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The Effects of Zinc Chloride on Sulfur Removal from Coal-Related Structures

by

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ABSTRACT

Compounds containing sulfur in structures similar to those present in coal were reacted in the presence of ZnCl₂. The catalyst was found to promote the removal of sulfur from sulfides and disulfides in which sulfur is bonded to a methylene group but had no effect on the elimination of sulfur from diaryl sulfides and disulfides or thiophenic structures. In those instances where sulfur was removed a significant portion was found to react with the ZnCl₂ phase.
INTRODUCTION

Organic sulfur in coal occurs primarily in the form of thiophenes. Smaller amounts of sulfur are also present in the form of thiols, sulfides, and disulfides\(^1-3\). The removal of sulfur is an important step in coal liquefaction and usually requires a catalyst to achieve a high degree of desulfurization. The present study was undertaken to determine the ability of \(\text{ZnCl}_2\) to catalyze the removal of sulfur from coal-related structures. This work was motivated by the recognition that while \(\text{ZnCl}_2\) has shown considerable promise as a coal liquefaction catalyst\(^4-7\), little is known concerning its desulfurization characteristics. To facilitate the identification of reaction products and pathways, the present studies were carried out using model compounds containing sulfur in structures resembling those found in coal.

EXPERIMENTAL

Experimental Apparatus and Procedure

Batch reactions of sulfur containing model compounds were carried out in a 300 cm\(^3\) 316 stainless steel, stirred autoclave (Autoclave Engineers, Inc. Model ABP-300) fitted with 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.

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 components were separated by filtration. The liquid products were identified using a Finnigan 4023 gas chromatograph/mass spectrometer. Quantitative analysis of these products was made by gas chromatography on a 1/8" x 10' column packed with 5% OV-225 on Chromosorb P. In some instances, gas products collected from the head space of the autoclave were analyzed by gas chromatography on a 3/16" x 15' column packed with Poropak Q.

Materials

The following compounds were used as models of sulfide and disulfide structures in coal: diphenyl sulfide (Eastman Organic Chemicals), dibenzyl sulfide (Eastman Organic Chemicals), diphenyl disulfide (Eastman Organic Chemicals) and dibenzyl disulfide (Eastman Organic Chemicals). Thiophenic structures were modeled by: thiophene (Aldrich), tetrahydrothiophene (MCB), and dibenzothiophene (Eastman Organic Chemicals). Each of the model compounds was used as obtained. Benzene (Mallinckrodt) and cyclohexane (MCB) were used as solvents for the reactants and products. Zinc chloride (Mallinckrodt) was used as received.
RESULTS AND DISCUSSION

The products, yields and conversion levels obtained from the reaction of sulfur-containing model compounds are summarized in Table 1. The length of reaction at temperature was 60 minutes in all cases listed. In this table, conversion is defined as the fraction of reactant which disappeared in the course of reaction. The percent theoretical yield is based on that amount of the product that could theoretically be obtained from the initial reactant. The discrepancy for a given reactant between the sum of the theoretical yields of products and the conversion can be ascribed to two causes. About 7% is due to incomplete recovery or products. The remainder of the discrepancy is due to formation of tars or resins and in some cases to complexing of reactants or products with the ZnCl₂. The tars are usually soluble, but have sufficiently high molecular weights to escape detection by gas chromatography.

**Dibenzyl Sulfide**

Dibenzyl sulfide is representative of a class of sulfur compounds which are capable of undergoing both thermal and catalytic reactions. As shown in Table 1, at 325°C in the presence of benzene and ZnCl₂, dibenzyl sulfide produces toluene, bibenzyl, stilbene and diphenylmethane. Under the same conditions but without ZnCl₂, toluene, bibenzyl and stilbene are again observed but not diphenylmethane, suggesting that the diphenylmethane arises from a reaction promoted by ZnCl₂. This conclusion is confirmed by the reactions of dibenzyl sulfide at 225°C. At this temperature, no reaction occurs in the absence of ZnCl₂.
With ZnCl₂ present, the sole product found is diphenylmethane (Table 1).

To gain some insight into the mechanism of the thermal reactions, a run was performed in which dibenzyl sulfide dissolved in benzene was heated to 325°C and then rapidly quenched. The products of this experiment showed an almost complete conversion of dibenzyl sulfide, a high ratio of stilbene to bibenzyl, and almost the same yield of toluene as that obtained following a one-hour run at 325°C. These results together with those presented in Table I suggest that dibenzyl sulfide rapidly reacts to toluene and stilbene, and that the hydrogenation of stilbene to bibenzyl occurs more slowly. A possible mechanism for these reactions is suggested by reactions 1 through 3.

\[
\begin{align*}
\text{O} & \quad \text{CH}_2\text{SCH}_2 & \quad \text{O} \quad \xrightarrow{-\text{H}_2\text{S}} \quad \text{O} & \quad \text{CH}=\text{CH} & \quad \xrightarrow{+\text{H}_2} \quad \text{O} & \quad \text{CH}_2\text{CH}_2 & \quad \text{O} \\
\text{fast} & & \text{slow} & & \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{CH}_2\text{SCH}_2 & \quad \text{O} \quad \rightarrow \quad \text{O} & \quad \text{CH}_2 & \quad + \quad \text{SCH}_2 & \quad \text{O} & \quad +\text{H}_2 \rightarrow \quad \text{O} & \quad \text{CH}_3 & \quad + \quad \text{O} & \quad \text{CH}_2\text{SH} \\
\text{2} & & & & & & & & \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{CH}_2\text{SH} \quad \rightarrow \quad \text{O} & \quad \text{CH}_2 & \quad + \quad \text{HS} & \quad +\text{H}_2 \rightarrow \quad \text{O} & \quad \text{CH}_3 & \quad + \quad \text{H}_2\text{S} \\
\text{3} & & & & & & & & \\
\end{align*}
\]

Since benzyl mercaptan is not seen as a product, for this mechanism to be plausible it must be assumed that any mercaptan formed is rapidly consumed.
The reaction of dibenzyl sulfide under the influence of ZnCl$_2$ results in the formation of diphenylmethane via reaction 4.

\[
\text{CH}_2\text{SCH}_2\text{-} + 2 \text{O} \rightarrow 2 \text{O} - \text{CH}_2\text{-} + \text{H}_2\text{S}
\]  

This process can be explained by two possible mechanisms, both of which involve the formation of benzyl carbonium ions through the action of the catalyst on the reactant.

The first mechanism is represented by reactions 5 through 8. The reaction is initiated through the formation and subsequent decomposition of an adduct between ZnCl$_2$ and dibenzyl sulfide, in a manner similar to that observed for diisopropyl sulfide$^8$. The benzyl carbonium ions produced in reactions 5 and 7 rapidly react with benzene to form diphenylmethane via reaction 6 and the catalyst is regenerated by reaction 8.

\[
\text{O} \text{CH}_2\text{SCH}_2\text{-} \rightarrow \text{O} - \text{CH}_2\text{+} + \text{O} - \text{CH}_2\text{S-ZnCl}_2\text{-}
\]

\[
\text{O} - \text{CH}_2\text{+} + \text{O} \rightarrow \text{O} - \text{CH}_2\text{-} + \text{H}^+ \]

\[
\text{O} - \text{CH}_2\text{S-ZnCl}_2\text{-} + \text{H}^+ \rightarrow \text{O} - \text{CH}_2\text{+} + \text{ZnCl}_2\text{SH}^- \]

\[
\text{ZnCl}_2\text{SH}^- + \text{H}^+ \rightarrow \text{H}_2\text{S} + \text{ZnCl}_2
\]

Reactions 9 through 12 comprise an alternative mechanism for generating benzyl carbonium ions. In this instance, ZnCl$_2$
reacts first with water, present as an impurity in the ZnCl₂ to form a Brønsted acid [i.e., H⁺(ZnCl₂OH)⁻]. This species then protonates the dibenzyl sulfide (reaction 10) thereby initiating its decomposition to a benzyl carbonium ion and a mercaptan (reaction 11) which in turn undergoes reaction to form a second benzyl carbonium ion (reactions 12 and 13).

\[
\text{ZnCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+(\text{ZnCl}_2\text{OH})^- \quad (9)
\]

\[
\begin{align*}
\text{O} & - \text{CH}_2\text{SCH}_2\text{O} + \text{H}^+(\text{ZnCl}_2\text{OH})^- \rightarrow \text{O} - \text{CH}_2\text{SCH}_2\text{O} + \text{ZnCl}_2\text{OH}^- \quad (10) \\
\text{O} & - \text{CH}_2\text{SCH}_2\text{O} \rightarrow \text{O} - \text{CH}_2^+ + \text{O} - \text{CH}_2\text{SH} \quad (11) \\
\text{O} & - \text{CH}_2\text{SH} + \text{H}^+(\text{ZnCl}_2\text{OH})^- \rightarrow \text{O} - \text{CH}_2\text{SH} + \text{ZnCl}_2\text{OH}^- \quad (12) \\
\text{O} & - \text{CH}_2\text{SH} \rightarrow \text{O} - \text{CH}_2^+ + \text{H}_2\text{S} \quad (13)
\end{align*}
\]

The two mechanisms suggested above are analogous to those proposed earlier for the reactions of dibenzyl ether catalyzed by ZnCl₂⁹ and the reactions of other ethers catalyzed by BF₃¹⁰,¹¹.

Comparison of the product composition obtained with and without the addition of ZnCl₂ shows that in the presence of the catalyst the yield of identifiable products and the ratio of bibenzyl to stilbene are lower. The lower yield may be the result of polymerization side reactions promoted by ZnCl₂ or complexing of Lewis basic species with ZnCl₂. The lower ratio of bibenzyl to stilbene suggests that the hydrogenation of stilbene may somehow be inhibited by ZnCl₂.

**Dibenzyl Disulfide**

The behavior of dibenzyl disulfide is very similar to that of dibenzyl sulfide, as can be seen from Table I. Toluene, bibenzyl
and stilbene are produced either in the presence or absence of ZnCl₂ and diphenylmethane is produced only in the presence of ZnCl₂. Here again, the catalyst appears to suppress the yield of products and the ratio of bibenzyl to stilbene.

It seems reasonable that the types of mechanisms proposed for both the thermal and catalyzed reactions of dibenzyl sulfide should also be applicable to dibenzyl disulfide. However, a broader spectrum of detailed reaction paths might be expected for the disulfide since it can decompose with rupture of either the carbon-sulfur or sulfur-sulfur bond. While it is conceivable that dibenzyl sulfide might be produced from dibenzyl disulfide, the rapid reaction of the sulfide would make its presence in the products unlikely.

**Diphenyl Sulfide**

The thermal reaction of diphenyl sulfide was studied in cyclohexane, since benzene is a likely reaction product in this case. At 325°C diphenyl sulfide was partially converted to benzene and thiophenol. In the presence of ZnCl₂ the conversion was lowered and benzene was the only observed product. If the catalyzed reaction is carried out in benzene, some diphenyl sulfide is lost from solution but no identifiable products are produced.

These results indicate that diphenyl sulfide does not undergo a ZnCl₂ promoted cleavage reaction. This is consistent with the proposed carbonium ion chemistry since cleavage aided by ZnCl₂ would require the formation of a highly unstable phenyl carbonium ion. The apparent inhibition of the thermal reaction by ZnCl₂ may be due to an acid-base interaction between diphenyl sulfide and ZnCl₂. A similar interaction might explain the absence of thiophenol as a product when ZnCl₂ is present.
Diphenyl Disulfide

Diphenyl disulfide undergoes thermal decomposition much more readily than diphenyl sulfide at 325°C. Diphenyl sulfide and thiophenol were the only products observed, since the reaction was carried out in benzene solution. The presence of ZnCl₂ decreased the conversion and increased the ratio of diphenyl sulfide to thiophenol formed. These observations again suggest that thermal rather than catalytic reactions are dominant. Most likely, reaction begins with rupture of the sulfur-sulfur bond. The pair of free radicals thus produced may react with benzene to form diphenyl sulfide or with hydrogen to form thiophenol. The inhibition of the reaction by ZnCl₂ may in some way arise from association of the catalyst with the diphenyl disulfide or with the diphenyl sulfide, preventing its further reaction to thiophenol. Such an interpretation might also explain the predominance of diphenyl sulfide over thiophenol in the presence of ZnCl₂.

Thiophene of Dibenzothiophene

Neither thiophene nor dibenzothiophene underwent thermal reaction at 325°C. The addition of ZnCl₂ resulted in a slight loss of reactant, probably due to the formation of an adduct with the catalyst, but did not result in observable reaction products.

Tetrahydrothiophene

Tetrahydrothiophene was found to be thermally stable at 325°C. When heated with ZnCl₂ at 225°C for one hour, nearly all of the tetrahydrothiophene was consumed from the solution, but no soluble products were observed. Analysis of the gases in the autoclave head space also failed to reveal any reaction products.
Thus, the only product appeared to be a complex of tetrahydrothiophene and ZnCl$_2$ which remained in the solid ZnCl$_2$ phase. This conclusion is supported by elemental analysis of the solids collected after reaction and previous reports that tetrahydrothiophene will form complexes with other Lewis acids$^{12,13}$.

When the reaction temperature is increased to 325°C, the complex of tetrahydrothiophene formed at lower temperature decomposes. The resulting products in the gas phase are saturated C$_1$ through C$_4$ hydrocarbons and H$_2$S. In the liquid phase, the primary product is sec-butylbenzene, along with some n-butylbenzene, iso-propyl-benzene, and toluene. These products are similar to those observed when tetrahydrofuran is reacted in the presence of ZnCl$_2$.$^9$

The production of sec-butylbenzene can be explained by a carbonium ion mechanism as shown below.

\[
\begin{align*}
\text{ZnCl}_2 & \rightarrow \text{S}_{\text{ZnCl}_2} \\
\text{S}_{\text{ZnCl}_2} & + \text{O} \rightarrow \text{O} + \text{H}^+ \\
\text{O} & + \text{H}^+ + \text{S} \rightarrow \text{O} + \text{S} + (\text{ZnCl}_2\text{SH})^- \\
\end{align*}
\]
Reaction 14 produces a secondary carbonium ion, which then reacts with benzene. Reaction 16 and 17 show a possible mechanism for abstracting hydrogen from tetrahydrothiophene to terminate the alkyl chain.

The presence of isopropylbenzene, toluene and C₁ through C₃ hydrocarbons in the products indicates that the four-membered carbon chain of tetrahydrothiophene is cracked. It is interesting to note that these gases are all saturated species. The source of hydrogen is unknown, though existence of a char in the solid phase suggests that a part of the reactant may have been condensed with a concurrent release of hydrogen.

It is also significant to note that while a some H₂S is found in the gaseous products, the majority of the sulfur remains in the solid phase. Part of this may be due to an incomplete reaction of the adduct formed between tetrahydrothiophene and ZnCl₂. The balance may be due to the reaction of H₂S with ZnCl₂ to form ZnS, a reaction which is thermodynamically favored. While analyses for ZnS were not obtained it seems very likely that this product may be formed not only during the reactions of tetrahydrothiophene but also of other substrates from which sulfur is released.

CONCLUSIONS

The present investigation has shown that ZnCl₂ promotes the removal of sulfur from sulfides and disulfides in which the sulfur atom is bonded to a methylene group. Reaction is initiated either by proton transfer from the Brønsted acid form of the catalyst or by direct complexing of the reactant to ZnCl₂. During subsequent steps a carbonium ion is produced which can participate in electrophilic substitution with an aromatic center. It is observed that a significant portion of the sulfur removed
is retained by the ZnCl₂ as a Lewis acid/base adduct or reacts with the ZnCl₂ to form ZnS. These studies have also demonstrated that ZnCl₂ does not promote the removal of sulfur from diphenyl, sulfide, diphenyl disulfide, thiophene, or dibenzothiophene.

ACKNOWLEDGMENT

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REFERENCES


   2, 12 as referred to in H. H. Lowry, "Chemistry of Coal


5. Zielke, C. W., Struck, R. T., Evans, J. M. Costanza, C. P.,
   5, 158.

6. Struck, R. T., Clark, W. E., Dudt, P. J., Rosenhoover, W. A.,
   Dev., 1969, 8, 546.

   Design Dev., 1976, 15, 144.

   and Grens, E. A., paper presented at AIChE National Meeting,
   Miami, November 1978.

   1975, 1177.

    1941, 63, 1722.


12. Mobley, D. P. and Bell, A. T., Univ. of California, Lawrence

    66, 2277.
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<th>Reaction Pressure (MPa)</th>
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</tr>
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<td>Tetrahydrothiophene</td>
<td>Benzene</td>
<td>21.5</td>
<td>2.98</td>
<td>325</td>
<td>15.8</td>
<td>Butanes, Propane, Hydrogen sulfide, Ethane, Methane, sec-Butylbenzene, Toluene, Isopropylbenzene, n-Butylbenzene</td>
<td>15, 13, 6, 3, 2, 2.4, 1.3, 0.9, 0.8</td>
<td>91.2</td>
</tr>
</tbody>
</table>

(1) Based on 2 moles product per mole reactant
(2) Based on 1 mole product per mole reactant
(3) Based on 4 moles product per mole reactant
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