DIHYDROQUINONE FOR ENHANCING COAL LIQUEFACTION YIELDS

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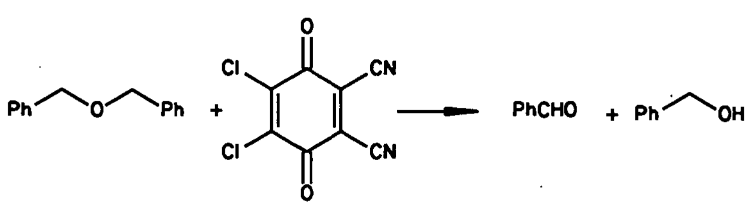
Abstract

Finding reagents and/or catalysts to enhance liquefaction of coal continues to be an area of active interest. During our studies directed towards the use of PI-acceptor induced bond cleavage reactions, we have found that 1,4-dihydroquinone enhances the yield of THF-extractables for a series of coals ranging from low rank sub-bituminous to high volatile bituminous. In certain cases, benzoquinone can also enhance the yields of THF extractables from coal. These reactions take place at surprisingly low temperatures (*i.e.*, 200°C).

Introduction

As part of our on-going effort to develop new ways to cleave bonds (1) through the use of electron transfer chemistry, we have been particularly interested in the reactions of quinones and their ability to cleave ether bonds (2). Representative of our work to date is the reaction of benzyl ether (**BE**) with 2,3-dichloro-5,6-dicyano-1,4-quinone (**DDQ**) which yields benzaldehyde and benzyl alcohol when heated together at 200°C in acetonitrile (CH_3CN) (2) as shown in eq (1).

(1)



BE **DDQ**

Although the use of quinones proved to be useful to bond cleavage in model compounds, quinones proved to have only a small effect on enhancing liquid yields liquids from coal under similar conditions to those used in model compound studies. Interestingly, small quantities of quinones did appear to have a small positive effect on achieving greater quantities of THF-extractables. One rationale for this lack of enhancement arises from the oxidizing nature of these compounds. Since the major goal for liquefaction seems to involve the addition of hydrogen to the molecular framework of the coal polymer as it unravels, we reasoned that dihydroquinones, as the redox couples of quinones (note eq (2)), might prove effect in increasing liquid yields. Although dihydroquinones have been used as part of a complex mixture for enhancing coal liquefaction, we report here that **DHQ** by itself is sufficient to enhance the amount of THF-extractable material from a number of coals.

(2)

Experimental

Samples of coal were obtained from the Argonne Premium Coal Sample Bank. Bakerstown coal and Sewell coal were obtained from the West Virginia Coal Sample Bank.

A given weight of coal and a given weight of the added reagent were added to 5 mL of acetonitrile (CH_3CN, freshly distilled from NaH) in a 10 mm glass tube. Oxygen was removed from the solution *via* 3 freeze-pump-thaw degassing cycles and the sample tube was then sealed *in vacuo*. The sample tube was placed in a tubing bomb reactor to which excess CH_3CN was added to equalize the pressure on the outside and inside of the glass. The tube was then placed in an oil bath at the indicated temperature for the indicated length of time. After removal from the oil bath, the contents of the glass tube are placed in a Soxhlett extractor and refluxed with THF for 24 h. After evaporation of the THF *in vacuo*, the weight of the extract and the weight of the insolubles were determined.

Results and Discussion

In order to evaluate the effect of a reagent on liquefaction of coal, control experiments were performed with no added reagent to establish the amount of extractables without reagent. In all cases, the coal was heated at 200°C for 48 h in the indicated solvent. Not surprisingly, the choice of solvent does have an effect upon the amount of THF-extractables obtained in these experiments. The results of these experiments are given in Table I. As expected, there is a solvent dependence on the amount of THF-extractability as evidenced by the effects shown on the Bakerstown coal. These experiments were mandated by the high mass balances afforded by acetonitrile (CH_3CN). Since all other solvents yielded mass balances less than 100%, we conclude that incorporation of CH_3CN into the insolubles and into the THF extractables occurs similarly in all experiments.

The results of adding a 1:1 weight ratio of dihydroquinone (**DHQ**) to the coal are shown in Table II. In these experiments, the coal and the **DHQ** have been heated together in the indicated solvent for 48 h at 200°C. In this table, the effects of the reagent are given by a Liquefaction Enhancement (L.E.) which has been defined by eq (3). In this equation, THF_{coal} and THF_{DHQ} are the amounts of extractables when either the coal or DHQ are treated alone. Normalization to the starting amount of coal is performed to enable comparison of one coal to another coal.

$$L.E. = \frac{(Total\ THF\ extract) - (THF_{coal} + THF_{DHQ})}{starting\ weight\ coal} \times 100\% \qquad \textbf{(3)}$$

As can be seen in Table II, reasonable enhancements in the liquid yields are obtained. These results are made more remarkable when one considers that these LEs were obtained for temperatures as low as 200°C. A solvent dependence is noted for this effect, with only CH_3CN and cyclohexane (C_6H_{12}) showing positive enhancements.

Although these results are still preliminary in nature, we speculate that **DHQ** serves primarily as a hydrogen donor. In support of this hypothesis, **DHQ** gives a greater LE than tetralin (L.E.=-12%) for Bakerstown coal under similar conditions. Since a limited amount of 1,4-benzoquinone (**BQ**) shows a small positive L.E., the use of **DHQ** offers the possibility that a catalytic cycle may be opened up, making the product(s) of **DHQ** (*i.e.*, **BQ**) effective for more liquefaction activity.

References

1. (a) Penn, J.H.; Lin, Z.; Deng, D.-L. *J. Am. Chem. Soc.*, **1991**, in press. (b) Penn, J.H.; Lin, Z.; Deng, D.-L. *Tetrahedron Lett.*, **1988**, *29*, 3635.

2. (a) Penn, J.H.; Lin, Z. *J. Org. Chem.*, **1990**, *55*, 1554. (b) Penn, J.H.; Deng, D.-L.; Aleshire, S.K. *J. Org. Chem.*, **1988**, *53*, 3572. (c) Penn, J.H.; Smith, R.S. *Tetrahedron Lett.*, **1986**, *27*, 3475.

Table I
Coal Extractability Without Added Reagent

Coal	Coal Rank	Solvent	%THF Extractable
Bakerstown		CH_3CN	19.9
		THF	25.9
		C_6H_6	21.7
		C_6H_{12}	4.8
Sewell		CH_3CN	19.5
Pittsburgh #8	HV Bituminous	CH_3CN	34.4
Blind Canyon	HV Bituminous	CH_3CN	26.4
Upper Freeport		CH_3CN	12.7
Beulah-Zap	Lignite	CH_3CN	5.4

Table II
Enhancements Using **DHQ** as a Co-reagent

Coal	Coal Rank	Solvent	L.E.
Bakerstown		CH_3CN	20.5
		THF	1.0
		C_6H_6	2.3
		C_6H_{12}	10.0
Sewell		CH_3CN	-1.9
Pittsburgh #8	HV Bituminous	CH_3CN	41.7
Blind Canyon	HV Bituminous	CH_3CN	7.8
Upper Freeport		CH_3CN	3.4
Beulah Zap	Lignite	CH_3CN	45.4