initial mode of reaction appears to be nucleophilic attack by the nitrogen lone pair, followed by bond scission and hydrogen donation in either a concerted or successive manner. Since tetralin is not a nucleophile, it cannot initiate similar reactions. The thiol produced with tetralin and diphenyldisulfide probably results from thermal scission of the disulfide, followed by hydrogen abstraction by the thio radical. Small amounts of thiol are formed when the tetralin is omitted in this experiment. In this case, with only H₂ available as a hydrogen donor, many of the thio radicals probably recombine. Since ester bonds are considerably stronger than disulfide bonds, it is not surprising that there is little reaction between tetralin and phenyl benzoate at 250°C. Diethylamine should be a more potent nucleophile than

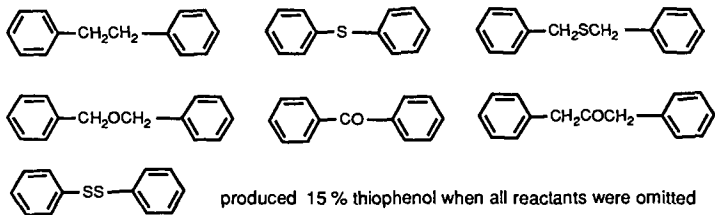
TABLE 2 MODEL COMPOUND STUDIES

Substrates	
Reactants	
THQ	 <p>100%</p>
Tetralin	 <p>100%</p>
Diethylamine	<p>50 % substrate recovered *</p>  <p>100%</p>

Conditions: 4 hrs at 250 C in FC-70 with 7 MPa H₂.

* Black, insoluble material was formed

The following substrates did not react with THQ under these conditions:



THQ, and indeed it does react with both diphenyldisulfide and phenyl benzoate at rates comparable to THQ. (The product of the disulfide reaction is a black, insoluble material that we have not yet been able to identify.)

In attempting to choose between esters and disulfides as the predominant bonds broken by THQ in our experiments, we must rationalize the observed attack of diphenyldisulfide by tetralin and both diphenyldisulfide and phenyl benzoate by diethylamine, while neither of these reagents are substantially effective in increasing coal solubility. Since tetralin has a similar boiling point and aromaticity to THQ, it is very difficult to explain the tetralin results if disulfide bonds are predominant. Diethylamine, however, with its lack of aromatic character, might find the coal environment much less favorable for selective partitioning. In addition, the high volatility of diethylamine would result in a substantial partitioning into the gas phase. Thus, the ineffectiveness of diethylamine with coal can be rationalized, and we prefer ester bonds as the primary linkages being attacked in our coal experiments. The surprising result that three very different coals all achieved very similar ultimate solubility upon long-term reaction with THQ in FC-70 at 250°C could most easily be explained by the postulate that these coals in their early stages of development all had similar concentrations of ester bonds in their macromolecular networks. At the so-called first coalification step, which occurs at ca. 78% carbon, coals lose CO₂, much of which comes from ester bonds, and the destruction of these bonds could account for the higher initial solubilities of PSOC 1098 and 1104. Van Bodegam *et al.* have reported that while low-rank coals contained ester bonds that could be broken in reactions with primary amines at temperatures of 120-180°C, no such bonds were found in medium and high-rank coals (6). Our work suggests that there are additional ester bonds in medium-rank coals that can be attacked by THQ at 250°C.

In both FC-70 and water, the amides generated by reaction of THQ with ester bonds in coal would show very little solubility, and thus it is not surprising that the coal does not dissolve in these media. With strongly basic water, however, further saponification of the amide occurs, with ionization of the resulting acids. The aqueous phase in this experiment therefore dissolves large concentrations of the coal fragments.

Acknowledgment

This work has been supported by the U. S. Department of Energy under contract DE-FG22-82PC50785. A grant from the Emory University Research Committee is also acknowledged. Provision of perfluorocarbon materials by 3M Corporation is greatly appreciated.

References

1. Panvelker, S. V., Shah, Y. T. and Cronauer, D. C., *Ind. Eng. Chem. Fundam.* **21**, 236 (1982).
2. Derbyshire, F. J., Odoerfer, G. A. and Whitehurst, D. D., *Fuel* **63**, 56 (1984).
3. Brucker, R. and Kolling, G., *Brennstoff Chemie* **46**, 41 (1965).
4. Kaufman, M., Jamison, W. C. L. and Liotta, D., *Fuel* **65**, 148 (1986).
5. Kaufman, M., Jamison, W. C. L., Gandhi, S. and Liotta, D., *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **31**, 296 (1986).
6. Van Bodegom, B., van Veen, J. A. R., van Kessel, G. M. M., Sinnige-Nijssen, M. W. A. and Stulver, H. C. M., *Fuel* **63**, 346 (1984); **64**, 59 (1985).