

HYDROXYL FUNCTIONAL GROUP DETERMINATION IN COAL TARS
AND PYROLYSIS OF O-METHYLATED COAL

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INTRODUCTION

The objective of this investigation was to study the hydroxyl functional groups of tar molecules and to determine their involvement in the mechanism of tar evolution during coal pyrolysis processes. Strong similarities exist between the infrared spectra of coals and their respective tars suggesting that the tar molecules are similar in structure to the parent coal and contain similar functional groups characteristic of the parent coal.(1) Clarification of the structure of tar molecules should lead to a better understanding of the parent coal structure. Our main concern has been centered on the identification of tar hydroxyl functional groups and the determination of their role in the mechanism of tar evolution. Whether hydrogen bonding through the hydroxyl functional groups is an important factor in tar evolution will be investigated through the pyrolysis studies of methylated coals. The process of methylation replaces most of the phenolic and carboxylic hydrogens in coal with methyl groups.(2,3) Thus hydrogen bonding via the phenolic or carboxylic hydrogens should be largely eliminated.

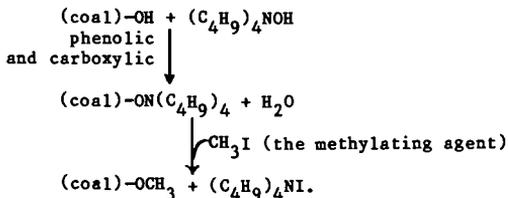
The experiments were designed so that tar molecules and other gaseous products of coal pyrolysis could exit the reaction zone rapidly and be trapped with inert nitrogen gas on a cold matrix surface. Matrix isolation studies of tar molecules produce better resolved FTIR spectra than those in a coal matrix, making structural characterization of the tar molecules a more definite possibility.

EXPERIMENTAL

The Rice University multisurface matrix isolation apparatus was used in the pyrolysis studies of four different ranks of coal and their respective methylated products. The four coal samples studied were Pittsburgh bituminous, Illinois #6, Rawhide sub-bituminous and Texas lignite. The samples were ground and sifted under inert nitrogen atmosphere to prevent oxidation. Only the -500 mesh size coal particles were used in the experiments.

The matrix isolation FTIR apparatus possesses 60 deposition surfaces which are useful for pyrolysis studies over a wide range of temperatures. Small changes occurring as a result of variations in reaction temperature can be readily detected. Gaseous pyrolysis products including the tar molecules were trapped in a nitrogen matrix at 12°K. One surface was used for every 40-100°C increment rise in temperature over a 10 minute trapping period. The frozen matrices were later analyzed off-line with an integrated IBM-FTIR spectrometer. Tar evolution was observed to occur within the same temperature range (150-600°C) for the four coals studied. Therefore the experimental temperature range studied was from room temperature to approximately 620°C. Detailed descriptions of the MI-FTIR apparatus and the pyrolysis reactor can be found elsewhere.(4,5)

Methylation of the coal samples was performed according to the procedures described by R. Liotta in "Selective Alkylation of Acidic Hydroxyl Groups in Coal".(2) The general reaction procedure may be described using the following equations:



Only -500 mesh coal particles were used in our methylation reactions. The experimental procedure for the pyrolysis of the methylated coals was identical to that of the original coal in order to determine if methylation in any way alters the pyrolysis behavior of the original coal.

RESULTS AND DISCUSSION

Determination of Hydroxyl Functional Groups in Tar

Hydroxyl functional group determination in coals has been undertaken both spectroscopically (6) as well as through a combination of chemical and spectroscopic means. (7) The spectroscopic method of hydroxyl determination relied on the measurement of the broad infrared absorption region between 3600-2000 cm^{-1} . This broad absorption range was complicated by the presence of KBr water absorptions as well as absorptions attributed to hydrogen bonded OH. The second method of hydroxyl functional determination involved the measurement of intensities of infrared bands (carbonyl stretching at 1770 and 1740 cm^{-1}) assigned to products of acetylation reactions of coal. Both methods involved indirect determination of OH functional groups in the parent coal matrix. Studies of coal pyrolysis processes using matrix isolation techniques have the advantage of actually isolating the individual tar molecules and other gaseous products in an inert matrix. Isolation of the individual tar molecules in an inert gas matrix at 12°K produced well resolved infrared spectra not observed in the FTIR spectra of tars in a coal matrix, thus making structural characterization of the tar molecules highly feasible. The matrix isolated tar should also be free of hydrogen bonding thus facilitating the identification of hydroxyl functional groups.

Figure 1 shows the matrix isolated FTIR spectra of the gaseous pyrolysis products of Pittsburgh bituminous from r.t. to 621°C. The evolution of tar molecules was initiated at temperatures as low as 130°C and continued until maximum evolution was reached at 470°C. Absorptions characteristic of tar molecules were broad bands at 3000-2800 cm^{-1} due to CH stretching, and 1550-1100 cm^{-1} due to CH bending and CO stretching. Study of the OH stretching region of the matrix isolated tar spectra should provide information concerning the hydroxyl functional groups present in the tar molecules. The presence of water OH stretching modes and absorptions due to water-tar complexes in this region complicated the identification of tar OH functional groups. Co-deposition of water (0.5 H₂O/100 N₂) with tar molecules resulted in noticeable increases in absorptions due to water-tar complexes. This is shown in Figure 2 which compares the matrix isolated FTIR spectra of Illinois #6 tar molecules with the results obtained from tar-water co-deposition experiments. As can be seen, two distinct broad absorptions at 3626.5 and 3580.9 cm^{-1} remained unaffected by the addition of water molecules. These were assigned to tar hydroxyl functional groups. The OH stretching frequencies of all four of the coal tar molecules studied are shown in Figure 3. Considerable amounts of hydroxyl functional groups were found in the tars of the two higher rank coals, Pittsburgh bituminous and Illinois #6, with Illinois #6 possessing greater amounts of hydroxyl functional groups. Considerably less hydroxyl absorption was observed for the two lower rank coal tars, Rawhide sub-bituminous and Texas lignite. The

observation of less hydroxyls for the lower rank coals is in accordance with lower rank coals possessing less aromatic character.

Comparison of OH stretching frequencies of phenol, 2-naphthol and cyclohexanol in nitrogen matrix with those of matrix isolated tar is shown in Figure 4. The broad tar OH absorption at 3626.5 cm^{-1} compares favorably with the OH stretching frequencies of phenol and 2-naphthol but not with cyclohexanol. In general, the less acidic alcoholic hydroxyls have OH absorptions at frequencies higher than 3630 cm^{-1} (OH stretching frequency of nitrogen matrix isolated methanol is 3664 cm^{-1}). The peak at 3626.5 cm^{-1} is thus assigned to a phenolic hydroxyl. One also concludes that alcoholic hydroxyls are not present in matrix isolated tar molecules. The less intense tar OH absorption at 3580.9 cm^{-1} is still under investigation. Since this absorption is lower in frequency than the phenolic OH, it is probably due to a more acidic OH functional group than the phenolic hydroxyl. Possibilities are carboxylic hydroxyls or phenolic hydroxyls with an adjacent thiophene group (hydroxy-benzothiophene). (8)

Pyrolysis of O-Methylated Coal

The role of hydroxyl functional groups in the mechanism of tar evolution is of great interest. Hydrogen bonding through the hydroxyl functional groups could be an important intermolecular bond in the structure of coal. If hydrogen bonding through the hydroxyl functional groups were the predominant factor in determining the volatility of the coal (determined by the ease of tar evolution and percent weight loss), then replacing the hydroxyl hydrogens with methyl groups should eliminate this hydrogen bonding and make the coal more volatile. Hydroxyl functional groups can also undergo water elimination reactions to form new C-O-C cross linkages. The formation of these new cross linkages would also act to reduce the volatility of coal and thus increase the tar evolution temperature. Methylation of the coal would eliminate the formation of these new cross linkages. More tar might also be evolved due to the increased volatility and decreased decomposition of the O-methylated coal.

If the evolution of tar during coal thermal decomposition occurred primarily through the cleavage of weak linkages such as methylene linkages, then methylation should not effect the volatility of the coal or the tar evolution temperature.

Slow pyrolysis studies of methylated coals were performed to determine if O-methylation in any way has altered the pyrolysis behavior of the original coal. Figure 5 shows the matrix isolated FTIR spectra of the pyrolysis products of methylated Pittsburgh bituminous from r.t. to 604°C . Comparison of pyrolysis results of the methylated coal (Figure 5) with those of the original coal (Figure 1) showed several differences indicative of coal structural changes after methylation. Tar evolution temperature has been reduced by approximately $150\text{--}200^{\circ}\text{C}$, indicating a more volatile coal after methylation. This was observed for all four ranks of coal studied. An increase of approximately 10% volatility was also observed for all four coals after methylation. Comparisons of the matrix isolated tars with their respective methylated tars are shown in Figure 6. For all four coals, O-methylation has changed the relative intensities of CH_3 to CH_2 groups in the tar molecules in favor of greater CH_3 absorptions as is to be expected since CH_2 groups have replaced all hydroxyl hydrogens in the methylated tar. Phenolic hydroxyl absorptions at 3626.5 cm^{-1} are also absent in the methylated tar molecules.

The increased volatility and the lowering of tar evolution temperature of the O-methylated coal suggest that methylene linkages are not involved in the mechanism of tar evolution. Our results from the pyrolysis of O-methylated coal suggest two possible mechanisms of tar evolution. The first involves breaking only hydrogen bonding of the hydroxyl groups as tar is evolved. A second mechanism envisions the formation of new cross linkages through decomposition of the hydroxyl groups at lower temperature. The temperature at which tar evolves in then set by the temperature at which the new cross linkages decompose. Isotopic enrichment studies are currently in progress to assist in distinguishing between the above mechanisms.

In any case, the large increase in volatility of the tar component of all four coals is quite remarkable and suggests a common bonding mechanism in all coals.

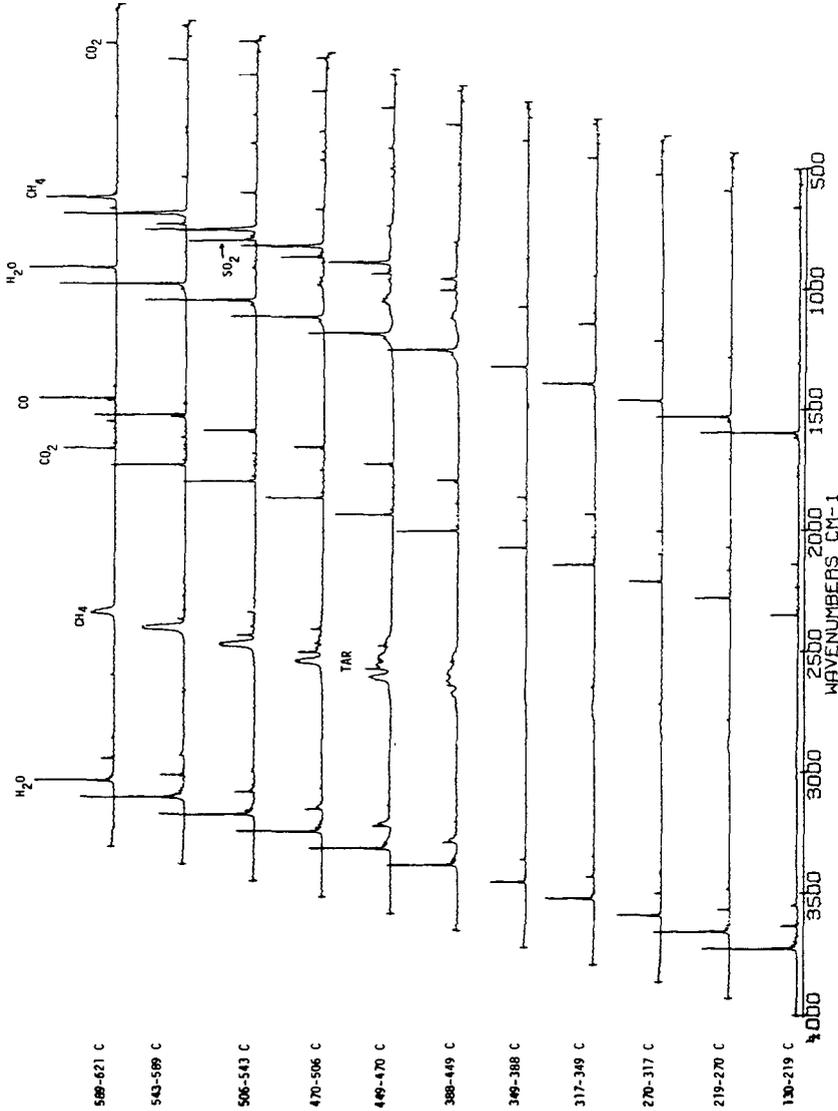
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Figure 1: Pittsburgh Bituminous Slow Pyrolysis



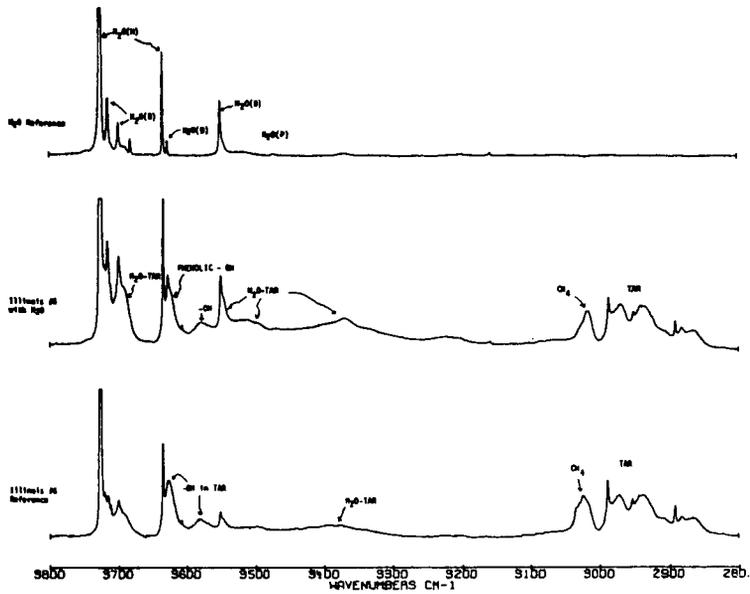


Figure 2. Co-Deposition of Illinois #6 Tar and H₂O in N₂ Matrix

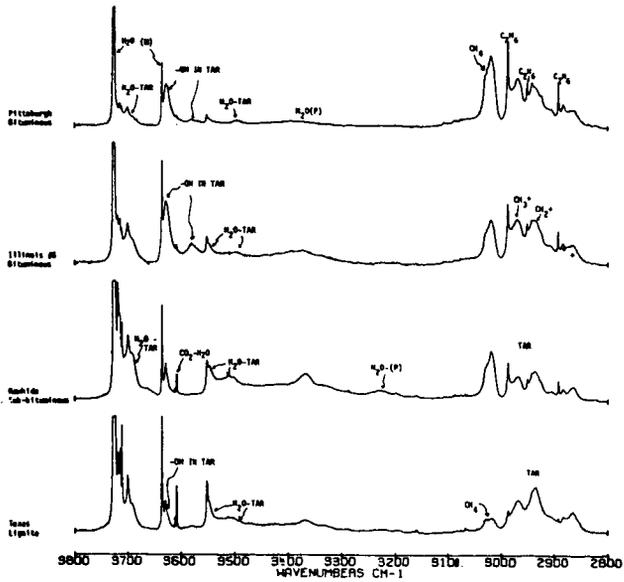
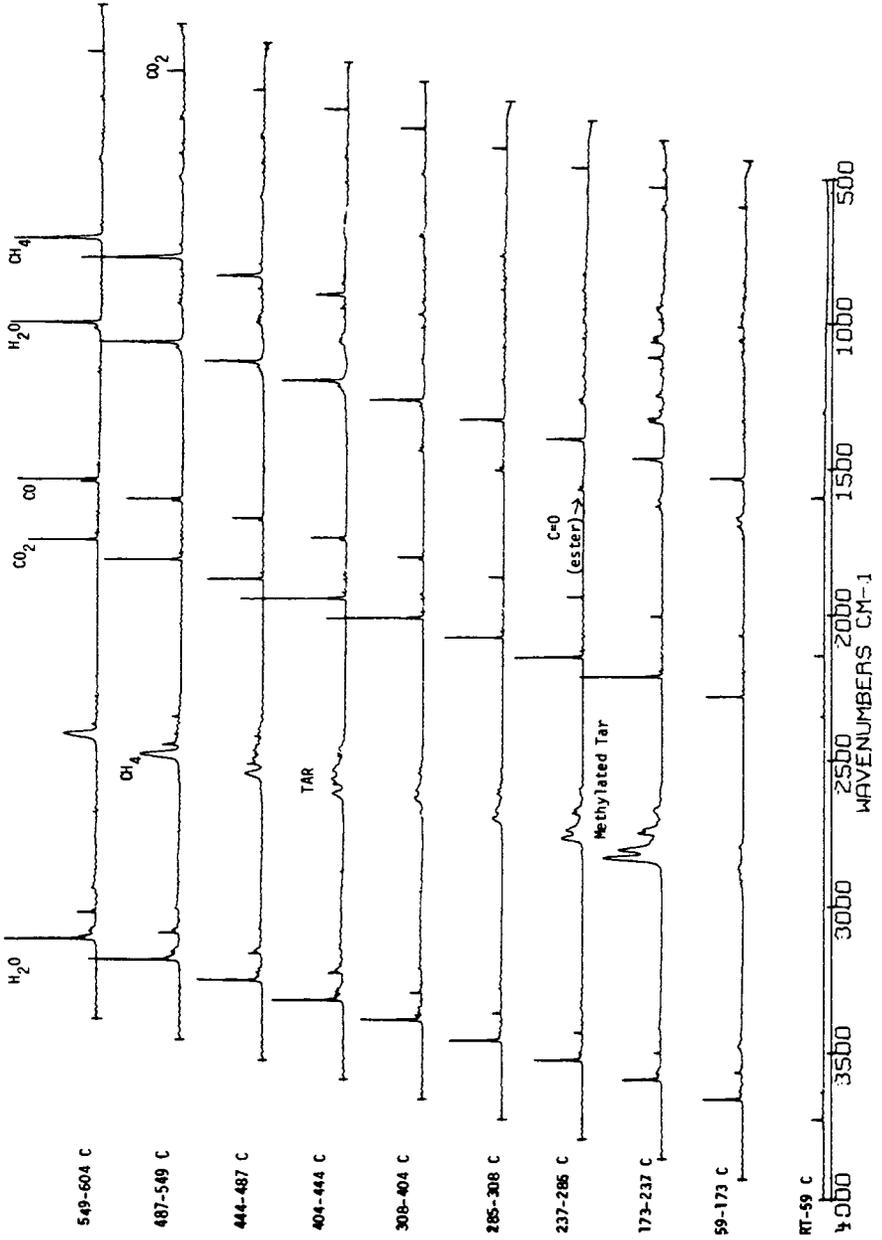


Figure 3. MI-FTIR Spectra of Four Coal Tars

Figure 5: 0-Methylated Pittsburgh Bituminous Slow Pyrolysis



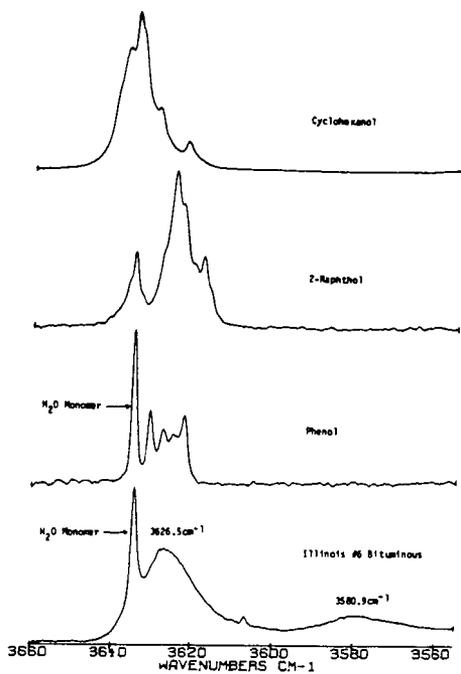


Figure 4. Comparison of Hydroxyl Stretching Frequencies in N_2 Matrix

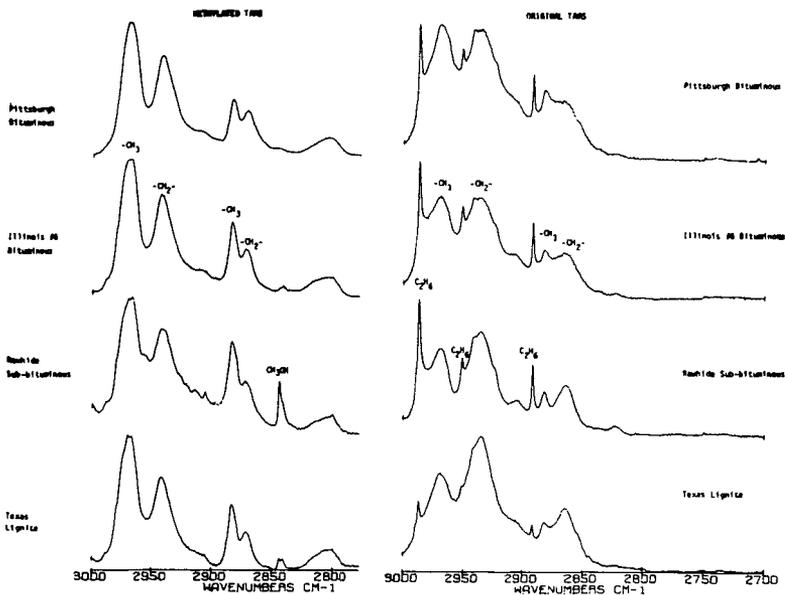


Figure 6. Comparison of CH Stretching Region of Tar and O-Methylated Tar