

THE 1600  $\text{cm}^{-1}$  BAND IN THE INFRARED SPECTRA OF CHARs AND COALS

R. A. Friedel and R. A. Durie

U.S. Department of the Interior, Bureau of Mines,  
Pittsburgh Coal Research Center, Pittsburgh, Pa.Commonwealth Scientific and Industrial Research Organization  
Coal Research Division, Chatswood, NSW, Australia

## ABSTRACT

One of the principal questions in the structure of low-temperature chars and of coals is the presence or absence of carbonyl groups as an important part of the structure. The infrared spectrum, particularly the 1600  $\text{cm}^{-1}$  absorption band, is a key point in this question. Assignment of this band, the most intense band in the spectra of both coals and chars, has not yet been settled. For coal, the original assignment of Cannon and Sutherland was to an aromatic CC stretching vibration.<sup>1/</sup> This was the generally accepted assignment until it was suggested that phenoxy compounds as well as hydrogen-bonded carbonyl structures may be involved. Investigations of the 1600  $\text{cm}^{-1}$  band by many workers have been concerned with these three possibilities: Aromatics, phenoxy compounds, and chelated carbonyl structures.

On the question of involvement of oxygen in the 1600  $\text{cm}^{-1}$  band, previous work on chars has indicated that there is such an involvement. n-Octacosane charred at 450° C in vacuo and anthracene charred at 500° C in vacuo gave spectra that showed practically no 1600  $\text{cm}^{-1}$  absorption. Oxygen was introduced into chars of these hydrocarbons by carrying out the charring in an oxygen atmosphere. Intense 1600  $\text{cm}^{-1}$  bands were produced. Conjugatively chelated carbonyl structures are strongly indicated by these experiments but the point is not proven. Though large amounts of oxygen were introduced into the chars it is still possible that the oxygen could be present in the form of phenoxy structures.

A more direct investigation of the specific structures responsible for the 1600  $\text{cm}^{-1}$  band in chars seemed desirable. Charring of compounds labeled with oxygen-18 was judged to be a direct method with good chances for success. If an unlabeled carbonyl group produces an absorption band at 1600  $\text{cm}^{-1}$  the corresponding labeled carbonyl group should produce a band shifted to 1560  $\text{cm}^{-1}$ . If the stretching vibration of the carbonyl structure is complex the shift obtained will differ somewhat from -40  $\text{cm}^{-1}$ . Several ketones, aliphatic and aromatic, are known to produce shifts of from -20 to -32  $\text{cm}^{-1}$  with O-18 labeling. Values less than theoretical indicate that mixing-in of other parts of the molecule into the carbonyl vibrations occurs, so that absorption is not localized on the carbonyl group. Only three O-18 labeled organic compounds were commercially available for this work: Linoleic acid, benzoic acid, and phenol. Chars were produced in the range of 500°-550° C for these three and for the sodium salts of benzoic acid and phenol. All of the chars were found to possess well-formed 1600  $\text{cm}^{-1}$  bands. But comparison of the spectra of the labeled and unlabeled chars showed that there was no detectable shift at 1600  $\text{cm}^{-1}$ . This result seemed to negate the hypothesis that carbonyl groups could be involved in the 1600  $\text{cm}^{-1}$  band. However, it was found that the carbonyl hypothesis could not

be discarded after all, for a comparison of the spectra of monomer and dimer benzoic acid, labeled and unlabeled, showed that moderately strong hydrogen bonding produced a significantly smaller shift. If a very strongly hydrogen-bonded system, such as a conjugatively chelated carbonyl, were labeled it would be possible to determine the effect of strong bonding on the shift. O-18 labeled dibenzoyl methane was prepared; the compound exists completely as the enol (hydrogen-bonded structure). No isotopic shift was observed. Thus, in this compound and possibly also in chars and coals, carbonyl structures can be present; the absence of isotopic shift indicates that the absorption process is not localized on an oxygen-containing functional group.

A further attempt to characterize the  $1600\text{ cm}^{-1}$  band has been carried out by a study of absorption band intensities. The infrared spectra of many different types of compounds have been studied; the integrated intensities for these compounds in the region of  $1600\text{ cm}^{-1}$  band have been compared with the corresponding values obtained from the spectra of chars and coals. One of the principal structures thought to be important, due to characteristic absorption at  $1600\text{ cm}^{-1}$ , namely polynuclear condensed aromatic hydrocarbons with oxygen substituents, cannot be important contributors at  $1600\text{ cm}^{-1}$  because of the weak intensities of these compounds. The only structure which, from intensity studies, appears capable of producing the intense absorption found is the conjugatively chelated carbonyl structure.

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1/ Cannon, C. G., and Sutherland, G.B.B.M. Trans. Faraday Soc., v. 41, 1945, pp. 279-288.