

Transformation Kinetics of Organic Sulfur Forms in Argonne Premium Coals During Pyrolysis

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The evolution of H₂S during pyrolysis of Argonne premium coal has been monitored with a mass spectrometer in Temperature Programmed Decomposition (TPD) experiments. X-ray Absorption Near Edge Structure Spectroscopy (XANES) and X-ray Photoelectron Spectroscopy (XPS) have been used to follow the changes that occur in the distribution of organic sulfur forms after pyrolysis of these coals to 400°C. The low temperature (T<400°C) elimination of aliphatic sulfur as H₂S is accompanied, in some cases, by the conversion of aliphatic sulfides to aromatic sulfur forms. This work explores the kinetics of H₂S formation. The method of heating rate variation was used in the TPD experiments to derive kinetic parameters for H₂S production during pyrolysis. The results indicate that the decomposition reaction of organic sulfides to form H₂S proceeds prior to most of the conversion of organic hydrocarbons to volatile matter during pyrolysis. This trend is consistent with XANES and XPS findings that there is very little sulfidic sulfur remaining after low temperature pyrolysis of different rank coals.

I. Introduction

Recent advances in the ability to directly quantify sulfur forms in coal by XANES and XPS [1-5] and gaseous sulfur pyrolysis products in a controlled environment [6-8] provides an opportunity to examine the detailed kinetics of the sulfur related chemistry that occurs during laboratory pyrolysis. The monotonic decrease in aliphatic sulfur forms with increasing coal rank has been established by direct measurement [4]. Another XANES and XPS study of several low rank coals has provided evidence that most of conversion of aliphatic sulfides to aromatic forms occurs under milder pyrolysis conditions than those required for the production of almost all of the organic volatile matter of coal [8]. In addition some of the aliphatic sulfur forms are eliminated as H₂S. Pyrolysis studies of model compounds show that organic sulfides are reactive at low temperature (T<750°C) while heterocyclic sulfur structures are not [6,7,9].

The current accuracy of XANES and XPS probes for quantitative determination of organic sulfur forms does not easily allow a detailed kinetic study of the transformation of aliphatic sulfur to aromatic forms during laboratory pyrolysis. While a direct relationship between the initial amount of aliphatic sulfur present in coal and H₂S formed during pyrolysis cannot be made it is certain that the reactions signified by H₂S evolution during pyrolysis of low rank coal are partially responsible for the relatively high levels of aromatic sulfur following mild (T < 400°C) pyrolysis [8]. A comparison of the TPD pattern of H₂S evolution for high rank coal with those of very low temperature chars made from low rank coals show that they are remarkably

similar [8]. The present work focuses on the thermal chemistry and the kinetics of the reaction of aliphatic sulfur forms in coals from the Argonne Premium sample program.

II. Experimental

The procedures for obtaining XPS and XANES spectra have been discussed elsewhere [1-4]. XANES experiments were conducted at the National Synchrotron Light Source at Brookhaven National Laboratory on line X-10C. Sulfur speciation was accomplished by spectra reconstruction based on third derivatives of the absorption spectra of model compounds. XPS spectra were obtained on a stand alone laboratory Vacuum Generators (VG) ESCA lab system using 5 channel detection. MgK α non-monochromatic radiation was used. Sulfur speciation was based on a self-consistent curve resolution methodology using experimental instrumental response functions and energy positions from pure model compounds. This methodology has been extensively described [2,4].

The TPD unit is comprised of an ultra high vacuum (UHV) compatible reaction vessel differentially pumped and attached to a UHV main chamber. H₂S detection was accomplished with a mass spectrometer located in the main chamber. The pressure rose to a maximum of 1×10^{-5} torr in the section where the reaction vessel was located and resulted in a maximum pressure rise of 5×10^{-7} torr in the main chamber. A typical coal sample size ranged from 0.5 to 5 mg, loaded into a 3mm x 15mm ceramic vessel. A fine chromel-alumel thermocouple was inserted into the center of the sample bed and the top of the vessel was packed with quartz wool. The vessel was indirectly heated by surrounding tantalum resistive heating elements. Linear heating rates of from 0.05 to 5.0°C/sec were used. Further details of this experimental arrangement appear elsewhere [8,10].

The method of heating rate variation was used to analyze the TPD data [11-13]. A plot of $\ln B/TP^2$ (vs) $1/TP$ where B equals the experimental heating rate and T_p equals the temperature of the peak maximum, produces a line with slope equal to $-(E_a/R)$ [11,12]. These Arrhenius parameters provide input for a more detailed discrete distribution of activation energy kinetic model.

The model is based on parallel first order reactions to describe the pyrolysis kinetics of H₂S evolution. The preexponential factor was determined from the experimentally derived activation energy and peak maximum. In order to describe the potential contribution from multiple kinetic processes to the TPD spectrum, a series of kinetic expressions was calculated at 2 kcal/mole increments about the experimentally derived energy value for the peak maximum while the preexponential factor was assumed to remain constant. The temperature of the peak maximum for each process is fixed by these constraints for a given heating rate. The level of contribution from each assumed first order reaction, calculated at 2 kcal/mole increments, is determined by a least squares fit of the calculated sum to the experimental data. Least squares calculations were done using a Cray X-MP/14se computer.

III. Results and Discussion

XANES and XPS were used to characterize the level of aliphatic sulfur initially present in fresh Argonne premium coal samples and following brief pyrolysis of coal at 400°C. Table I shows the results. The change in the relative aliphatic content is most pronounced for lower rank that have high initial aliphatic sulfur

contents. Most of the aliphatic sulfur is converted to aromatic sulfur forms or eliminated as H_2S during this mild pyrolysis. The XANES data for Illinois #6 char produced at $700^\circ C$ show that there is little further decline in the aliphatic content.

The evolution of H_2S measured by TPD from Argonne Premium coals at a fixed heating rate of $0.23^\circ C/sec$ is shown in Figure 1. The position of the peak maximum occurs at a lower temperature as the coal rank decreases. The very sharp H_2S evolution spike seen at high temperature in all cases is associated with pyrite decomposition. This sharp spike is not apparent in coals with high organic sulfur and very low inorganic sulfur. As an example of this, the sharp spike is not observed with samples of depyritized Illinois #6 coal nor with samples of extracts of Illinois #6 coal since neither contains pyrite. Lower rank coals such as Wyodak and Illinois #6 show a distinct peak near $400^\circ C$ in the TPD H_2S trace. For higher rank coals such as Pocahontas the onset of evolution occurs at much higher temperature and appears almost as a shoulder on the sharp pyrite related spike. Coals such as Wyodak and Illinois #6 provide the opportunity for more accurate and detailed analysis.

Ion peaks of evolved gases during TPD experiments at varying heating rates were measured for Illinois #6 and Wyodak coal. The kinetic behavior of gases other than H_2S have been extensively studied [14-16] and their kinetic behavior is important to tie the present work to other kinetic studies. The resultant Arrhenius plot for H_2S , CH_4 and light hydrocarbons ($m/e = 41$; C_3-C_9) determined in this work are shown in Figure 2. The different products show distinct kinetic patterns that will be discussed below. The resultant activation energies derived from the slopes of the lines in Figure 2 appear in Table II along with the calculated preexponential factor. The activation energy is based on least squares analysis. The comparable data for Wyodak coal is also found in Table II.

The position of the $m/e = 41$ peak is closely related to the position of the peak maximum for tar production as measured by infrared at the same heating rate for the Argonne Premium coals [17]. The activation energy and preexponential factor for hydrocarbons from Illinois #6 coal are in good agreement with those of previous studies [15,16]. The kinetic parameters for hydrocarbons from Wyodak coal also agree with previous findings [15] except in one where roughly a 10 kcal/mole higher activation energy was found [16]. The rate constants, however are similar. The present findings appear more reliable since only 3 different heating rates were used in reference [16]. While the results of the present work are based on a larger number of experiments.

The kinetic parameters for H_2S evolution from Argonne Premium coals have not been previously examined. Table II shows those for H_2S are significantly different than those for hydrocarbons. The reactions responsible for the elimination of H_2S from Illinois #6 and Wyodak coals happens faster than those that produce most of the volatile hydrocarbons during thermolysis. It is recognized that a single first-order reaction does not provide a good description of the complex hydrocarbon pyrolysis processes of coal [16]. While a single first-order expression is inadequate for a complete description of the H_2S TPD data, most of the H_2S evolution at different heating rates can be accounted for using a small number of Arrhenius for each coal. The TPD data for H_2S were analyzed in the context of the discrete distribution of activation energy kinetic model described in the Experimental section. Table III shows the results of the analysis. Figure 3 shows the TPD spectrum

of H₂S from Wyodak coal at a heating rate of 0.2 deg/sec and the simulated TPD spectrum based on the results of the discrete distribution of activation energy kinetic model. Contributions related to the pyrite H₂S spike are not considered. Table III shows that processes with activation energy lower than the value of the main peak contribute more in the case of Wyodak, a lower rank coal relative to Illinois #6.

It is interesting to note that the present kinetic results can be examined in the context of the early stages of coal metamorphism. Extrapolation of the results for H₂S derived here for Wyodak and Illinois #6 coal, to geological temperatures and times (several million years below 100°C) would predict that much of the H₂S would have been eliminated prior to the loss of much of the other hydrocarbon matter. The relative hydrocarbon kinetic reference is taken as that of the m/e = 41 peak. The H₂S is predicted to be progressively eliminated over extremely long times at low temperature as coal rank increases. The present kinetic data for H₂S along with XANES and XPS data on the depletion in the relative level of aliphatic sulfides still leaves open the possibility that the organic reactions specific to sulfur that occur during laboratory pyrolysis may be related to those that occur during the early stages of coal metamorphism.

IV References

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Table i

Mole percent aromatic Sulfur by XPS and XANES for Argonne Premium Coal Samples Before and After 400°C Pyrolysis

Coal	% Carbon (dmmf basis)	XANES		XPS	
		Fresh	Char	Fresh	Char
Beulah-Zap	74.05	63	94	55	-
Wyodak-Anderson	76.04	67	89	63	84
Illinois #6	80.73	67	95	69	87
Blind Canyon	81.32	76	95	65	-
Pittsburgh #8	84.95	78	95	75	-
Lewiston	85.47	80	91	86	-
Upper Freeport	88.08	87	96	81	-
Pocohontas	91.81	87	94	100	-

Table II

Kinetic Parameters for Pyrolysis Products Determined by the Method of Heating Rate Variation

Coal	Product	Preexponential Log A	Activation Energy kcal/mole	Number of Experimental Observations
Wyodak	H ₂ S	11.8	44.7 (+1.1)	6
Illinois #6	H ₂ S	11.9	45.0 (+2.3)	7
Wyodak	C ₃ :C ₈	13.0	50.8 (+1.2)	17
Illinois #6	C ₃ -C ₈	12.9	50.6 (+1.0)	11
Wyodak	CH ₄	11.8	50.0 (+2.0)	14
Illinois #6	CH ₄	11.8	50.4 (+2.1)	10

Table III

Distribution of Activation Energies Found to Simulate H₂S Evolution. The Contribution of Each Kinetic Process is Calculated Using a 2 kcal/mole Energy Increment. The Amount Due to Processes >+4 and those <-4 kcal/mole Have Been Combined in the Table. All Values Are Listed as the Percentage of the Total.

Coal	<-4	-2	Main Peak	+2	>+4
Wyodak	16	20	26	16	22
Illinois #6	3	13	41	11	32

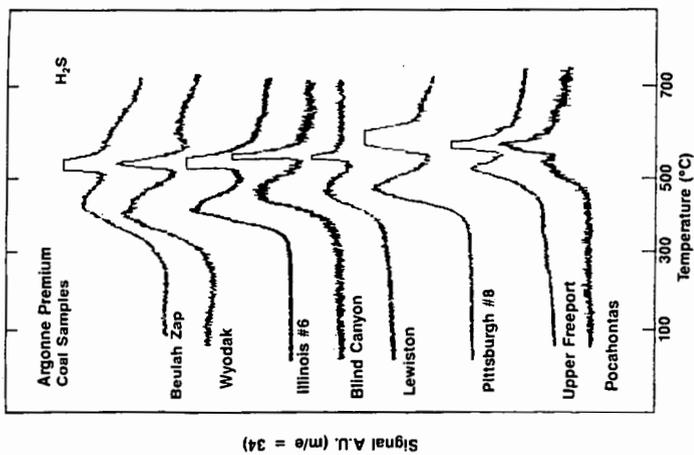


Figure 1
The H₂S TPD Spectra of Argonne Premium Coals.
The Heating Rate Was 0.23 deg/sec.

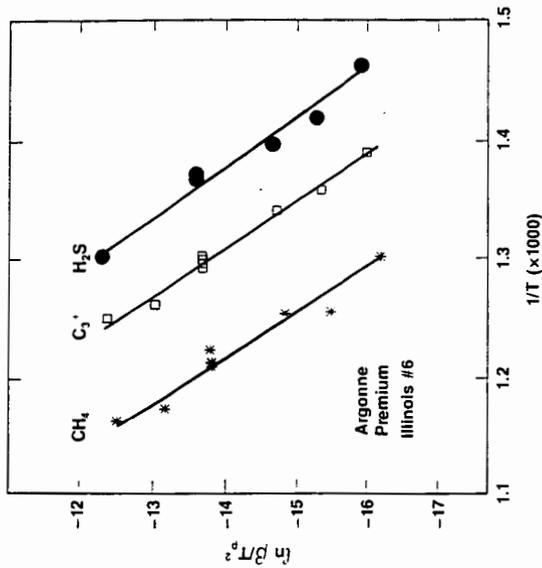


Figure 2
Arrhenius Plot Derived From the Method of Heating
Rate Variation For Argonne Premium Illinois #6 Coal.

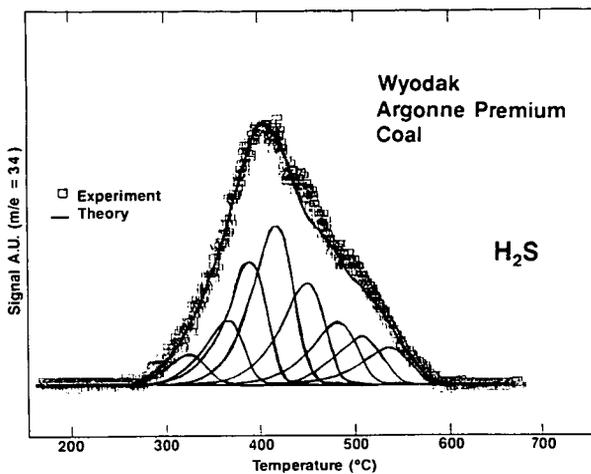


Figure 3

An Example of the H₂S TPD Spectrum of Argonne Premium Wyodak and the Simulated Spectrum Based on the Discrete Distribution of Activation Energy Kinetic Model. The Heating Rate Was 0.23 deg/sec. The Sharp Pyrite Related H₂S Spike Is Not Considered.