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The Effects of Zinc Chloride on the Cleavage of Ether
Structures Present in Coal

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Abstract

A number of compounds which model the ether structures found in coal were subjected to reaction in the presence of ZnCl_2 . Both cyclic and non-cyclic ethers reacted provided at least one methylene group was present adjacent to the ether oxygen atom. Complete elimination of oxygen to form water was achieved with dibenzyl and cycloaliphatic ethers but oxygen bonded directly to a phenyl or naphthyl group was converted to an unreactive phenolic hydroxyl group.

Introduction

Recent studies have suggested that ether oxygen plays an important role in linking the macromolecular units or clusters present in coal. Takegami et al.¹ concluded from a study of mild hydrogenation of bituminous coal that the formation of asphaltenes might be ascribed to the cleavage of ether linkages. More recently, Ignasiak and Gawlak² examined the molecular weights of products obtained from reductive alkylation of a high-rank vitrinite. They concluded that the macromolecular network of vitrinite is composed of relatively small units (no. av. mol. weight 600-700) which are linked primarily by ether oxygen atoms. Ruberto et al.³ deduced from solvation studies of coal that sub-bituminous coal appears to consist primarily of two- and three-ring condensed aromatic structures linked mainly by oxygen atoms. It was estimated that roughly half of the oxygen content of the coal is involved in such ether structures. Finally, Wachowska and Pawlak⁴ noted that while the extent of ether linkages varies widely with coal rank, ether groups represent the main linkages between aromatic clusters.

The reactions which ether groups undergo during the conversion of coal to liquid products is not well understood. In studies of the solvent refining of coal Whitehurst et al.⁵ observed that the consumption of hydrogen required to achieve a given level of conversion correlates closely with the amount of oxygen removed as water. A similar

correlation was noted earlier by Weller et al.⁶ in their studies of coal liquefaction using a SnCl_2 catalyst. Both of these observations strongly suggest that the hydrogen consumed is required to remove oxygen atoms from ether linkages present between aromatic clusters. Such an interpretation is not unreasonable since the cleavage of ether linkages is energetically favorable compared to, say, the cleavage of aliphatic linkages.

It is anticipated that the presence of a catalyst during coal liquefaction may accelerate the cleavage of ether linkages. A catalyst of particular interest in this regard is ZnCl_2 . Extensive work ^{7,8,9} has shown that ZnCl_2 promotes the liquefaction of coal with only a moderate consumption of hydrogen. In recent studies it has also been demonstrated¹⁰ that ZnCl_2 will promote the conversion of a sub-bituminous coal to pyridine soluble components at temperatures below which pyrolysis can occur ($<350^\circ\text{C}$). Furthermore, initial evidence ^{has been} ~~was~~ obtained¹¹ to suggest that the degree of conversion correlates with the removal of oxygen from the coal. These latter results suggest that ZnCl_2 may catalyze the cleavage of ether linkages and thereby promote a reduction in molecular weight.

The present studies were undertaken to determine the extent to which ZnCl_2 catalyzes the cleavage of ether linkages. To facilitate the identification of reaction pathways and products our studies were conducted with model

compounds chosen to reflect ether structures present in coal. Ethers containing phenyl, benzyl, and naphthyl groups were studied as well as cyclic ethers.

Experimental

Batch reactions of oxygen containing model compounds were carried out in a 300 cm³ 316 stainless steel, stirred autoclave (Autoclave Engineers, Inc. Model ABP-300). To minimize contact with the autoclave walls the reaction mixture was contained in a glass liner. In a typical experimental run, the reactant, solvent, and catalyst were weighed and introduced to the glass liner. A sample of the solution was taken for analysis before the catalyst was introduced to the mixture. The filled liner was then placed in the autoclave and the autoclave was sealed and pressurized to obtain the desired cold starting pressure.

The reaction mixture was brought to reaction temperature and pressure by means of an electric heating mantle surrounding the autoclave. This phase took from 20 minutes (to reach a temperature of 225°C) to 30 minutes (to reach a temperature of 325°C). The reactor was maintained at the reaction temperature for 60 minutes, and was then rapidly quenched. Quenching was accomplished by both an internal cooling coil and an external cooling jacket. This method of cooling enabled the autoclave contents to be cooled to less than 100°C within 2 minutes of the start of quenching and to be brought to room temperature in 15 to 20 minutes.

Throughout the heat-up, reaction, and cool-down phases the autoclave contents were stirred at 600 RPM. Since the reaction was run as a closed system, no gas was fed to or bled from the autoclave during these periods. The final cold pressure was noted and compared with the starting cold pressure to determine whether gas had been consumed or generated in the course of the reaction.

After the autoclave contents had reached room temperature, they were removed from the autoclave, together with the glass liner. The recovered products were weighed and the solid and liquid products were separated by filtration. The liquid products were analyzed by gas chromatography on a 1/8" x 10' column packed with 5% OV-225 on Chromosorb P. A second column, packed with 3% Dexsil 300 on Chromosorb W/HP was used for analysis in the cases where products of reaction had higher boiling points than could be eluted from the OV-225 column. Product identification was made using a Finnigan 4023 GC-MS. In some instances products were identified from infrared and ^1H -NMR spectra of collected chromatographic fractions.

Experiments were run with each model compound and solvent without the ZnCl_2 present to insure that the observed reactions were indeed catalytic.

The following compounds were used as models of ether linkages: diphenyl ether (Eastman Organic Chemicals), dibenzyl ether (Eastman Organic Chemicals), benzyl phenyl

ether (Frinton Laboratories), and benzyl α -naphthyl ether (Eastman Kodak Co.). Four cyclic ethers were also examined: furan (Aldrich), tetrahydrofuran (Mallinckrodt), 2,3-dihydrobenzofuran (Aldrich), and tetrahydropyran (Aldrich). Each of the model compounds was used as obtained. As solvents for the reactants and products we used: benzene (Mallinckrodt), cyclohexane (MCB), and tetralin (Eastman Organic Chemicals). ZnCl_2 (Mallinckrodt) was also used as received.

Results and Discussion

Non-cyclic Ethers

The products obtained upon reaction in the presence of ZnCl_2 of model compounds containing ether linkages are summarized in Table 1. In this table, conversion refers to the amount of reactant which disappeared in the course of the reaction, while the percent theoretical yield of the individual products is calculated on the basis of the initial amount of reactant. Since the percent theoretical yield is also based on the amount of product actually recovered, some of the deviation from theoretical yields can be attributed to system losses, which averaged 7%.

The reaction pattern exhibited by dibenzyl ether is characteristic of other model compounds and hence will be discussed first. As seen from Table 1, dibenzyl ether reacts in benzene to produce diphenylmethane in high yield via the following reaction

Similarly, when tetralin is used as a solvent instead of benzene, the α and β isomers of benzyltetralin are obtained. However, when the solvent is cyclohexane, tars are formed and no lower molecular weight products are observed in significant yield.

The reaction products obtained from dibenzyl ether can be interpreted in terms of mechanisms used to describe Friedel-Crafts chemistry¹². The essential feature of these mechanisms is the formation of a benzyl carbonium ion through the ZnCl_2 -promoted cleavage of the dibenzyl ether. The carbonium ion thus formed then attacks an aromatic center, if one is available, to yield the benzylation product.

Formation of the benzyl carbonium ion may be envisioned to occur by pathways similar to those used to explain ether cleavage by other Lewis acids. For example, following the mechanism proposed by Monacelli and Hennion¹³ for the cleavage of ethers by BF_3 , a benzyl carbonium ion could be formed by decomposition of the addition product formed between ZnCl_2 and dibenzyl ether (reaction 2).

The remaining fragment of the addition product proceeds to form a second carbonium ion (reaction 4). The carbonium ions thus formed react with benzene to yield diphenylmethane via reaction 3. Finally, the catalyst is regenerated in reaction 5.

Burwell¹⁴ observed that at least some ethers require the presence of strong Brønsted acids to undergo cleavage in the presence of BF_3 . This suggests a second mechanism (reactions 6-9) in which the ether must first be protonated to form the oxonium ion before it decomposes to the carbonium ion.

The active catalytic species in this instance is a Brönsted acid. If, as is usually the case, ZnCl_2 is not completely dry, sufficient water will be present to generate the protonic species $\text{H}^+(\text{ZnCl}_2\text{OH})^-$ via reaction 6¹⁵. The alcohol generated by the oxonium ion decomposition forms a second carbonium ion as in reaction 9. The carbonium ions again form products by attack on an aromatic center as in reaction 3 above.

The present study contains no evidence to distinguish between these mechanisms. Indeed, it is plausible that both mechanisms could operate simultaneously. The second mechanism could be promoted by the formation of water as a product of the first mechanism, which does not require water as an initiator.

The carbonium ion mechanism can also explain the reactions of dibenzyl ether in cyclohexane. In this case, the only aromatic center available to the benzyl carbonium ions is dibenzyl ether itself. As a result, reaction of the carbonium ion leads to polymer and tar formation via condensation reactions. Reactions 10 and 11 exemplify the types of propagation reactions which might be involved in the condensation process.

The role of gaseous hydrogen in the reactions dibenzyl ether was also investigated. As seen in Table 1, substitution of nitrogen for hydrogen had virtually no effect on the yield or distribution of products. These results and experiments in which the H_2 pressure was varied suggest that gaseous H_2 does not participate in the reaction mechanism.

Finally it should be noted that while the data presented in Table 1 refer to 225 to 230°C, experiments were conducted with dibenzyl ether at temperatures between 136 and 305°C. No other products were observed in these experiments and only the yield declined with reduction in the temperature.

In contrast to dibenzyl ether, diphenyl ether does not react, either in the presence of benzene or tetralin. This result agrees with those of earlier investigators who found diaryl ethers to be unreactive under the same conditions at which other ethers could be cleaved by Lewis acids^{16,17,18}. The stability of diphenyl ether is also consistent with the proposed mechanism of ether cleavage which would require the formation of a highly unstable phenyl ion.

From the above results, one would expect an alkyl aryl ether to undergo an assymetric cleavage. This is in indeed the case, as can be seen from the results of experiments using benzyl phenyl ether and benzyl naphthyl ether (Table 1).

In the case of benzyl phenyl ether, the cleavage mechanism can be described as follows:

The expected phenol and diphenylmethane are seen in fairly high yields. In addition, however, hydroxy-1,2-diphenylmethane is observed, as a result of benzylation of the phenol. The appearance of hydroxy-1,2-diphenylmethane can probably be ascribed to the higher activity of phenol than benzene for electrophilic attack, a factor which compensates for the higher concentration of benzene than phenol. The effect of ZnCl_2 on pure benzyl phenyl ether has previously been reported by Short¹⁹ with similar results.

In an attempt to see whether the nature of the aromatic group associated with the ether alters the rate of ether cleavage, reactions were conducted with benzyl naphthyl ether. The products obtained are analogous to those obtained in the reaction of benzyl phenyl ether, showing no differences in the type of reaction. However, the product yields were noticeably smaller than with benzyl phenyl ether.

Cyclic Ethers

Table 2 summarizes the products formed during the reactions of cyclic ethers in the presence of ZnCl_2 . In general, it is observed that the products obtained from these reactions are much more numerous and the yields of identifiable products are much lower than those obtained in the reaction of noncyclic ethers. A second general result is that α,β -saturated cyclic ethers (i.e. tetrahydrofuran, tetrahydropyran, and 2,3-dihydrobenzofuran) are reactive, while unsaturated cyclic ethers, such as furan, appear to be stable.

The predominant product obtained from the reaction of tetrahydrofuran in benzene is sec-butyl benzene. The higher abundance of this product with respect to n-butylbenzene is again consistent with a carbonium ion mechanism and reflects the greater stability of a secondary carbonium ion. The first steps of this mechanism are shown in reactions 15 and 16.

The presence of the n-butylbenzene among the products, however, suggests the possibility of a concerted-step mechanism. In either case the hydrogen necessary to complete the process probably comes from a portion of the tetrahydrofuran as shown below.

The presence of significant amounts of isopropylbenzene along with small amounts of ethylbenzene and toluene indicates that cracking of the carbon chain occurs. The closed-ring products (i.e. 1-methylindan and tetralin) could arise from a second attack on the benzene ring by the activated carbon chain, starting with the product of reaction 16, for example.

The products obtained from the reaction of tetrahydropyran in benzene are similar to those of tetrahydrofuran. However, there are apparent differences in product distributions. For example, while sec-amylobenzene is the major product, no significant amount of the n-amylobenzene isomer is seen. In addition, 1-methyltetralin (in analogy

to 1-methylindan above) is present in high relative abundance. Small amounts of the isomers of methylnaphthalene are seen, indicating some dehydrogenation of the methyl tetralins as they are formed.

As was noted before, tetrahydrofuran and tetrahydropyran gave low product yields. This can be partially attributed to consumption of some of the reactants to provide hydrogen for the reactions. In addition, during the reaction some of the reactant is likely to associate with the ZnCl_2 and remain in the ZnCl_2 phase during product work-up, thus not being accounted for in the liquid product.²⁰

A saturated cyclic ether structure more representative of those found in coal is 2,3-dihydrobenzofuran. The reactions of this compound are somewhat different in nature to those of the cyclic ethers discussed above. Whereas no significant thermal reactions were noted with other model compounds, dihydrobenzofuran undergoes some cleavage to form 2-ethylphenol in the absence of a catalyst.

In the presence of ZnCl_2 , the principle products are phenol, ethylbenzene and hydroxy 1,2-diphenylethane. It is proposed that the first steps result in a disproportionation of the 2,3-dihydrobenzofuran to yield 2-ethylphenol and benzofuran.

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The hydroxy-1,2-diphenylethane is produced by a reaction analogous to those of the cyclic ethers discussed above. The bond between the oxygen and adjacent saturated carbon is cleaved, leaving an alkyl fragment which is activated to attack an aromatic center, namely benzene. The presence of other products, principally toluene, indicate fragmentation of the alkyl chain. Here again, we note that the reaction products are not greatly dependent on the gas used (H_2 or N_2), although the product distributions are somewhat different.

No cleavage products were observed when furan was heated up to $325^\circ C$. in benzene containing $ZnCl_2$ but some of the furan was consumed. The absence of cleavage products ^{Could} attributed to the fact that a stable carbonium ion cannot be formed from cleavage of furan. The disappearance of a significant amount of furan can be ascribed to the formation of a stable complex with $ZnCl_2$ which remains in the $ZnCl_2$ phase, and to the formation of some tar. While the hydrogenation of furan to tetrahydrofuran would make further reaction possible, there was no evidence for tetrahydrofuran formation at a hydrogen pressure of 13.9 MPa.

Conclusions

The present study has shown that both cyclic and non-cyclic ethers react readily provided that the ether oxygen is adjacent to at least one methylene group. During the initial steps of cleavage both types of ether form fragments which rapidly alkylate aromatic centers.

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For dibenzyl and cyclo-aliphatic ethers the oxygen atom is removed completely to form water. However, if the oxygen is bonded to a phenyl or naphthyl group then a phenolic hydroxyl group is formed, which is ^{stable}~~refractory~~ to further reaction. The distribution of products obtained from different substrates and the effects of different solvents can be interpreted in terms of carbonium ion mechanisms similar to those used to explain Friedel-Crafts chemistry. Both the experimental results and the proposed reaction mechanisms suggest that gaseous hydrogen is not involved in forming the observed products.

Based upon the results reported here it is possible to predict the effects of ZnCl_2 on ether linkages present in coal. Linkages of the form $\text{Ar-CH}_2\text{-O-CH}_2\text{-Ar}$ should cleave with the elimination of oxygen as water. The remaining benzylic carbonium ions should then react with aromatic moieties present in the solvent. Structures of the type $\text{Ar-O-CH}_2\text{-Ar}$ will also undergo cleavage. However, in this case the oxygen atom will be retained as a phenol. Cleavage of both types of linkage should result in a reduction in the molecular weight of the coal structure and an increase in the solubility of the fragments in aromatic and hydroaromatic solvents. By contrast, oxygen atoms present in diaryl ethers and in furan, benzofuran, and dibenzofuran-type structures are not expected to undergo reaction at temperatures below 350°C and in the presence of ZnCl_2 . Likewise, phenolic hydroxyl groups will also be unaffected.

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