

THE DESULFURIZATION OF COAL AND MODEL COAL COMPOUNDS IN AMBIENT TEMPERATURE MOLTEN SALTS

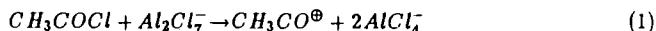
David S. Newman, Ellen M. Kurt, and Denguan Chen
Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

ABSTRACT

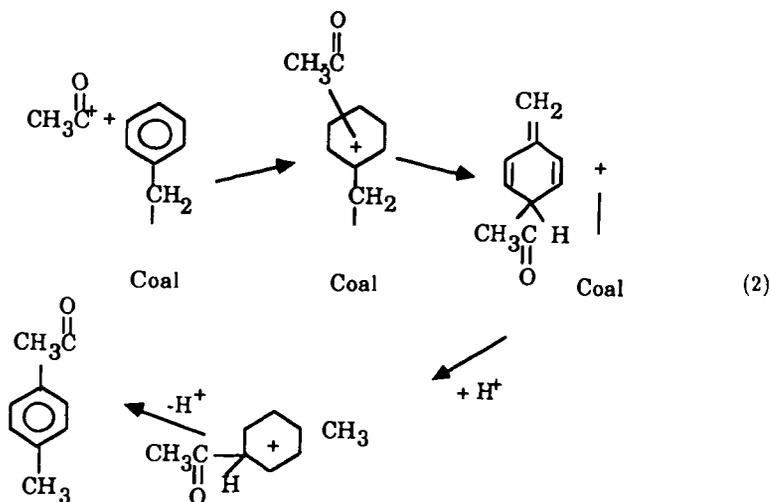
An ambient temperature molten salt, $C_5H_5N^+ \cdot Al_2Cl_7^-$ (pyridinium heptachloroaluminate) containing dissolved $CdCl_2$ was used as the reaction medium and catalyst for the acylation and concomitant desulfurization of IL #6 coal and several model coal compounds. The reactions were done at $40^\circ C$ and 1 at. pressure and, in the case of the model compounds, products were identified and mechanisms proposed.

INTRODUCTION

Gaseous byproducts of the combustion of coal are the major contributors to acid rain. Since a gradual change from a primarily petroleum-based economy to a coal-based economy is virtually inevitable, cleaning, liquefying, gasifying, and generally modifying coal have become major goals of chemistry and chemical engineering. Ideally, coal should be modified by means of chemical scission reactions which remove designated portions of the coal or break specific chemical bonds via a known mechanism. Moreover, these scission reactions should occur at ambient temperature and atmospheric pressure so that unwanted side reactions occur at a minimal rate. To this end we have developed a series of Friedel-Crafts acylations and alkylations that take place in the ambient temperature molten salt $C_5H_5N^+ Al_2Cl_7^-$ (pyridinium heptachloroaluminate). (1,2,3,4) For Example, we found that F-C alkylation of PSOC 244 high sulfur coal increased its solubility in a 3:1 benzene/methanol solution approximately five fold relative to the untreated demineralized coal. (1,2) We also found that acylating IL #6 coal with acetyl chloride in this medium increased its solubility in 3:1 benz/methanol by about a factor of five. (3,4) The increased solubility is caused by hydrogen ions breaking the methylene chains holding the sub units of the coal macromolecule together. The mechanism for the acylation and accompanying depolymerization is most likely: (3,5,6)



followed by:



The proton then reacts with $AlCl_4^-$:

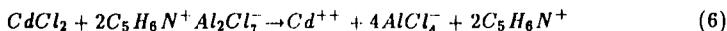


Both $AlCl_3$ and HCl have been identified as reaction products. The net reaction is



In 1980 Mobley and Bell found that $ZnCl_2$ catalyzed the removal of sulfur from the model coal compounds dibenzyl sulfide and tetrahydrothiophene and a variety of solid sulfides were identified. The net result of the $ZnCl_2$ -model compound interaction was the breaking of the aliphatic -C-S bond in each of the model compounds. (7) The $ZnCl_2$ had little effect on aromatic C-S bonds in thiophene and diphenyl thiophene. The mechanism suggested by Mobley and Bell for the catalytic reaction is somewhat similar to the mechanism for the F-C acylation or alkylation of coal or model compounds in pyridinium heptachloroaluminate. Since $CdCl_2$ is more soluble in this melt, (8) and also has a great affinity for sulfur, we

decided to dissolve CdCl_2 in the heptachloroaluminate melt. The dissolution reaction is probably,



The $\text{C}_5\text{H}_6\text{NAl}_2\text{Cl}_7$ acts as an acid and the CdCl_2 acts as a base. We then used the Cd^{++} containing melt as both catalyst and reaction medium for the removal of sulfur from model compounds and from coal. We also thought that the scission of C-C- and C-S bonds, as well as the formation of sulfides, would be facilitated by the F-C reactions and by the aluminum ion which forms an extremely stable sulfide. Hydrogen ions, arising from a variety of sources, would also be expected to facilitate the formation of H_2S .

The F-C experimental conditions were similar to those used in earlier studies. (2,3,4)

RESULTS AND DISCUSSION

Reactions of Model Coal Compounds

1. Dibenzyl Sulfide

Dibenzyl sulfide (0.0041 moles) was dissolved in 0.1143 moles of pyridinium heptachloroaluminate to which 0.0071 moles of acetyl chloride and 0.0027 moles of CdCl_2 were added. The mole fraction of CdCl_2 in the slurry was 0.022. The reaction was allowed to proceed under N_2 for 20 hours at 40°C whereupon it was quenched with water. The inorganic compounds $\text{HCl}(\text{g})$, $\text{H}_2\text{S}(\text{g})$ and $\text{AlCl}_3(\text{g})$ were isolated and identified as reaction products. The organic reaction products tentatively identified by GC/MS are listed in Table 1 in order of abundance.

In addition to the compounds listed in Table I, unidentifiable polymeric material was obtained. A second mixture with different concentrations (melt, 0.1200 moles; dibenzyl sulfide, 0.0076 moles; acetyl chloride, 0.0615 moles; CdCl_2 , 0.0081 moles) was allowed to react under N_2 for 20 hours at 40°C . The same products, in different proportions, were identified.

Some of the original cadmium was found in the aqueous layer, and some was incorporated into a black precipitate which formed during the reaction. It is not clear what percentage of the model compound's C-S bonds were broken, but our estimate is that approximately half were cleaved under the reaction conditions used. We think that if reaction conditions were optimized for sulfur removal, all of the C-S bonds in dibenzyl sulfide could be broken.

2. Thiophene

Thiophene (0.0106 moles) was allowed to react with acetyl chloride (0.0625) moles in the Cd^{++} containing melt. $\text{H}_2\text{S}(\text{g})$ was identified along with $\text{HCl}(\text{g})$ and $\text{AlCl}_3(\text{g})$. A yellow filtrate was collected upon filtration of the quenched reaction products. A solid precipitate formed which consisted of brownish-white crystals and a few black crystals. Both Cd and Al were found in the precipitate, as well as some polymeric material that could not be identified. The yellow liquid contained unreacted thiophene, acylated thiophene, and several species which have not been identified yet. Since the H_2S and probably the Cd and Al found in the precipitate arose from a reaction of the thiophene with the melt, aromatic C-S bonds had to have been broken! This was not found to occur with ZnCl_2 even though the reaction conditions were much harsher (250°C , 10 atm pressure). (7)

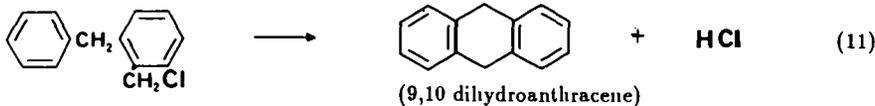
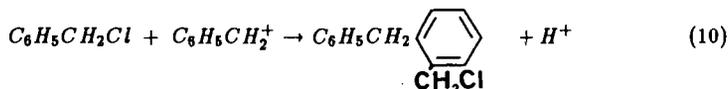
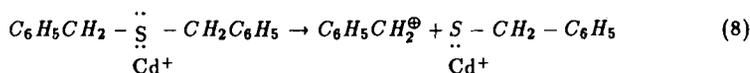
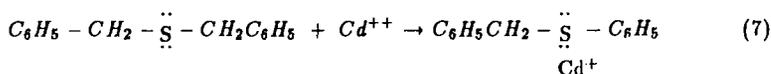
3. Dibenzothiophene

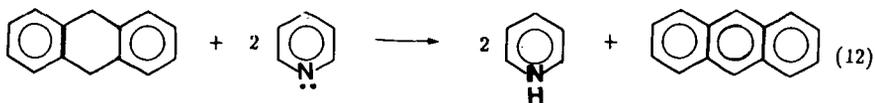
Dibenzothiophene did not react to a measurable degree under the previously described experimental conditions.

II. IL #6 Coal

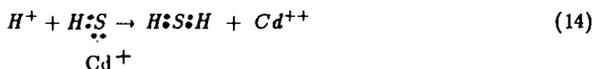
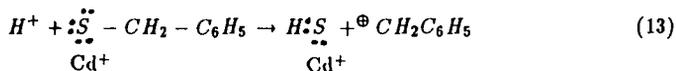
A 1 g sample of HF/HCl demineralized IL #6 coal (batch # I.D. 301.00135) was slurried in 50 ml of Cd^{++} containing heptachloroaluminate molten salt to which 1 g of acetyl chloride was added. The reaction was allowed to continue for 16 hours under nitrogen atmosphere. The procedure is similar to that used in earlier studies. (1,2,3) The coal's solubility was then measured in 3:1 benz/methanol and found to be 11.7%. A small quantity of H_2S was identified as a reaction product of the F-C acylation by allowing the N_2 carrier gas to pass through an aqueous $CdCl_2$ solution and observing the precipitation of CdS . The total sulfur content of the insoluble and soluble portions of the coal were analyzed and compared with the sulfur content of the original demineralized coal. The difference between the sulfur content of the reacted and original coal is assumed to have formed H_2S . The data are shown in Table II. The sulfur containing compounds formed during the reaction will be identified where possible and the results reported at a later date.

The formation of anthracene or phenanthrene from dibenzyl sulfide is perhaps the most unexpected aspect of the model coal compound study. A plausible mechanism that fits all of the data is the following:





In order to substantiate this mechanism, benzyl chloride was added to the melt and allowed to react for 20 hours at 40°C. GC/MS of the precipitate gave the same spectrum as authentic anthracene alone. To establish the presence of 9,10 dihydroanthracene as an intermediate in the reaction, authentic dihydroanthracene was added to the neat melt and allowed to react for 20 hours at 40°C. GC/MS of the precipitate showed the same spectrum as anthracene alone did. The mechanism for H₂S formation is probably as follows:



The Cd⁺⁺ thus serves as a catalyst for the reaction. Al⁺³ also reacts very strongly with sulfur and its role in the desulfurization mechanism is currently under investigation.

CONCLUSION

The extremely mild conditions used for the solubilization and desulfurization of coal and model coal compounds indicate that the molten salt may be an extremely useful medium for coal chemistry. If the soluble coal compounds can be identified, the nature of the sulfur containing fragments of the coal macromolecule can also be determined with some degree of assurance because their structure is the same as, or at least mechanistically related to their structure, in the original coal. Furthermore, if reaction conditions are optimized, a very high percentage of a coal's sulfur can be removed at room temperature and atmospheric pressure.

ACKNOWLEDGMENT

We would like to thank the Alumni Undergraduate Research Program at Bowling Green State University and the Research Challenge Program of the State of Ohio for their support. We would also like to thank the Premium Coal Sample Program at Argonne National Laboratory for contributing the coal samples.

LIST OF REFERENCES

1. D. S. Newman, R. E. Winans, "Proceedings of the Third International Symposium on Molten Salts," G. Mamantov, M. Blander, G. P. Smith, Editors, The Electrochemical Society Softbound Series, p. 425, Pennington, NJ, 1981.
2. D. S. Newman, R. E. Winans, R. L. McBeth, *J. Electrochem. Soc.* **131**, 1079 (1984).
3. D. S. Newman, T. H. Kinstle, G. Thambo, "Proceedings of the Joint International Symposium on Molten Salts," G. Mamantov, M. Blander *et al.* Eds., The Electrochemical Society, Pennington, NJ 1987, p. 991-1001.
4. D. S. Newman, T. H. Kinstle, G. Thambo, R. E. Winans, R. Hayatsu, R. L. McBeth, "Energy and Fuels," submitted for publication, 1988.
5. J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.* **51**, 480 (1986).
6. J. A. Boon, S. W. Lander, J. A. Levisky, J. L. Pflug, L. M. Skizynecki-Cooke, J. S. Wilkes, "Proceedings of the Joint International Symposium on Molten Salts," G. Mamantov, M. Blander *et al.* Eds., The Electrochemical Society, Pennington, NJ 1987, p. 979-990.
7. D. P. Mobley and A. T. Bell, *Fuel* **59**, 507 (1980).
8. R. R. Rhinebarger, Ph.D. Thesis, Michigan State University (1986).

Table I. Organic Reaction Products of Dibenzyl Sulfide at 40°C

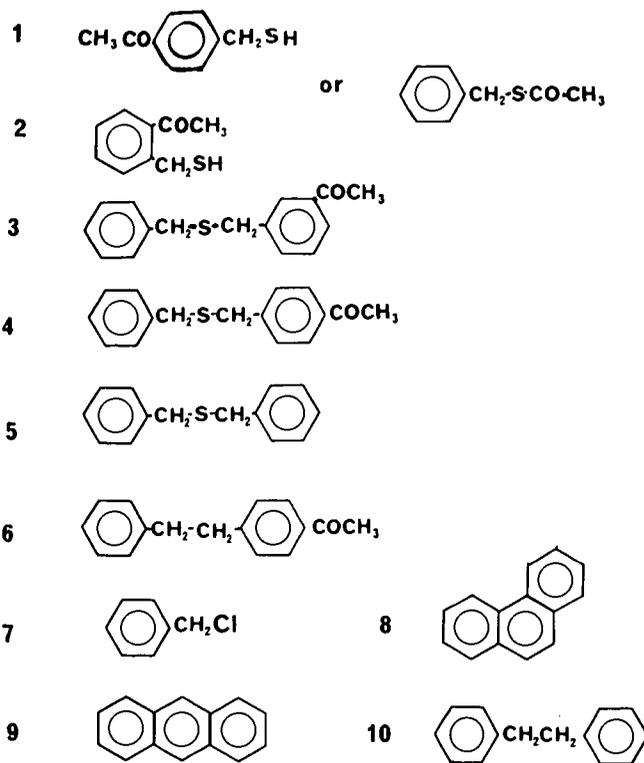


Table II. Weight Percent Sulfur in Coal Samples

Original Coal	Insoluble Portion	Soluble Portion
4.57	3.37	2.42

This page intentionally left blank