

THE CHEMISTRY OF MOLTEN HYDROXIDE DESULFURIZATION USING MODEL SYSTEMS

Bruce R. Utz, Steven K. Soboczinski, and Sidney Friedman

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

INTRODUCTION

The TRW "Gravimelt" Molten Hydroxide Desulfurization Process is being developed to remove sulfur from coal [1]. While the chemistry for removing inorganic sulfur is being examined actively [2], little research has been done on the removal of sulfur from organosulfur moieties in coal. The objective of this study is to determine how molten hydroxides remove organosulfur from coal. The two model compounds used initially to examine the chemistry of organosulfur removal are benzothiophene and dibenzothiophene. These model compounds were chosen because they simulate sulfur compounds in coal. Thermal decomposition reactions of intermediate products were also studied, and based on the results, a proposed pathway for desulfurization is suggested. The potential role of water in molten hydroxide desulfurization was determined by varying the amount of water present in the hydroxide mixture. Results demonstrate that water does not play an important role in the removal of sulfur from organosulfur moieties. Since both sodium hydroxide and potassium hydroxide have typically been used in the TRW Molten Hydroxide Desulfurization Process, the importance of each hydroxide was examined. It was found that the relative amount of each hydroxide may be critical in removing organosulfur and that potassium hydroxide is the important species. Continuing research will examine the importance of the cation in molten hydroxide reactions and the use of other molten salts for the removal of sulfur from organosulfur species.

EXPERIMENTAL

All molten hydroxide desulfurization reactions were performed using 1/2-inch Monel Swagelok unions as reactors. Similar 316-stainless-steel reactors developed cracks and leaks, resulting in loss of volatile components. In a typical reaction, 3.1 to 4.0 g of powdered sodium hydroxide and/or potassium hydroxide, 0.3 to 0.6 g organosulfur compound, and a 1/4-inch-diameter stainless-steel ball (to ensure adequate mixing) were added to the reactor under nitrogen. Product yields were slightly less without the stainless-steel ball. In some cases, the hydroxide mixture was added in two steps, to reduce the free volume of the reactor. Elimination of free volume ensured that the reactant would be in the condensed phase and in intimate contact with the molten hydroxide. This was accomplished by melting most of the powdered base in the reactor at 350°C, with subsequent addition of the organosulfur compound and 0.3 to 0.5 g of additional base. The end caps were then tightened to 35 ft lb.

The reactor was bolted to a bracket assembly and immersed in a Tescom SBL-2 fluidized sand bath that was preheated to reaction temperatures. Reaction temperatures ranged from 350°C to 400°C, and reaction times varied from 10 minutes to 3 hours. Vigorous mixing was accomplished by using a Burrell mechanical wrist-action shaker. The reactors were cooled rapidly by immersion in room-temperature water.

The reactors were opened, placed in 50 mL of CH_2Cl_2 , and sonicated for 5 minutes. This allowed partial removal of neutral organics and, more important, minimal evaporative losses of volatile organics. The CH_2Cl_2 was decanted and 1 mL of a solution containing an internal standard was added (a solution containing an

internal standard was added to all CH_2Cl_2 extracts before GC analysis). The reactor was then sonicated with 50 mL of deionized water until all the base was dissolved (20-30 minutes). The basic solution was decanted and the reactor was washed with an additional 10 mL of water to ensure complete removal of its contents. The H_2O solutions were combined and extracted with two 25-mL portions of CH_2Cl_2 to remove any of the remaining neutral organics. Using litmus paper as the indicator, the water layer was neutralized with 4 to 6 mL of concentrated HCl. The neutralized solution contained acidic products that had previously remained in the aqueous phase as soluble salts. The neutralized water layer was then extracted with two 25-mL portions of CH_2Cl_2 . Solutions containing internal standards were added to each portion to determine quantitatively the amounts of individual components and to determine material balances. Material balances of approximately 95% were achieved.

The three methylene chloride portions were analyzed using an HP 5740 gas chromatograph with a 50-meter SE-54 capillary column. In most cases, flame ionization was used to detect the individual components of the reaction. The CH_2Cl_2 was removed by rotoevaporation, and the products were further characterized by proton NMR; FTIR; and low-voltage, high-resolution MS. Some loss of the more volatile components was observed.

Thermal decomposition reactions were conducted using aromatic thiols and their respective salts. The aromatic thiol (0.2 g) and a stainless-steel ball(s) were added to the reactor, and the reactor was heated to 375°C for 30 minutes. Thermal decomposition of the salt of the aromatic thiol was examined by adding 0.2 g of the aromatic thiol, 3.5 g of powdered KOH and NaOH (60:40) and a stainless-steel ball to the reactor. Reaction conditions were the same as those for the aromatic thiol. Reaction products were dissolved in 50 mL of CH_2Cl_2 and quantified using capillary GC and an internal standard.

RESULTS AND DISCUSSION

Reaction of Benzothiophene

A weight ratio of 1:1 (KOH:NaOH) was chosen for the initial model-compound study, based on the ratio that the TRW process is using for bench-scale experiments with coal [1]. Preliminary experiments at 375°C and 30-minute reaction times indicated that benzothiophene, chosen as the initial model compound, had reacted partially with the molten hydroxide to form two principal products. Capillary GC, high resolution mass spectrometry, FTIR, and NMR identified the major product as o-thiocresol. The minor product was toluene.

Extending the reaction time to 3 hours gave a considerably different distribution of products. Not only had all the benzothiophene reacted, but the major product was toluene. These results indicate that the overall reaction of benzothiophene with molten hydroxide involves a ring opening and elimination of a carbon to form o-thiocresol, followed by a slower sulfur elimination to form toluene (Figure 1). These results are supported by the observations of Weissgerber and Seidler [3], who identified small amounts of o-thiocresol and formic acid when reacting benzothiophene with KOH at 300°-310°C. Apparently extended reaction times or higher temperatures are two means to remove sulfur from the sulfur species completely. The individual steps of the mechanisms are being examined.

Effect of KOH:NaOH Ratio

Because of some inconsistencies in product yield, a series of experiments was conducted using varying amounts of KOH and NaOH. Varying the relative amounts of KOH and NaOH clarified the problem and determined the importance of each hydroxide. Hydroxide mixtures having different ratios of KOH and NaOH were

prepared, and their activities were compared by determining the extent of benzothiophene conversion to the initial product, o-thiocresol, or the subsequent product, toluene. Weight percents of KOH:NaOH used for this study were the following: 0:100, 40:60, 45:55, 48:52, 50:50, 52:48, 55:45, 60:40, 75:25, 90:10, and 100:0. Figure 2 shows the results of these experiments. Note that at approximately a 45:55 ratio of KOH:NaOH, the conversion of benzothiophene to o-thiocresol increases dramatically. The lack of any significant reaction at lower percentages of KOH was unexpected. Increasing the weight percent of KOH in the hydroxide mixture resulted in an increase in the concentration of o-thiocresol and a corresponding increase in toluene formation, since the formation of toluene represented a decomposition of the intermediate product, o-thiocresol. Maximum yields of desulfurized product (toluene) were obtained by using pure KOH. Since conversions varied dramatically at approximately a 45:55 ratio, all subsequent experiments were done with a 60:40 ratio of KOH:NaOH.

From these results, it can be seen that the amount of KOH within the hydroxide mixture may be critical in removing organosulfur from coal. While the particular role of KOH has not been determined, evidence from the literature has shown that the size of the cation may be important in stabilizing intermediate carbanions. Wallace et al. [4] conducted a series of base-catalyzed, beta-elimination reactions with isopropyl sulfide and measured the amount of olefin production. The proposed mechanism involved an initial formation of a carbanion with subsequent elimination of the sulfur moiety (which can be considered a good leaving group) to form the olefin (Figure 3). It was shown that the rate of olefin production was dependent on the size of the metal cation (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+) of the base. The increase in olefin production with an increase in cation size was explained as a stabilization/solubilization effect, wherein the intermediate carbanion was more effectively stabilized by the larger cations, causing an increase in the rate of olefin production. Certain possible reaction pathways for the conversion of benzothiophene also require a carbanion intermediate. Increases in benzothiophene conversion with increasing amounts of K^+ support this type of intermediate.

Thiol Thermochemistry

The mechanism for the formation of o-thiocresol has not been clearly established, although evidence to support a pathway for the desulfurization of the aromatic thiol (o-thiocresol) has been obtained. Experiments using model compounds showed that the thermal decomposition of aromatic thiols is different from that of their respective salts (salt formation occurs in molten hydroxide). The thermal decomposition of thiols can be complicated because the incipient free-radicals tend to react with other thiol molecules and provide a variety of products. Reports in the literature demonstrate that certain aromatic thiols decompose thermally to form the corresponding sulfide [5]. Thermal decomposition reactions in our reactor (375°C for 30 minutes) using thiophenol or o-thiocresol produced diphenyl sulfide or 2,2'-dimethyldiphenyl sulfide respectively. Although the mechanism is not known, one can be suggested. The bond dissociation energy of the S-H bond for aromatics is approximately 75 kcal/mole, and at 375°C, the molecule most likely dissociates to $\text{Ar-S}\cdot$ and $\text{H}\cdot$ [6]. Attack of $\text{Ar-S}\cdot$ on the aromatic thiol with subsequent loss of the stable thiyl radical would produce a monosulfide and hydrogen sulfide (Figure 4).

The behavior of the aromatic thiol salt was studied by conducting thermal decomposition reactions in the molten hydroxide mixture (60%KOH:40%NaOH). It was assumed that hydroxide was present only to allow formation of the thiol salt. In molten hydroxide, the aromatic thiol loses a proton to form the conjugate base, which is not likely to lose an electron to form $\text{Ar-S}\cdot$ and a free solvated electron. The bond dissociation energy of the aromatic C-S bond is approximately 85 kcal/mole and represents a likely thermolysis pathway [6]. Thermal decomposition of the thiophenolate salt produced about 60%-70% insoluble material and

approximately 30% benzene. The formation of insoluble material may be a result of phenyl radical reactivity, leading to radical polymerization reactions. This hypothesis was tested by conducting the same reaction in the presence of formate ion. Formate ion is known to react with hydroxide and generate hydrogen, carbon monoxide, and carbonate salts [7]. In situ generation of H_2 might allow capping of intermediate free-radicals (phenyl radicals) and thus inhibit free-radical polymerization reactions. Thermal decomposition of the thiophenolate salt in the presence of formate yielded approximately 80% benzene, supporting the hypothesis that homolysis occurs at the C-S bond. Based on these results, it is suggested that the conjugate base of the intermediate product, o-thiocresol, undergoes thermal decomposition to toluene. The absence of polymer may be due to a low concentration of o-thiocresol at any given time.

Reaction of Dibenzothiophene

Dibenzothiophene was much less reactive than benzothiophene. Reactions at 375°C for 30 minutes in our laboratories demonstrated that dibenzothiophene was unreactive and quantitatively recovered. Maijgren and Hubner [8] observed, using dibenzothiophene as a model, that under similar reaction conditions (75%KOH and 25%NaOH, 370°C for 60 minutes), 81% of dibenzothiophene was recovered, but no reaction products were identified. Wallace et al. also found that dibenzothiophene was unreactive when heated at 200°C for 20 hours in a KOH - white oil mixture [9]. The severity of the reaction conditions in our laboratory was increased to 400°C for 3 hours. Under these conditions dibenzothiophene reacted quantitatively, producing approximately 50% CH_2Cl_2 insoluble material, 35% o-phenylphenol, and 10% biphenyl. These results indicate that dibenzothiophene will react with molten hydroxide and desulfurize if the reaction conditions are sufficiently severe.

Role of Moisture

Since A.C.S. reagent grade KOH has a moisture content of 13%-15%, it was thought reasonable to test whether water might be playing an important role in the desulfurization reaction using molten hydroxides. Reactions were conducted with a high-purity KOH that contained less than 1 wt.% of water, and the same results (complete conversion) were obtained. Also, an equivalent amount of water (13 wt.%) was added to experiments conducted in pure NaOH, and in each case, no conversion occurred. Based on these results, it appears that water has neither a deleterious nor an advantageous effect on the removal of sulfur from organosulfur compounds using molten hydroxides. These results also indicate that a considerable cost savings in the energy required for drying recycled caustic may be possible.

CONCLUSION

Experiments carried out in microautoclaves demonstrate that sulfur can be removed from organosulfur model compounds using molten hydroxides. Based on these results, it can be seen that the ratio of KOH and NaOH may be critical in removing sulfur from organosulfur moieties in coal and that the reaction temperatures and reaction times might determine which type of organosulfur species is being removed and to what extent. A large improvement in sulfur removal using the molten hydroxide desulfurization process might be possible by varying the amount of KOH and NaOH. While sulfur might be removed from benzothiophene moieties in coal at 375°C, it appears that more severe conditions are necessary to remove sulfur from dibenzothiophene moieties. Efficiency of organosulfur removal may be partially dependent on the type of organosulfur species in coal, and therefore continued efforts to characterize the types of organosulfur moieties in coal are necessary.

ACKNOWLEDGMENT

We gratefully acknowledge the technical assistance of Bonnie Brooks and Thomas Williams in obtaining technical data from the molten hydroxide experiments. We also acknowledge the Oak Ridge Associated Universities (ORAU) Postgraduate Research Associate Program, in which Steven K. Soboczinski participated.

REFERENCES

- [1] "Gravimelt Process Development," Final Report, TRW Energy Development Group, Contract No. DOE/PC/42295-T7, June 1983.
- [2] C.W. Fan, R. Markuszewski, and T.D. Wheelock, Am. Chem. Soc. Div. Fuel Chem. Preprints, 29(4), 319 (1984).
- [3] R. Weissgerber and C. Seidler, Ber. Dtsch. Chem. Ges. B., 60, 2088 (1927).
- [4] T.J. Wallace, J.F. Hofmann, and A. Schriesheim, J. Am. Chem. Soc., 85, 2739 (1963).
- [5] E. Emmet Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 6, pp. 27-29, Chemistry Publishing Company, Inc., N.Y. (1963).
- [6] R. Shaw, in "The Chemistry of the Thiol Group," (S. Patai, ed.), Part 1, pp. 151-161, John Wiley and Sons, N.Y. (1974).
- [7] M.C. Boswell and J.V. Dickson, J. Am. Chem. Soc., 40, 1779 (1918).
- [8] Conf. on Coal Science, Pittsburgh, Pa., April 15-19, 1983, pp. 256-259.
- [9] T.J. Wallace and B.N. Heimlich, Tetrahedron, 24, 1311 (1968).

DISCLAIMER

Reference in the report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

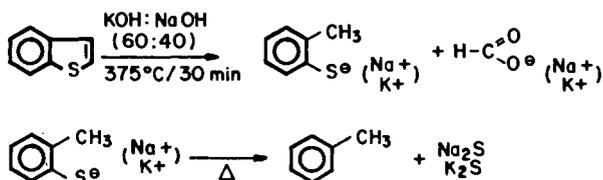


Figure 1. Desulfurization of Benzothiophene in Molten Hydroxide

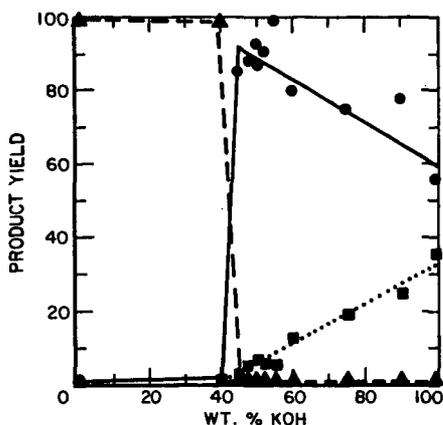


Figure 2. Reactions of Benzothiophene with Molten KOH/NaOH Mixtures at 375°C for 30 minutes.

---▲--- BENZOTHIOPHENE
 —●— O-THIOCRESOL
■..... TOLUENE

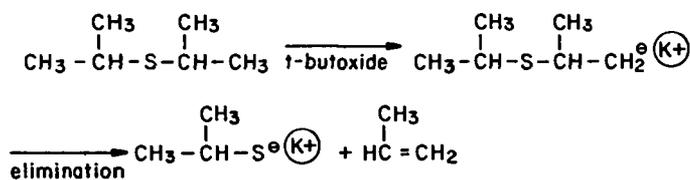


Figure 3. Base-Catalyzed Elimination of Sulfide [4]



Figure 4. Thermal Decomposition of Thiophenol