ON THE ROLE OF SULFUR COMPOUNDS IN COAL LIQUEFACTION

C.B. Huang and L.M. Stock

Department of Chemistry
University of Chicago
Chicago, Illinois 60637

Introduction

The sulfur content of a coal is an important factor in the success of its conversion reactions (1-5). Sulfur minerals and organic sulfur compounds in the coal may contribute significantly to the conversion which begins with the fragmentation reactions ends with product improvement reactions. Prior investigations have focused on the role of sulfur compounds in the mineral matter and special emphasis has been given to the iron sulfides that are prominent in many coals (6). An investigation of the hydrogen atom transfer reactions of tetralin with coals, coal products, diphenylmethane, and the molecular constituents of coal revealed that [(phenylmethyl)thio]benzene considerably accelerated the rate of transfer of hydrogen between the benzylic positions of these molecules (equation 1) (7). Indeed, the catalytic influence of this

$$\text{T-d}_{12} + C_6H_5CH_2C_6H_5 \xrightarrow{400°C} \text{T-d}_{11} + C_6H_5CHDC_6H_5 \qquad 1)$$

thioether was much greater than that observed for many other compounds. Subsequent work has established that some sulfur compounds significantly increase the rate of liquefaction of Illinois No. 6 coal in tetralin. These intriguing observations prompted us to study the role of organic sulfur compounds and sulfur minerals in the hydrogen atom transfer reactions that are so essential in successful conversion processes. For this purpose, we have examined the influence of sulfur-containing compounds on the exchange reaction between tetralin-d_{12} and diphenylmethane (equation 1). The catalytic activity of aromatic and aliphatic thiols and thioethers has been investigated as has the activity of some metal sulfides. Metal sulfide-hydrogen sulfide and metal sulfide-phenol cocatalysts have also received attention. In addition, the impact of representative catalysts upon the rate of decomposition of 1,3-diphenylpropane and upon the rate of liquefaction of Illinois No. 6 coal in tetralin have been examined.

Results and Discussion

Organic Sulfur Compounds. Heterocyclic sulfur compounds such as 2,3-benzothiophene and dibenzothiophene do not enhance the rate of exchange of hydrogen atoms between tetralin-d_{12} and diphenylmethane (8). However, unstable thioethers such as [(phenylmethyl)thio]benzene considerably accelerate this exchange reaction. It was postulated that this compound en-

hanced the rate via the reactions shown in equations (2)-(6) where T-d_{12} represents the initial labeled tetralin and 1-T-d_{11}· represents the benzylic radical formed from this labeled compound. It is well known that benzene-

$$C_6H_5CH_2SC_6H_5 \rightarrow C_6H_5CH_2\cdot + \cdot SC_6H_5 \qquad 2)$$

$$C_6H_5CH_2\cdot + T\text{-}d_{12} \rightarrow C_6H_5CH_3 + 1\text{-}T\text{-}d_{11}\cdot \qquad 3)$$

$$C_6H_5S\cdot + T\text{-}d_{12} \rightarrow C_6H_5SH + 1\text{-}T\text{-}d_{11}\cdot \qquad 4)$$

$$1\text{-}T\text{-}d_{11}\cdot + C_6H_5CH_2C_6H_5 \rightarrow C_6H_5\dot{C}HC_6H_5 + T\text{-}d_{11} \qquad 5)$$

$$C_6H_5\dot{C}HC_6H_5 + T\text{-}d_{12} \rightarrow 1\text{-}T\text{-}d_{11}\cdot + C_6H_5CHDC_6H_5 \qquad 6)$$

thiol and other thiols are very effective hydrogen transfer agents (9). Consequently, the decomposition of the thioether provides a reactive product, benzenethiol, which may also accelerate the exchange reaction. Several other compounds were studied to assess their catalytic activity. Representative results are presented in Table 1.

Table 1. The influence of organic sulfur compounds on the deuterium-hydrogen exchange reaction between tetralin-d_{12} and diphenylmethane at 400°C.[a]

Additive	Time (min)	Deuterium content of the 1-position of diphenylmethane (%)
None	30	15
[(Phenylmethyl)-thio]benzene	4	59
Diphenyldisulfide	2	66
Benzenethiol	5	51
1-Naphthalenethiol	5	58
	30	73
Benzenemethanethiol	30	55
	10	68
1-Butanethiol	30	37
Hydrogen sulfide[c]	30	28

[a]Diphenylmethane (0.376 mmole), tetralin-d_{12} (0.377 mmole) and the additive (0.045 mmole) were reacted in a glass vessel. The exchange occurred almost exclusively at the benzylic position of tetralin.

[b]Reference 8.

[c]A lesser quantity (0.020 mmole) of this additive was used.

Diphenyldisulfide is an even more effective catalyst than [(phenylmethyl)thio]benzene. The deuterium content at the benzylic positions of the exchanging molecules reaches equilibrium in less than 3 min at 400°C in the presence of this catalyst. The reaction also proceeds rapidly at 350°C. Aromatic thiols including the benzene, 1-naphthalene, and 2-naphthalene derivatives as well as dithiols such as 4-methyl-1,2-benzenedithiol are also very active reagents. The aliphatic thiols and hydrogen sulfide are moderately less effective than the aromatic thiols in this exchange reaction. These observations suggest that compounds which form aromatic thiyl radicals are especially good catalysts for the selective exchange of the benzylic hydrogen atoms. The reactivity of the thiols is not surprising inasmuch as compounds of this class are known to be especially effective chain transfer agents in polymerization reactions at much lower temperatures (9). The information available from such studies indicates that no universally applicable order of reactivity can be established for thiols. Thus, the parallel observed between the effectiveness of the catalyst in the exchange reactions of tetralin-d_{12} and the strength of the S-H bond* may not be manifest with all reactive substrates.

Compounds that promote the exchange reactions of benzylic hydrogen atoms sometimes also promote the rate of the decomposition of hydrocarbons (10). 1,3-Diphenylpropane was selected for study because such structures may be labile constituents of many bituminous and subbituminous coals. To test the effectiveness of organic sulfur compounds for the catalysis of the decomposition reactions of such compounds, we studied the rate of decomposition of 1,3-diphenylpropane, Table 2.

The thiol and the thioether are both very effective catalysts for the decomposition of the propane. The reaction path outlined in equations (7) and (8) emphasizes the role of the thiyl radical in increasing the concen-

$$C_6H_5S\cdot + C_6H_5CH_2CH_2CH_2C_6H_5 \rightleftharpoons C_6H_5SH + C_6H_5\dot{C}HCH_2CH_2C_6H_5 \qquad 7)$$

$$C_6H_5\dot{C}HCH_2CH_2C_6H_5 \rightarrow C_6H_5CH{=}CH_2 + C_6H_5CH_2\cdot \qquad 8)$$

*The bond dissociation energies of aliphatic thiols are about 10 kcal. $mole^{-1}$ greater than that of the aromatic thiols (11).

tration of the benzylic radical that decomposes via a familiar β-scission reaction to yield the fragmented products.

The thiol and the thioether are also very effective catalysts for the conversion of Illinois No. 6 coal to pyridine-soluble products, Table 3.

Table 2. The influence of certain organic sulfur compounds on the rate of decomposition of 1,3-diphenylpropane in tetralin at 400°C.[a]

Additive	Time (min)	Decomposition (%)	Product Distribution	
			Toluene	Ethylbenzene
None	30	25	77	23
Illinois No. 6 coal (51 mg)[b]	30	43	58	42
[(Phenylmethyl)-thio]benzene[b]	30	77	73	27
Thiophenol	30	80	78	22

[a]1,3-Diphenylpropane (0.758 mmole), tetralin (0.757 mmole), and the additive (0.09 mmole) were used in each reaction in a glass vessel.

[b]Reference 10.

Table 3. The influence of sulfur compounds on the reaction of Illinois No. 6 coal with tetralin.[a]

Additive	Reaction Conditions		Solubility (%)		
	Temp (°C)	Time (min)	Pyridine	Toluene	Hexane
None	400	4	58	24	15
[(Phenylmethyl)-thio]benzene	400	4	88	13	10
Thiophenol	400	4	87	18	13

[a]Illinois No. 6 coal (0.76g), tetralin (1.57g) and the additive (1.35 mmole) were reacted in a 4.6 ml stainless steel reactor.

In summary, the observations presented in Tables 1-3 demonstrate the effectiveness of organic sulfur compounds for the promotion of benzylic exchange reactions, hydrocarbon decomposition, and coal dissolution processes. This chemistry strongly suggests that organic sulfur compounds in coals can have a major influence on the rates of low severity coal dissolution reactions. It is pertinent that Attar and Dupuis have reported that about 50 atom percent of the organic sulfur in an Illinois No. 6 coal is present in thiol groups or molecules that are readily converted to thiols (12). This is equivalent to 0.05 gm moles of thiol per 100 gm of this coal. Such high concentrations must exert an important influence on the course of these reactions. Of course, the distribution of sulfur compounds among the various functional groups varies considerably in coals of different rank and it is unlikely that the reactivity of coals will, in a general way, correlate with the percentage of organic sulfur. Moreover, the hydrodesulfurization reactions which occur during the liquefaction reactions presumably convert heterocyclic sulfur compounds to reactive aromatic thiols (13). These reactions also convert aromatic thiols to less reactive hydrogen sulfide. Consequently, the effective use of the sulfur compounds in the coal as naturally-provided disposable catalysts requires careful selection of the reaction conditions.

Metal Sulfides.--Previous workers have reported that iron sulfides and other minerals increase the conversion of coals to soluble products (5,6). To examine this aspect of the chemistry, we also studied the influence of some sulfides and minerals on the exchange reaction (equation 1). Representative results are presented in Table 4.

None of the iron sulfides are effective catalysts for the exchange reaction. Chromium(III) and molybdenum(IV) sulfide are similarly unreactive. However, molybdenum(VI) and tungsten(IV) sulfide catalyze the exchange of the benzylic and aromatic hydrogen atoms of tetralin and diphenylmethane. The manner in which these catalysts accelerate the exchange of the aromatic hydrogen atoms has not yet been investigated. However, the observation that molybdenum(VI) sulfide, which decomposes to molybdenum(IV) sulfide and sulfur under the experimental conditions (14), is highly reactive may be related to the finding that sulfur is also deposited during the reduction of pyrite to pyrrhotite (2,6). Such results imply that the sulfur and the hydrogen sulfide produced in the presence of the unstable metal sulfides are the actual catalysts or cocatalysts for the exchange and conversion reactions (2,6). Inasmuch as sulfur would be converted to hydrogen sulfide during the oxidation the hydroaromatic compounds in coal under these experimental conditions, we elected to study the cocatalytic influences of hydrogen sulfide. Representative results are presented in Table 5.

A modest cocatalytic effect is realized with these metal sulfides. These observations, therefore, provide support for the view that sulfur and the hydrogen sulfide formed from it through the reduction or decomposition of minerals actively promote the liquefaction reaction.

While it is clear that the sulfur and hydrogen sulfide can contribute significantly to the enhanced reactivity of the coals rich in minerals, it is also necessary to consider the possibility that such substances might

Table 4. The influence of metal sulfides on the hydrogen-deuterium exchange reaction between diphenylmethane and tetralin-d_{12} at 400°C.[a]

Metal sulfide	Deuterium content (%)				
	Diphenylmethane		Tetralin		
	Ar	1-	Ar	1-	2-
None	0	15	91	91	91
Pyrite, FeS_2	0	13	93	89	92
Iron(II) sulfide, FeS	0	16	93	90	90
Pyrrhotite, $Fe_{1-x}S$	0	18	92	92	92
Bornite, Cu_5FeS_4	0	17	93	92	91
Sphalerite, ZnFeS	0	18	92	92	92
Chromium(III) sulfide, Cr_2S_3	0	15	91	93	93
Molybdenum(IV) sulfide, MoS_2	2	12	90	93	92
Molybdenum(VI) sulfide, MoS_3	41	32	54	71	72
Tungsten(IV) sulfide, WS_2	14	13	60	92	90

[a]Diphenylmethane (0.377 mmole), tetralin-d_{12} (0.377 mmole), and the potential catalyst (0.045 mmole) were reacted in a glass vessel for 30 min. The initial deuterium content of the tetralin was 94% Ar-d, 95% 1-d, and 92% 2-d.

Table 5. The influence of hydrogen sulfide-metal sulfide catalysts on the exchange reaction between diphenylmethane and tetralin-d_{12} at 400°C.[a]

Catalyst	Deuterium content at the 1 position of diphenylmethane (%)
None	15
Hydrogen sulfide	25
With pyrite	30
With pyrrhotite	32
With molybdenum(IV) sulfide	24

[a]Diphenylmethane (0.376 mmole), tetralin-d_{12} (0.377 mmole) and the catalysts (0.02 mmole of each compound) were reacted for 30 min. The exchange occurred selectively at the 1 position of tetralin.

exert their beneficial effects upon liquefaction through the direct or indirect formation of highly reactive thiols as illustrated in equation (9).

$$\text{Metal sulfide} + \text{ArOH} \rightarrow \text{ArSH} + \text{Metal oxide} \qquad 9)$$

We found that the iron sulfides were no more active in the presence of 1-naphthol than in its absence. The direct transfer reaction is apparently too slow to be effective. However, the exchange reaction between tetralin-d_{12} and diphenylmethane was enhanced significantly in the presence of sodium sulfide and 1-naphthol. This simple sulfide also enhanced the reactivity of phenyl benzyl ether. To explore this aspect of the chemistry more thoroughly, we studied the influence of hydrogen sulfide and phenols, Table 6.

Table 6. The influence of hydrogen sulfide-phenol cocatalysts on the hydrogen-deuterium exchange reaction of diphenylmethane and tetralin-d_{12} at 400°C.[a]

Catalyst	Deuterium content at the 1 position of diphenylmethane (%)
None	15
Hydrogen sulfide alone	25
With phenol	25
With 1-naphthol	30
With 9-phenanthrol	30

[a]These experiments were performed as described in Table 5.

These results suggest that the multiring phenolic compounds can act as cocatalysts for the exchange reaction. Other work with sodium sulfide and 1- and 2-naphthol, 9-phenanthrol and 2,3-naphthalenediol supports this interpretation.

Conclusion

Sulfur compounds that can yield thiols catalyze the exchange reaction, the decomposition of 1,3-diphenylpropane, and the conversion of Illinois No. 6 coal to soluble products. Although certain metal sulfides may intervene directly with the organic compounds present in coals, our results suggest that indirect pathways may be more significant. As already mentioned, this research supports the view that the sulfur and hydrogen sulfide produced from the minerals in decomposition or reduction reactions accelerate the free radical processes essential for facile coal conversion. The observation that the reactivity of hydrogen sulfide appears to be enhanced in the presence of phenolic compounds suggests, in addition, that modest quantities of the sulfides may be converted to highly catalytically active thiols even under the conditions of low severity reactions.

Experimental Part

The preparation of tetralin-d_{12} and its use in exchange reactions with a variety of organic compounds has been described previously (7,8). Similar procedures were used in this work. The metal sulfides were obtained from commercial sources or from the Illinois Geologic Survey through the courtesy of Dr. Carl Kruse. These catalysts were introduced into the glass reaction vessels as fine powders. The influence of particle size on these reactions has not yet been examined. The reaction products were studied by gas chromatography and nuclear magnetic resonance spectroscopy at 270 or 500 MHz.

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