

DETECTION BY PHOTOACOUSTIC INFRARED FOURIER TRANSFORM SPECTROSCOPY
OF SURFACE PEROXIDE SPECIES IN CHEMICALLY AND THERMALLY MODIFIED COALS

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ABSTRACT

Work in our laboratories over the last three years has demonstrated that PhotoAcoustic infrared Fourier Transform (PAIFT) spectroscopy provides unique qualitative and quantitative information about the surface functionalities of bituminous coals.

We now report evidence detected by PAIFT techniques of new carbonyl-type oxygen functionality in such coals, which is generated both by base-promoted and thermal decomposition of precursor peroxide species, which we propose are ubiquitous constituents of the surfaces of all except the most freshly prepared samples of powdered bituminous coals.

INTRODUCTION

Over the past three years, PhotoAcoustic Infrared Fourier Transform (PAIFT) spectra of coal samples have been acquired in our laboratory for a data base now amounting to some 6000 spectra. Various preliminary reports of our results have been presented (1-5).

Among the manifold advantages of PAIFT spectroscopy in the study of coals are minimal sample preparation, insensitivity of signal to degree of subdivision, and the ability to observe surface infrared absorbing features generated by chemical manipulation. Subtraction to yield difference spectra revealing such introduced features is straightforward and avoids arbitrary scaling procedures.

Although it is often stated that application of FTIR spectroscopy has revitalized the applications of infrared spectroscopy to coals, the truly new results reported as a consequence of this revitalization are very limited, and the recent literature contains several examples of unwarranted and probably incorrect conclusions arising from subjective applications of curve-resolving techniques and calibrations of relative intensities of spectral features.

In this paper, we report detection by PAIFT spectroscopy of new oxygen functionality produced by base-promoted decomposition of precursor peroxide species ubiquitously present at the surface of all except the most freshly prepared samples of powdered bituminous coals. The occurrence of this reaction process has escaped detection previously since KBr-pellet transmission FTIR and Diffuse Reflectance FTIR measurements involve randomization of the superficial infrared-absorbing groups as a consequence of the grinding procedures associated with sample preparation using these techniques.

EXPERIMENTAL

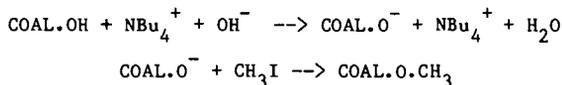
PAIFT spectra were acquired using a Bruker IFS110 purge-type Infrared Fourier System employing a Ge on KBr beamsplitter. The spectrometer was interfaced to an E G & G Princeton Applied Research Model 6003 Photoacoustic Accessory equipped with a zinc selenide window and the amplified photoacoustic output was transmitted to the data acquisition system of the IFS110. The purge flow was interrupted during scanning.

Coal samples were ground to finer than 60 mesh under liquid nitrogen using Brinkmann Pulverizer, and dried at 100 degrees C under vacuum before transfer to the sample cup of the photoacoustic accessory. For routine operation, 10-50 mg of dried coal were placed in the sample cup, and 128 photoacoustic interferograms were collected at 8 cm^{-1} resolution with a zero-filling factor of 2, corresponding to a final transformed spectrum encoded every 4 cm^{-1} . Photoacoustic spectra were obtained by ratioing against the energy output (black-body response) from a similarly prepared sample of Fisher Carbon Lampblack C-198.

The interferometer mirror velocity was $0.08333 \text{ cm s}^{-1}$, and spectra were acquired from $400\text{-}4,000 \text{ cm}^{-1}$.

DISCUSSION AND RESULTS

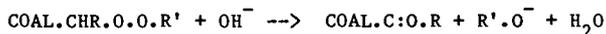
Bituminous coal samples may be methylated quantitatively using the phase-transfer catalyzed process developed by Liotta and co-workers at Exxon Research and Engineering Company (6,7). The procedure involves initial formation of anionic centres and associated swelling of the coal by treatment with tetrabutylammonium hydroxide in aqueous tetrahydrofuran under nitrogen, followed by $\text{S}_{\text{N}}2$ reaction with methyl iodide, that is:



PAIFT spectra for a typical sample of freshly ground, newly mined bituminous coal (from Cape Breton Island, Nova Scotia) and of its quantitatively methylated species are reproduced in the two spectra of Figure 1.

In previous work (1-4) we observed that many methylated coals exhibit distinct carbonyl absorption in the region $1680\text{-}1705 \text{ cm}^{-1}$, which is not present in the starting coal. Although we thought at first that a high-frequency shift of a pre-existing carbonyl species (occurring as a consequence of the elimination of hydrogen-bonding interactions) accounted for this phenomenon, further work shows that the new carbonyl is generated irreversibly at the stage of formation of the coal anions (that is, before methylation) (see the overlay spectrum of Figure 2), and is unchanged by re-acidification of the reaction mixture; thus the new peak cannot involve displacement of a carboxylate/carboxylic acid ratio, nor a simple frequency shift accompanying methylation.

We attribute the formation of the new absorbing entity to the base-promoted decomposition of peroxide species, that is:



R = alkyl or aralkyl, R' = H, alkyl, or aralkyl

This is a well documented reaction (8-10) whose possible relevance to coal transformations has not been recognized previously to our findings. The difference spectrum between the sample of Figure 1 and the corresponding reprotonated (re-acidified and washed) "coal anion", which was presented in overlay form in Figure 2, is reproduced as Figure 3, and exhibits a maximum at 1686 cm^{-1} . We have been able to define the nature of the carbonyl feature as ketonic, since it is quantitatively reduced to an alcohol species by tetrabutylammonium borohydride in aqueous tetrahydrofuran.

Derivatization of the same coal through acetylation using the standard procedure where the coal is heated to reflux with acetic anhydride dissolved in pyridine does not produce added ketone-type carbonyl species (see Figure 4). Under these conditions, we suggest that it is likely that the peroxide species transfers oxygen directly to the pyridine solvent, and the formed pyridine-1-oxide undergoes the known rearrangement/hydrolysis to give 2-acetoxypyridine and thence 2-pyridone.

Although the overlay and difference spectra referred to above bear a general resemblance to those observed for oxidation at higher temperatures (see Figures 5 and 6), the band shapes are different, with the carbonyl peaks from the base-generated ketones obviously being simpler, and the carbonyls shown in Figure 6 possessing multiple contributing components. Also we wish to point out that the intensity of the ketone carbonyl peaks in the difference spectra derived from base-treatment of coals stored in the laboratory at around 20°C for six and for twelve months (Figures 7 and 8) increases progressively: "fresh" coal, 0.020 intensity units, after six months, 0.059; after 12 months, 0.089.

Finally, we find that thermal decompositions of these coal samples occur in vacuo between 150 and 200 degrees C to generate carbonyl functions whose origin we are confident lies with surface peroxides, although the course of these reactions is more complex than for the base-promoted decompositions.

CONCLUSIONS

PAIFT spectroscopy of coals treated with phase-transfer base followed by reacidification provides evidence that previously unquantified and undetected peroxide species are significant features of coal surfaces exposed to air at ambient temperatures; thermal decompositions at coal surfaces similarly involve contributions from peroxide \rightarrow carbonyl conversions. The proportion of peroxides on a coal surface is surely playing an important, hitherto unguessed, role in determining the course of coal pyrolyses.

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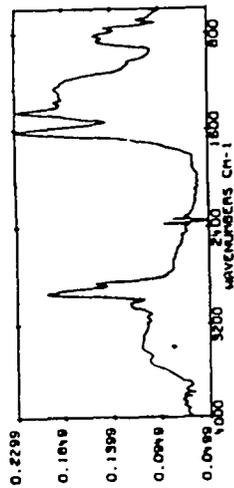


Figure 1. Typical PAFT spectra of Cape Breton Island bituminous coal and of its product of quantitative methylation.

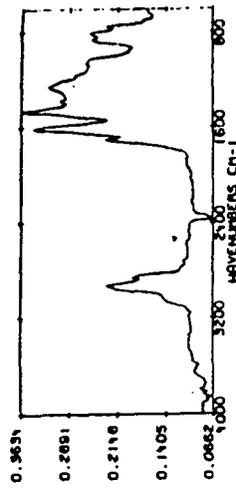
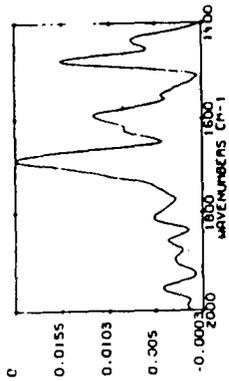


Figure 2. Overlay spectrum of the coal of Figure 1, before and after coal anion generation.



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Figure 3. Difference spectrum, coal after minus before coal anion generation.

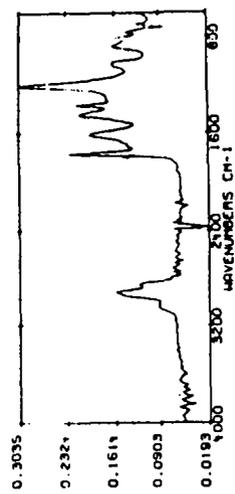


Figure 4. PAFT spectrum of quantitatively acetylated bituminous coal of Figure 1.

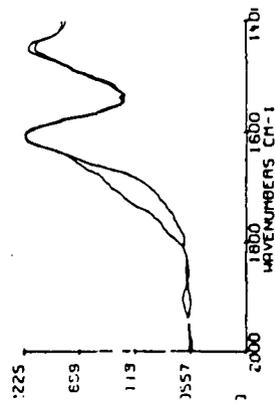


Figure 5. Overlay spectrum of thermally oxidized bituminous coal (before and after 192 h oxidation in air at 105°C).

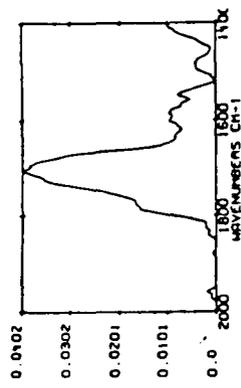


Figure 6. Difference spectrum, thermally oxidized coal (see Figure 5).

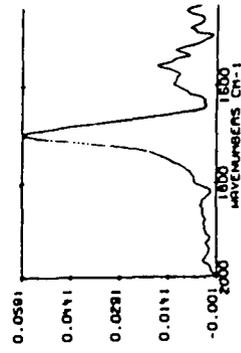


Figure 7. Difference spectrum, after minus before coal anion formation, for coal of Figure 1 stored six months.

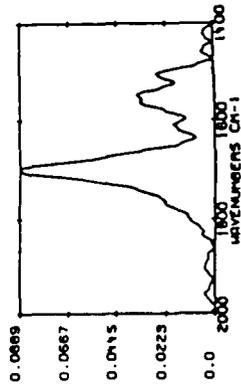


Figure 8. Difference spectrum after minus before coal anion formation, for coal of Figure 1 stored twelve months.