OXYDESULFURIZATION OF COAL. FURTHER STUDIES OF OXY-ALKALINOLYSIS

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Although it is clear that increasing amounts of coal will be burned each year for decades, no satisfactory technology for the chemical "deep cleaning" of coal has been developed. This situation arises from the fact that the forms of organic sulfur in coals are chemically reduced, and therefore, relatively unreactive under most desulfurization conditions. Early attempts to develop "oxy-desulfurization" processes failed to take into account that organic sulfur is no more susceptible to free radical oxidation than are carbon and hydrogen; and thus, even though pyritic sulfur is removed by these processes no selective removal of organic sulfur can be accomplished.

The use of more sulfur-selective electrophilic oxidants to chemically clean coal was introduced by the Jet Propulsion Laboratory's development of a chlorine based process (1-3). Unfortunately, this powerful oxidant also chlorinates coal, replacing some of the carbon-hydrogen bonds with carbon-chlorine bonds; and as many as 20 chlorines per 100 carbons are introduced (1, 3). Removal of this inadvertently introduced chlorine became a new problem which has proved very difficult to solve. JPL has attempted to dechlorinate the intermediate product using a variety of conditions including hydrogenation at temperatures up to 700°C (2).

In the meantime, TRW, Inc. had shown that substantial amounts of organic sulfur are apparently removed from coal by heating it with molten caustic (4-6). Since the replacement of oxidized sulfur functions as well as chlorine by hydroxide ions are common reactions in both aliphatic and aromatic chemistries, we reasoned that electrophilic oxidation followed by treatment with strong base would be superior to either treatment alone.

On this basis, we developed a two-step process for the desulfurization of coal in which the coal is first mildly oxidized and then heated with alkaline materials. In our first report (7), oxy-alkalinolysis was demonstrated to be more effective than either chlorination or alkali fusion. We now wish to present results using bromine as the first stage oxidant and add a few model studies which shed additional light on the chemistry underlying the processes.

EXPERIMENTAL

General

Western Kentucky No. 9 coal from the Ames Lab coal library, which had been prepared and stored under O_2-free conditions, was used. Bromination of the coal and the alkali fusion of the brominated samples were carried out under N_2 atmosphere. Before use, the coal was sized to pass through a 200 US mesh screen. Methylene

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chloride, potassium hydroxide pellets (85%), potassium iodide, sodium thiosulfate, potassium dichromate, and soluble starch, all certified ACS grade, were used as obtained from commercial sources. AR grade bromine was used in the bromination of coal. The analysis of the samples were carried out by the Ames Lab Analytical Services.

Bromination of Coal

A typical procedure for the bromination of coal samples is described below:

To a well stirred mixture of 70 ml of CH_2Cl_2 and 50 ml of water was added an accurately weighed (about 2.50 g) sample of coal. While stirring the mixture vigorously, 3 ml (58.6 mmol) of bromine was introduced in three equal portions. Stirring was effected by ultrasonic irradiation. After a total of 60 min., the mixture was filtered through a previously weighed fluoropore filter (3 m, Millipore). The coal residue was thoroughly washed 8-10 times using 20-25 ml of water each time. The brominated coal was then dried under vacuum in an oven at 110°C. After drying, the gain in weight of coal was recorded.

Estimation of Bromine

In a separate series of experiments, the bromine left unreacted after the bromination of coal was estimated by adding excess of KI to the filtrate and titrating the liberated I_2 with $Na_2S_2O_3$ previously standardized with $K_2Cr_2O_7$ using starch. This enabled us to determine the amount of Br_2 consumed by coal (0.5 g) during oxidation. The incorporated Br_2 was estimated from the elemental analyses.

Alkali Fusion

In a typical experiment 15-10 g KOH was at first fused at 380° in a steel reactor placed in a salt ($NaNO_3$+$NaNO_2$+KNO_3) bath and fitted with a N_2 inlet-outlet device, paddle stirrer and a port for loading coal. The molten mass of KOH was held at 380° until no more water was expelled. About 0.5 g of coal was then introduced and the molten mass was stirred at 380°-390° for 30 min. After cooling, the contents of the reactor vessel were mixed with water and the resulting slurry was acidified with 1:1 HCl. The mixture was then kept over a steam bath for 30 min. and finally filtered through fluoropore (3 m, Millipore), washed very throroughly with warm water, dried in an oven under vacuum at 110° overnight.

RESULTS

In order to understand the data, we will express changes in the coal on oxidation and KOH fusion in terms of atom ratios, most usually atoms per one hundred carbon atoms, xX/100C. This is equivalent to gram-atoms of X per 100 gram-atoms of carbon. This approach allows careful focus on changes in the organic fraction of the coal without regard to changes in the mineral matter.

The results of coal bromination are given in Tables 1 and 2 and a number of aspects of the reaction of bituminous coal with bromine are illustrated in Figure 1. Up to a ratio of more than 10 mmol of bromine per 100 g-atom of carbon, all of the bromine is consumed within the 60 minute reaction time. The weight of product increases markedly during the early stages of bromination, increasing by about one-third when 15 moles of bromine per 100 gram-atoms of carbon is

used. Increasing the ratio beyond 15 gives no further weight increase. As seen in Table 2, about one-fourth of the hydrogen in the coal is lost (see Figure 2a), even in the most lightly brominated samples, and sulfur falls off slowly and steadily with increased bromine consumption (See Figure 3a).

Table 3 shows the results of subjecting the preoxidized samples to fusion with KOH for 30 minutes at 380°C. Note that under these conditions, the sulfur level of the raw W. Kentucky #9 coal treated with KOH alone is reduced from 1.9S/100C to 0.7S/100C. There is a small increase in the sulfur level after fusion when insufficient bromine is used, but in general, the sulfur levels attainable in 30 minute KOH fusions for preoxidized samples decreases with increasing bromine consumption (See Figure 3b). Under the best condition a level of 0.1S/100C (94% desulfurization) is achieved. Bromine levels after fusion are uniformly low, confirming that organic halogen is removable by KOH fusion.

DISCUSSION

The Oxidation Step

Our previous paper established that chlorine is an effective oxidant (7); however, gaseous chlorine is not as easy to study in detail as is bromine because chlorine cannot be introduced as accurately nor kept in solution as easily. Therefore, we have determined the stoichiometry of the oxidation of coal with bromine, assuming that the result can be generalized to the other halogens.

Bromine is consumed in four phenomenologically identifiable processes: (1) substitution for hydrogen; (2) dehydrogenation of the coal; (3) oxidation of iron pyrite to sulfate and ferric iron; and (4) oxidation of divalent sulfur compounds to the tetravalent state, equations 1-4 respectively.

$$-\overset{|}{\underset{|}{C}}-H + Br_2 \longrightarrow -\overset{|}{\underset{|}{C}}-Br + HBr \qquad (1)$$

$$-\underset{H}{\overset{|}{C}}-\underset{H}{Z} + Br_2 \longrightarrow -\overset{|}{C}=Z + 2\ HBr \qquad (2)$$

(Z = C, N, O, S)

$$2\ FeS_2 + 15\ Br_2 + 16\ H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4 + 30\ HBr \qquad (3)$$

$$R\text{-}S\text{-}R + 2\ H_2O + 2Br_2 \longrightarrow R\text{-}SO_2\text{-}R + 4\ HBr \qquad (4a)$$

$$R\text{-}SH + 3\ H_2O + 3\ Br_2 \longrightarrow R\text{-}SO_3H + 6\ HBr \qquad (4b)$$

Given the following data: (1) the total bromine consumed, (2) the amount of bromine incorporated into the coal, and (3) the loss of hydrogen from the coal; one can calculate the amount of bromine consumed by processes 1 and 2, and then by difference, the amount of bromine consumed in oxiding sulfur.

Table 4 shows that even at a bromine consumption level of 14 Br_2/100C, virtually all of the consumed bromine is accounted for without sulfur oxidation. The conclusion that some non-sulfur-oxidizing processes are very fast is also borne out by careful comparison of hydrogen loss versus sulfur reduction. Fifty-seven percent of the sulfur is removed under the most severe bromination conditions; roughly one-third of this sulfur is removed at a bromine-to-carbon ratio of 0.12. On the other hand, three-fourths of the

hydrogen consumed under the severest conditions has been removed at a ratio of 0.12.

Bromine in carbon tetrachloride or in water is used in most qualitative organic analysis schemes to diagnose the presence of (1) carbon-carbon unsaturation, (2) phenols, (3) compounds with relatively stable enol forms, (4) many amines, most notably anilines, and (5) other easily oxidized functional groups (8). Divalent organic sulfur compounds fall in this latter category along with hydroquinones and a few compounds possessing a very activated carbon-hydrogen bond. Thus, the concommitant consumption by coal of bromine in processes which do not oxidize sulfur is not surprising, and has been suggested before (9, 10); however, the extent to which it occurs is disconcerting.

The Alkali Fusion Step

The ratio of sulfur to carbon in the brominated coals drops modestly (from 1.5S/100C to 0.8S/100C) when the bromine to carbon ratio increases from 0.12 to 0.40 (See Figure 3a). However, over the same range, the susceptibility of the product to subsequent sulfur removal by KOH fusion is markedly enhanced. Fusion of the aforementioned samples with KOH leads to final sulfur values of 0.8S/100C and 0.1S/100C respectively (See Figure 3b). The organic sulfur in the sample treated with 40 Br_2/100C is clearly different from that in the sample treated with 12 Br_2/100C. On the basis of model compound studies reported previously (7), we are confident that it is the oxidation state of sulfur which has changed.

CONCLUSIONS

This study shows that preoxidation of coal samples by bromine markedly increases the efficiency of sulfur removal by molten caustic treatment. Under conditions which give a 65% sulfur reduction with KOH fusion alone, a preoxidized sample can be 94% desulfurized. That some hydrogen substitution and dehydrogenation processes are faster than sulfur oxidation has been demonstrated. The substitution reactions are probably phenol brominations and the replacement of active aliphatic hydrogen by bromine. The dehydrogenation reactions probably involve oxidation of easily oxidized carbon-carbon and cabon-oxygen bond systems.

Table 1. Bromine consumed by W. Ky. #9 Coal.*

$\left(\frac{\text{mol } Br_2}{\text{g-atom C}}\right)_{used} \times 100$	$\left(\frac{\text{mol } Br_2}{\text{g-atom C}}\right)_{cons'd} \times 100$
0	0
13.3	12.2
16.5	13.0
26.2	18.5
33.0	21.6
39.1	23.3

*One gram of W. Ky #9 coal contains .7086g (0.059g-atom) of carbon.

Table 2. Product Analytical Data for Brominated W. Ky. #9 Coal.

Run No.	$\left(\frac{\text{mol } Br_2}{\text{g-atom C}}\right)_{used} \times 100$	$\left(\frac{\text{g-atom}}{\text{g-atom C}}\right) \times 100$ Br	H	S
1	0	0	86.0	1.9
2	11.9	7.1	68.3	1.5
3	15.9	8.3	68.5	1.2
4	23.8	8.6	65.6	1.1
5	31.8	9.4	62.2	0.8
6	39.7	9.8	61.9	0.9

Table 3. Product Analytical Data for KOH Fused Samples.

Run No.	$\left(\frac{\text{g-atom}}{\text{g-atom C}}\right) \times 100$ S	Br	H
1	0.7	0.0	45.4
2	0.8	0.1	41.2
3	0.6	0.2	46.9
4	0.3	0.3	43.0
6	0.1	0.1	45.1

Table 4. Relative Stoichiometries of Bromine Consumption.

Run No.	(mol Br_2/100 g-atom C)$_{consumed}$ Substitution for H Process 1	Dehydrogenation Process 2	Sum of processes 1 and 2	Obs.	Obs.-(1+2)*
6	9.8	7.2	17.0	23.2	6.6
5	9.4	7.2	16.6	20.2	3.4
4	8.6	5.9	14.5	17.0	2.7
3	8.3	4.6	12.9	13.8	0.5
2	7.1	5.3	12.4	11.9	-0.5

*FeS_2 requires 3.4 Br_2/100 C; depending on functional group distribution, organic S requires 1.9-2.8 Br_2/100 C; total required for S oxidation is 5.3-6.2 Br_2/100 C.

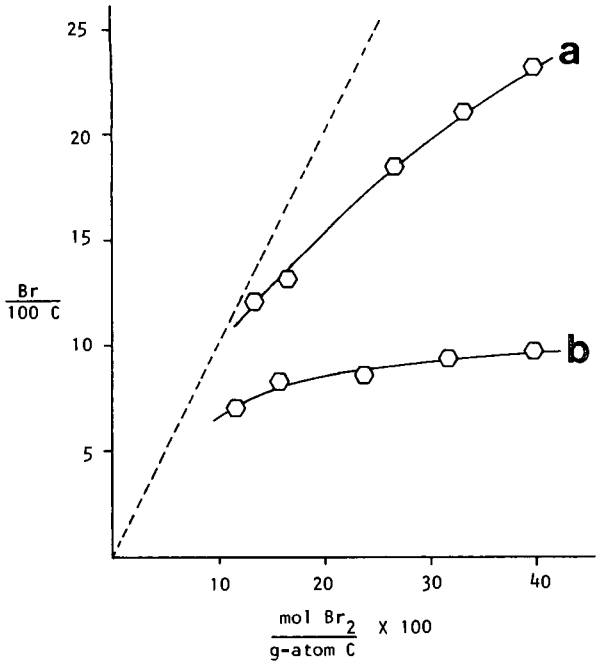

Figure 1. Reaction of Bromine with W. Ky. #9 Coal: (a) Consumption of Bromine and (b) Incorporation of Bromine as Functions of the Bromine to Coal Ratio (60 Minute Reaction).

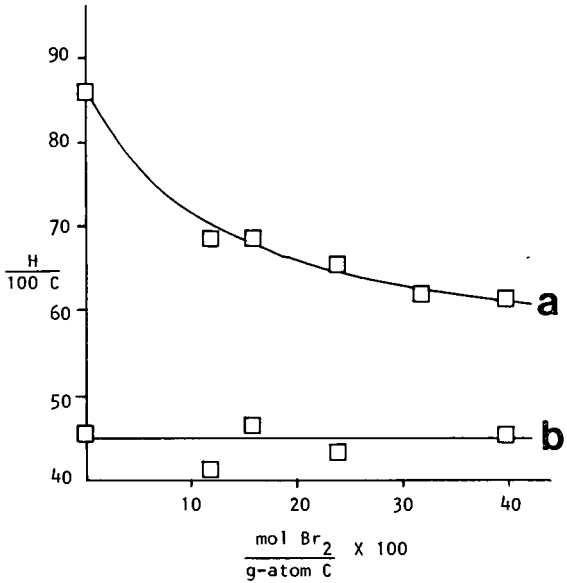

Figure 2. Hydrogen to Carbon Ratio in W. Ky. #9 Coal: (a) after Bromination for 60 Minutes, and (b) after KOH Fusion of the Brominated Samples.

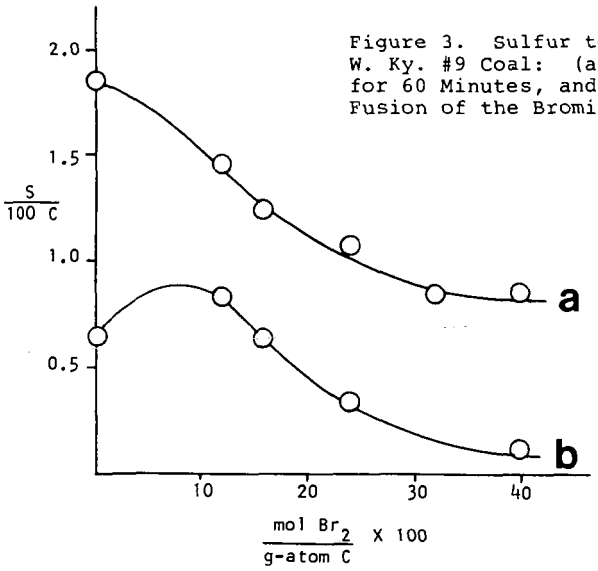

Figure 3. Sulfur to Carbon Ratio in W. Ky. #9 Coal: (a) after Bromination for 60 Minutes, and (b) after KOH Fusion of the Brominated Samples.

REFERENCES

1. Vasilakos, N. P.; Corcoran, W. H. Fuel 1983, 62, 1111 and references therein.
2. Hsu, G. C.; Kalvinskas, J. J.; Ganguli, P. S.; Gavalas, G. R. Am. Chem. Soc. Symp. Ser. 1977, 64, 206; and personal communications.
3. Vasilakos, N. P.; Corcoran, W. H. Fuel 1983, 62, 795.
4. Masciantonio, P. X. Fuel 1965, 44, 169.
5. Meyers, R. A.; Hart, W.D.; McClanathan, L.C.; paper presented to the 17th Intersociety Energy Conversion and Engineering Conference, Los Angeles, CA, August, 1982. We wish to thank Dr. Meyers for kindly supplying us with a preprint of his paper.
6. Meyers, R. A.; Final Report, U. S. Department of Energy Contract No. DE-AC22-80PC30141, TRW, Inc., Redondo Beach, CA.
7. Aida, T.; Venier, C. G.; Squires, T. G. Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 1982, 27(3-4), 328.
8. Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds"; Fifth Ed., Wiley, New York, NY, 1964, pp. 121-124.
9. Cunningham, A. C.; Ladner, W. R.; Wheatley, R.; Wyss, W. F. Fuel 1966, 45, 61.
10. Weiler, J. F. Fuel 1935, 14, 190.