

MATRIX ISOLATION EPR STUDIES OF COAL TAR MOLECULES

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ABSTRACT

EPR studies of matrix isolated tar molecules have demonstrated for the first time the presence of free radical sites in the original gaseous tars evolved from coal over the 350-500°C temperature range. Matrix isolated tars exhibit considerably more structure than does the coal itself. It is initially isolated in carbon dioxide at liquid nitrogen temperature. The EPR spectra suggest the presence of four or more randomly oriented planar free radical molecules, some of which may be assignable to sulfur, nitrogen and oxygen containing heterocyclic aromatics. The parallel component ($g_{||}$) is sensitive to the structure and/or composition of tar. The respective perpendicular (g_{\perp}) components are insensitive to tar structure and similar to the free electron value. The free radical species disappear as the coal tar is warmed to room temperature. This strongly suggests that the usual tar products that are formed from devolatilized coal are free radical polymerized polymers which are formed from smaller free radical species.

INTRODUCTION

Considerable literature (1-5) has been published concerning the existence of free radical ESR signals in coals. The reported coal ESR literatures have been mainly concerned with either coal, pyrolyzed coal, solvent refined coal or coal liquefaction products. The g -values of a large number of coals have been studied extensively by Retcofsky(1) and Yen (4) independently. It was found that g values are dependent on the heteroatom contents of the coal. In general, the higher the nitrogen, oxygen and sulfur contents, the higher the g values from that of the free electron. Evidence also suggests that the coal free radical ESR signal is associated with the organic structure of coal and not the mineral matter.

We have studied extensively the pyrolysis processes of coals using matrix isolation FTIR techniques. Since the primary step in coal gasification and coal pyrolysis presumably involves the thermal decomposition of coal to produce free radicals, it would be of interest to study the primary pyrolysis products to determine the existence of free radicals. This involves experimental techniques which allow the formation of primary pyrolysis products and the utilization of matrix isolation techniques which traps the reactive intermediate free radicals in an inert matrix gas at low temperatures and quenches further reaction. Using these techniques, we have identified all of the slow pyrolysis products of four different ranks of coal through matrix isolation FTIR spectroscopy (6,7), however, evidence of free radical formation was not observed except in the case where tar molecules were flash pyrolyzed at 1100°C and methyl radicals were observed for the first time. Other slow pyrolysis products identified through matrix isolation FTIR are: CO, CO₂, H₂O, CH₄, C₂H₄, C₂H₆, HCN, H₂S, CS₂, COS, SO₂, and tar molecules. If the existence of free radicals were to be found from the thermal decomposition of coal, the most likely free radicals would be that of tar molecules which are structurally similar to the parent coal and are considered to be smaller fragments of the original coal. To consider this possibility and the existence of other free radicals not identifiable through matrix isolation FTIR, we have matrix isolated tar molecules along with other pyrolysis products of four coals, Pittsburgh bituminous, Illinois #6, Rawhide sub-bituminous and Texas Lignite, and studied them by Electron Spin Resonance or Electron Paramagnetic Resonance Spectroscopy.

EXPERIMENTAL

Studies were performed on four coals donated by Exxon Research and Engineering Co., Baytown, Texas. They are:

1. Illinois #6, high volatile C bituminous
2. Pittsburgh, high volatile A bituminous
3. Rawhide, sub-bituminous C rank, Wyoming
4. Texas lignite, lignite rank

Elemental analysis of these coals are listed in Table I and slow pyrolysis behavior of these four coals has been described in detail in another paper.(6,7) The coal samples were ground and sifted under inert nitrogen atmosphere to prevent oxidation and only the -500 mesh coal particles of less than 25 microns were used in the experiments.

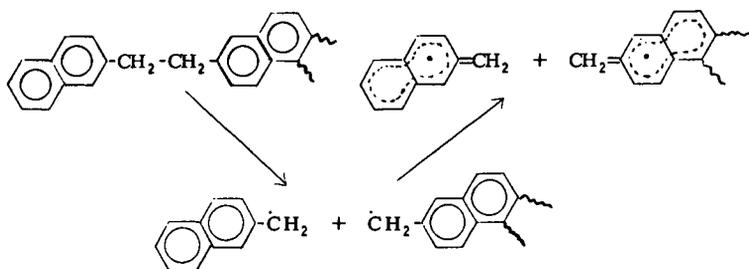
A detailed schematic diagram of the matrix isolation EPR apparatus is shown in Figure 1. The apparatus is constructed of stainless steel and pumped by a mechanical pump - 4" diffusion pump combination and maintained at 10^{-7} torr pressures except during deposition when the pressure rises to 10^{-5} torr due to excess inert matrix gas. The entire apparatus is mounted between the magnets of a Varian E-9 EPR spectrometer. The coal sample was placed in a slow pyrolysis reactor (6,7) situated in the furnace chamber directly facing a single crystal sapphire rod cooled to 77K. The coal particles were slowly heated to promote the evolution of pyrolysis products which exit the reactor and are then immediately co-condensed onto the liquid nitrogen temperature sapphire rod with carbon dioxide as the matrix gas. After deposition, the sapphire rod attached to a moveable liquid nitrogen cooled tube is slowly lowered into a 1/2" o.d. thin wall quartz tube situated in the microwave cavity and an EPR spectrum of the products obtained.

RESULTS AND DISCUSSION

Results obtained from the matrix isolated EPR spectra demonstrated for the first time the presence of free radical sites in the original gaseous tars evolved from coals over the 350-500°C temperature range. The assignment of the observed EPR spectrum to volatilized tar molecules is based on the temperature at which EPR spectra first begin to appear (i.e., <350°C). EPR spectra of Illinois #6 tar molecules are shown in Figure 2 which illustrates the appearance and gradual increase of the EPR spectra from 314°C to 564°C. FTIR matrix isolation studies of the coals also indicate extensive evolution of tar at <350°C to 500°C. This temperature range has been designated as the high temperature tar evolution temperature range. Another less intense low temperature tar evolution was observed from FTIR studies at ~100°C to 300°C. It is interesting to note that the low temperature tars (100-300°C) do not exhibit free radical character. Thus only the high temperature tars are formed by actual bond breakage. It seems likely that the low temperature tars are formed through the dissociation of hydrogen bonding in the coal. We have found that a disruption of the hydrogen bonding in coal by O-methylation of the coal hydroxyl functional groups dramatically increases the evolution of low temperature tar but not that of high temperature tar.(8)

Retcofsky et.al. (5) have reported the EPR behavior of a heat treated Ireland Mine hvAb coal. The results show an increase in spin concentration for the coal heat treated to 450°C, approximately 7 times that of the original unheated coal. The same coal heat treated to 350°C showed only a slight increase in spin concentration. Khan (9) has also reported increases in electron spin

concentration, in the same order of magnitude as Retcofsky, for Pittsburgh and Illinois #6 coals heat treated to 460°C. These results complement our findings since concurrent with the observation of free radical tar formation at 350°C to 500°C, the pyrolyzed residual coal particles must also be experiencing a gradual increase in electron spin concentration as more free radicals are formed through bond breakage in this temperature region. Retcofsky reported that the g value obtained for the heat treated coal at 450°C is 2.0028 which is in the spectral range generally attributed to π -hydrocarbon radicals. The observed g -anisotropy of the matrix isolated tar spectra is understandable if the tar molecules are also of a π -hydrocarbon free radical type. This indicates that during the tar evolution process, the σ -type free radicals formed as a result of bond breakage of linkage groups in coal are not as stable as π -hydrocarbon free radicals. Therefore the σ -free radical site must be preferentially transferring and delocalizing the free electron to adjacent aromatic π -ring systems, i.e.,



The smaller π -free radical fragments formed evolve as tar molecules and the remaining π -free radicals attached to the main skeletal structure of the coal stay in the residue and are the cause for the observed increase in spin concentration of the heat treated coal.

The EPR spectra of the randomly oriented but rigidly held tar molecules of the four coals are shown in Figure 3. The spectra obtained are similar to a "powder pattern" spectra exhibiting g anisotropy and no hyperfine splitting. The matrix isolated EPR spectrum of Illinois #6 tar is compared to the EPR spectrum of the original coal powder diluted in high vacuum grease in Figure 4. It is clear that the matrix isolated tar molecules exhibit considerably more structure than the coal itself. In fact peaks labeled a, b, c, and d can be identified with distinctly different free radical sites in the tar molecules. From similarities between the matrix isolated tar spectrum and the spectrum simulated by Weltner (10,11) of randomly oriented and rigidly held planar aromatic molecules, peaks a-d can be labeled as parallel components representing different free radical tar species. The parallel components ($g_{||}$) are apparently sensitive to the structure and/or composition of tar. The respective perpendicular (g_{\perp}) components are relatively insensitive to tar structure and similar to the free electron value.

Differences in the parallel ($g_{||}$) components of the tar are clearly observed between the four coals (Figure 3). The relative abundance of the a-d peaks varies significantly from coal to coal. In fact, the coal exhibiting the most distinct $g_{||}$ components is Illinois #6. Since it is known that the g values of the coal are dependent on the heteroatom contents of the coal,^(1,2,4) tar

molecule g values must also be effected by the heteroatom contents. Flash pyrolysis studies of the coal tars at 1100°C has shown the tar molecules to contain considerable sulfur, nitrogen and oxygen heteroatoms.⁽¹²⁾ Illinois #6 contains a much higher percentage of sulfur than the other coals (see Table I), this suggests that one of the g_{II} peaks may be associated with a sulfur containing free radicals. The other peaks may be attributed to either a pure aromatic free radical or nitrogen and oxygen containing heterocyclic aromatic free radicals. The experimentally calculated g_{II} , g_I and g^0 ($g^0=1/3(g_{II}+2g_I)$) values for the four matrix isolated tars are listed in Table II. Table III lists the g values of some of the possible organic free radicals in coal compiled by Petrakis and Grandy.⁽²⁾ By comparing the ordering of the tar g^0 values to that of the g values for hetero-atom containing free radicals (see Table IV), one can assign peak a to sulfur containing, peak b to oxygen containing, and peak c to nitrogen containing π aromatic free radicals. Peak d, nearest to the g_I component of the tar, is assigned to pure π aromatic free radicals containing no hetero-atoms. The higher g^0 values of the tar molecules may be a result of matrix isolation and will be further investigated. The assignment of peaks a-d indicates that potential exists for a direct measurement of the relative amounts of nitrogen, sulfur, and oxygen heterocyclics. Figure 5 shows the disappearance of the free radical species as the coal tar is warmed to room temperature. The tar molecules were initially isolated in carbon dioxide at liquid nitrogen temperature. This strongly suggests that the usual tar products formed from devolatilized coal are re-polymerized polymers formed from smaller free radical species.

More work will be done to conclusively characterize the types of free radicals present in tar. Work with model polymers containing appropriate heterocyclic aromatic structures will be very useful. It is already clear, however, that volatilized tars can be distinguished by the number and types of free radical sites present. An understanding of these differences could play a very important role in the choice of other processing steps which lead to the production of useful fuels.

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Table I. Analytical Data of Four Coal Samples*

	<u>Texas</u> <u>Lignite</u>	<u>Rawhide</u> <u>Sub-bitum.</u>	<u>Illinois #6</u> <u>Bituminous</u>	<u>Pittsburgh</u> <u>Bituminous</u>
Moisture, Wt%	21.1	15.4	10.3	7.6
Ash, Wt%	9.35	8.64	9.28	6.04
Mineral matter, Wt%	6.9	7.1	10.9	7.8
Vol. matter, Wt%	48.2	47.3	41.6	37.2
Carbon, Wt%	68.0	68.3	70.9	78.9
Hydrogen, Wt%	4.99	4.84	5.08	5.25
Nitrogen, Wt%	1.06	0.82	1.18	1.28
Sulfur, total, Wt%	0.96	0.92	3.94	2.29
Sulfur, pyritic, Wt%	0.04	0.01	1.17	0.69
Sulfur, organic, Wt%	0.92	0.91	2.77	1.60
Oxygen, organic, Wt%	18.3	18.2	9.4	5.6
Density, g/cc	1.44	1.45	1.37	1.33
Btu/lb	11720	11710	12857	14312

*Samples supplied by Exxon Research and Engineering Co.

Analysis based on moisture free coal.

Ash contents of samples supplied may not be same as those indicated.

TABLE II. g Values for Matrix Isolated Tars*

Coal ----	g_{11} ---	g_1 ---	g^0 ---
Illinois #6			
a	2.037	2.002	2.014
b	2.029	2.002	2.011
c	2.025	2.002	2.010
d	2.010	2.002	2.005
Pittsburgh			
a	-----	-----	-----
b	2.030	2.003	2.012
c	-----	-----	-----
d	2.011	2.003	2.006
Rawhide			
a	-----	-----	-----
b	2.029	2.001	2.010
c	-----	-----	-----
d	2.010	2.001	2.004
Texas Lignite			
a	2.038	2.003	2.014
b	2.030	2.003	2.012
c	-----	-----	-----
d	2.011	2.003	2.006
O-methylated Illinois #6			
a	2.037	2.002	2.014
b	2.029	2.002	2.011
c	2.025	2.002	2.010
d	2.011	2.002	2.005
Coal (unheated)			2.0025-2.0045
Free Electron			2.0023
Graphitized carbon film			2.0107

$$*(g^0=1/3(g_{11}+2g_1))$$

Table III. g Values of Possible Free Radicals in Tars⁽²⁾

<u>Free Radical</u>	<u>g Value</u>	
Aromatic Hydrocarbons		
π Radicals	2.0025	(cation)
1-5 Rings	2.0026-2.0028	(anion)
7 Rings	2.0025	(cation)
7 Rings	2.0029	(anion)
Aliphatic Hydrocarbons		
σ Radicals	2.0025-2.0026	(neutral)
Oxygen Containing Free Radicals		
σ Type	2.0008-2.0014	(neutral)
π Type		
Quinones 1-3 rings	2.0047-2.0038	
Ethers		
i-ring, Mono-, Di-, Trimethoxybenzene	2.0035-2.0040	
N-Containing Radicals	2.0031	
S-Containing Radicals	2.0080-2.0081	
Graphite	2.0025-2.015	

Table IV. Comparison of Tar g-Values with Other Free Radicals

Tar	$\frac{a}{2.014}$	$\frac{b}{2.011}$	$\frac{c}{2.010}$	$\frac{d}{2.005}$
π Aromatic Free Radicals	$\frac{\text{Sulfur}}{2.008}$	$\frac{\text{Oxygen}}{2.004}$	$\frac{\text{Nitrogen}}{2.003}$	$\frac{\pi \text{ Aromatic}}{2.0025}$

Moveable Liq. He or N₂ Cooled Tube

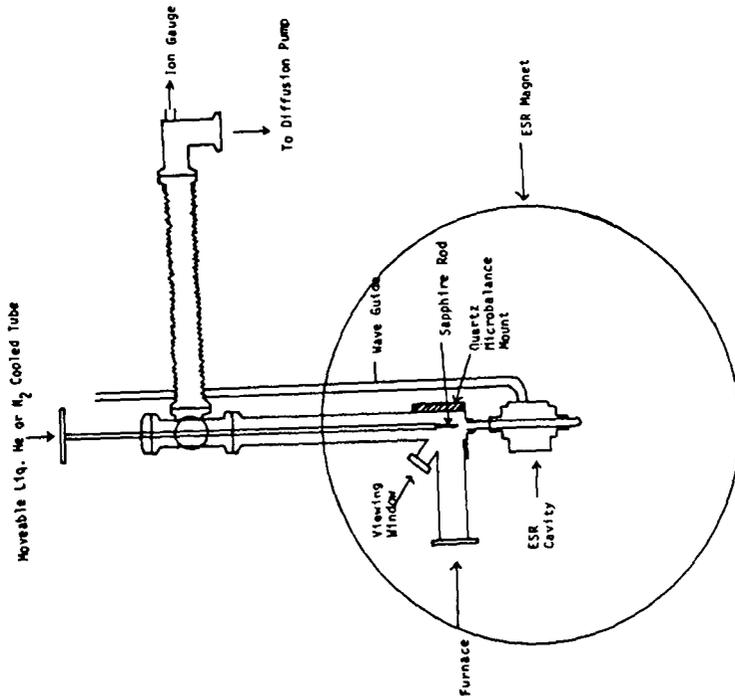


Figure 1. Matrix Isolation ESR Apparatus

Figure 2. EPR of Iodoanis #6 at 77K Showing Evolution of Tar Molecules

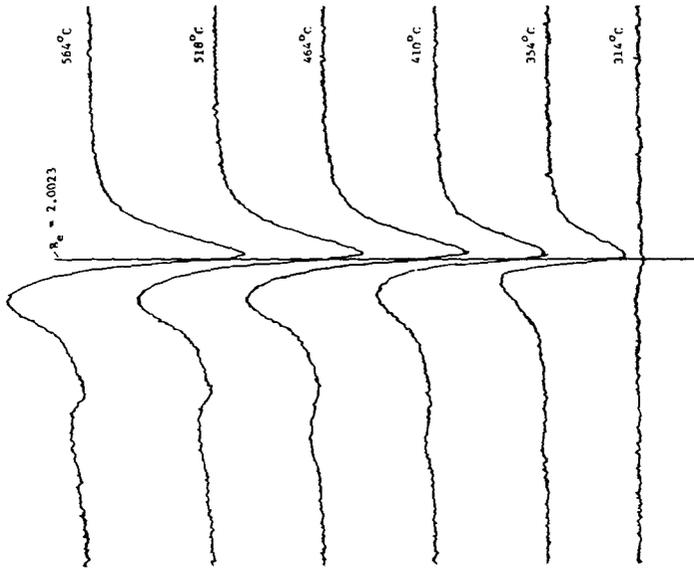


Figure 4. Comparison of Illinois #6 and Its Matrix Isolated Tar

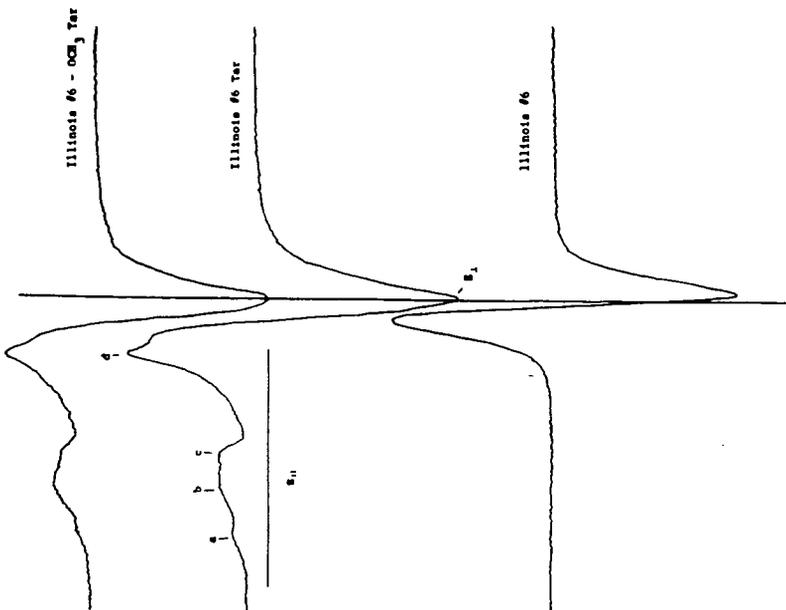


Figure 3. EPR of Matrix Isolated Tar Molecules at 77K

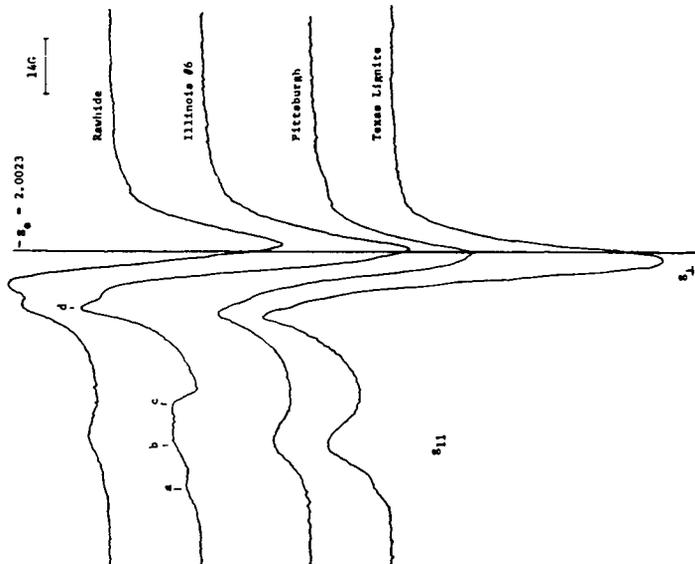


Figure 5. Warm Up of Matrix Isolated Illinois #6 Tar

