INFRARED SPECTRA OF OXYGEN-18 LABELED CHARS

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SUMMARY

Chars of four O-18 labeled compounds were prepared. Infrared spectra were examined for isotopic shifts. On the basis of a few published results on pure compounds the shifts for $C=O^{18}$ at 1600 cm^{-1} were expected to be -20 cm^{-1} or more. The observed shifts are less than 5 cm^{-1}; this result may indicate that chelated carbonyls are not involved. However, very strong hydrogen bonding as in chelated, conjugated carbonyl structures may be responsible for the small shifts. An O^{18}-labeled chelate is being prepared at the CSIRO laboratories in order to investigate this point.

Introduction

Chars

Since the early work at the Bureau of Mines on carbohydrate chars[1,2] the infrared spectra of chars ($\leq 500°$ C) of various chemicals have been studied.[3,4,5] Spectral investigations of structure of chars have included studies of the effect of elemental constitution; the effect of introducing oxygen into chars of hydrocarbons indicated that spectral absorption bands, particularly the intense 1600 cm^{-1} band, were attributable to oxygenated structures.[4,6,7] Isotope-labeling of chars has been utilized; a successful study of deuterium labeling was carried out by comparing infrared spectra of chars of an aliphatic hydrocarbon and a corresponding deuterocarbon. From this study definite evidence was obtained for assignment of the 730-910 cm^{-1} absorption bands to CH out-of-plane aromatic vibrations.[6,7] Also, further indications were found that the most intense band in char spectra, 1600 cm^{-1}, was attributable to oxygenated structures.

A more direct investigation of the specific structures responsible for the 1600 cm^{-1} band seemed desirable. Charring of compounds labeled with oxygen-18 was judged to be a direct method with good chances for success. Three structures were considered on the basis of their intense absorption, near 1600 cm^{-1}, to be possible sources of the 1600 cm^{-1} band in chars:

(1) Carbonyl groups in ketones, quinones, or conjugated chelate structures should show a shift to low frequency in going from $C=O^{16}$ to $C=O^{18}$; (2) aromatic nuclei should produce no change in spectral frequency; (3) aromatic nuclei with enhanced intensities due to oxygenated substituents on the ring should not undergo any appreciable frequency shift in the 1600 cm^{-1} region; a shift should occur in the C-O stretch region at 1100 cm^{-1}.

Coals

Studies of the 1600 cm^{-1} band in char spectra may produce information on the origin of the same band in the spectra of coals. Spectral data from chars of carbohydrates would be particularly applicable for comparison with coal spectra as carbohydrate chars produce spectra nearly identical to spectra of coals.[1,2] Unfortunately O^{18}-labeled carbohydrates are not available.

Information on the intense 1600 cm^{-1} band in coals has been obtained in studies of absorption intensities for many pure compounds in an effort to determine what structures could produce the 1600 cm^{-1} absorption.[8] The principal type of structure found to have sufficient intensity is the conjugated chelated carbonyl group. These groups can only produce the 1600 band if all or nearly all of the oxygen in the coal is in the form of hydroxyl chelated carbonyl groups.

O^{18}-Labeled Compounds

The minimum spectral shift in the infrared spectra for a labeled carbonyl group ($C{=}O^{18}$) relative to an unlabeled group ($C{=}O^{16}$) is -40 cm^{-1}, on the basis of the simple ratio of the reduced masses. Hooke's law for the stretching vibration of $C{=}O^{16}$ is: $\nu_{16} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{16}}}$, where

$$\mu_{16} = \frac{m_C + m_{O^{16}}}{m_C m_{O^{16}}} \; ; \; \nu = \text{frequency, cm}^{-1}; \; k = \text{constant};$$

For $C{=}O^{18}$ the same equation applies; dividing,

$$\frac{\nu_{16}}{\nu_{18}} = \sqrt{\frac{\mu_{16}}{\mu_{18}}} = \sqrt{1.05}$$

or $$\nu_{18} = \frac{\nu_{16}}{\sqrt{1.05}}$$

For ν_{16} = 1600 cm^{-1}, ν_{18} = 1560 cm^{-1}; $\Delta\nu$ = -40 cm^{-1}. If this 1600 cm^{-1} band in a char or coal spectrum is due to a simple carbonyl structure, the corresponding labeled carbonyl group should produce an absorption band shifted to 1560 cm^{-1}. If the stretching vibration of the carbonyl structure is complex the simple value obtained from the reduced mass calculation will differ somewhat from 40 cm^{-1}. A ketone investigated by Karabatsos[9] showed an appreciable deviation; 2,3-dimethyl-3-pentanone-O^{18} shows a shift of 31 cm^{-1} instead of the expected 40. This shift is in the neighborhood predicted by Francis[10] for a mixed vibration composed of about 80 percent C=O stretch and 20 percent C-C stretch. With conjugation the shift does not change for the benzenoid carbonyl compounds: Benzoic acid, two benzoates, benzophenone, and benzoquinone.

	$\Delta\nu$, cm^{-1}
Benzoic acid (monomer)	-32[11]
Methylbenzoate	-31[11]
Cinnamyl nitrobenzoate	-30[12]
Benzophenone	-30[13]
p-Benzoquinone	-30[14]
Benzoylchloride	-25[11]
Benzamide	-24[15]

The decreased shift for benzamide is attributable to greater participation of other groups of the molecule in the carbonyl vibration.[15] Apparently the same explanation may be given for the decreased shift observed for benzoylchloride. It is surprising that the shifts observed indicate no particular increase due to conjugation with an aromatic ring. (A large effect due to ring conjugation is observed by comparison of the spectra of nitromethane-O^{18} and nitrobenzene-O^{18}.[16,17]) Future investigations of more aliphatic ketones may produce different results.

The only published indication of the effect of conjugated chelation is on benzoic acid dimer:

	$\Delta\nu$, cm^{-1}
Benzoic acid dimer	-20
Benzoic acid monomer	-32

Thus hydrogen bonding is seen to produce a significant decrease in the O^{18} shift of a conjugated carbonyl system. It was anticipated that the spectra of chars having carbonyl groups enriched in O^{18} may show shifts for the 1600 cm^{-1} band of -20 to -30 cm^{-1}. Such shifts in char spectra would be measurable, even though absorption bands are broad.

Experimental

On the initiation of this work only three usable O^{18}-labeled organic compounds were commercially available. They were investigated in the following order: Linoleic acid, phenol, and benzoic acid; sodium phenate and sodium benzoate-O^{18} were also prepared and charred. First the unlabeled compounds were charred under various conditions in order to determine the most favorable condition for producing intense 1600 cm^{-1} bands. Temperatures required to eliminate the absorption of monosubstituted benzenes in order to produce coal-like absorption bands in the 730-900 cm^{-1} aromatic band region were usually so high that other spectral details, including the 1600 cm^{-1} band, were weakened.

Samples of O^{16} compounds were placed in a glass tube or a steel bomb, sealed or unsealed, in vacuo or under nitrogen. Amounts of sample used were 50-100 mg because of the scarcity of O^{18} samples. Pyrolysis temperatures were varied from 350° C to 620° C; times were varied from 1 to 58 hours.

Linoleic acid-O^{18}

Two samples were investigated: (a) A sample of 22 percent O^{18}-enriched acid (kindly given by Dr. A. Miko, of the Yeda Research and Development Co., Rehovoth, Israel), and (b) a commercial sample of 38 percent enriched acid. The best conditions found for obtaining 1600 cm^{-1} bands were 400° C, 2 hours, under 1 atmosphere of nitrogen in a sealed pyrex tube. The 22 percent enriched sample was donated, with the warning that polymerization probably had occurred; it is also possible that polymerization occurred in the 38 percent enriched sample. Yeda has taken linoleic acid-O^{18} off the market.

Phenol-O^{18}, 86 percent

Pyrolysis of phenol of 86 percent O^{18} enrichment was carried out at temperatures near 550° C for about 18 hours in a sealed tube under nitrogen.

Sodium phenate

The O^{18}-labeled phenate was not prepared because of insufficient phenol-O^{18}. Sodium phenate-O^{16} was prepared from ordinary phenol and charred. Conditions were similar to those used for phenol.

Benzoic acid-O^{18}, 95.6 percent

Conditions were similar to those used for phenol.

Sodium benzoate-O^{18}

A nitrogen atmosphere and a temperature of 500° C were used. Pyrolysis times were about 24 hours.

In all samples except the sodium phenate and sodium benzoate, char was obtained in the form of a thin film on the walls of the sealed tube. These films were sufficiently thin to give spectra of good quality directly; data obtained from such films was qualitative or semi-quantitative as thicknesses of the film varied considerably. In all cases spectra were also obtained by means of KCl pellets which were better for quantitative absorption measurements.

Spectra were determined first on gases produced. Then the samples were washed with hexane and/or benzene and the spectra of the soluble products were obtained. The benzene-insoluble char was then investigated.

Ultimate analyses of all of the chars are given in table 1.

Results and Discussion of Results

Results obtained on the four substances investigated show that the spectral shifts are very small or negligible (table 2); no shift was definitely detectable for any of the chars. In figure 1 the spectra of chars from benzoic acid-O^{16} and -O^{18} are given; they are practically identical, including the positions of the two 1600 cm^{-1} bands.

1600 cm^{-1} bands were obtained in all chars but in no case were they intense bands. This is a possible indication that carbonyl groups may not have been involved. For linoleic acid and benzoic acid it is nearly certain that no oxygen-containing group could be an important contributor to the 1600 cm^{-1} band, as the oxygen contents of the chars were found to be negligible. Hydrocarbon structures could have produced the weak bands found.

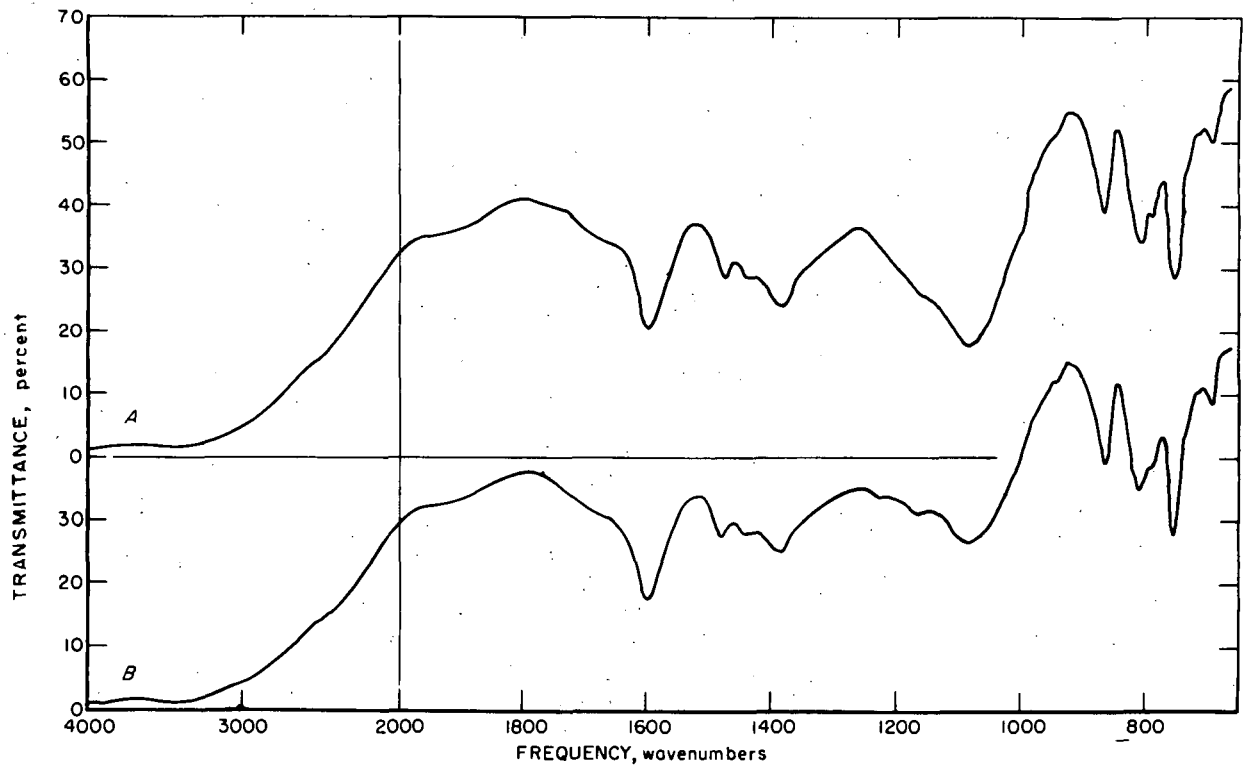

Figure 1. Infrared spectra of chars prepared from 50 mg heated at 550 C for 72 hours. KCl pellets, 2 percent in 100 mg KCl. Curve A, benzoic acid; curve B, benzoic acid-O^{18}.

Table 1.- Ultimate analyses of chars

	C	H	O	State
Benzoic acid	96.2	3.8	< 0.5	Film
Benzoic acid	70.08	2.86	(6.35)2/	Powder
Benzoic acid-O^{18}	95.17	3.89	1.35	Film
Sodium benzoate	93.00	3.71	3.88	Powder
Sodium benzoate-O^{18}	91.47	3.22	2.60	Powder3/
Phenol	71.80	3.35	20.0	Powder
Phenol	93.26	3.46	3.42	Film
Phenol-O^{18}	91.20	3.81	3.73	Film.
Sodium phenate	76.76	2.98	19.4	Powder
Linoleic acid1/	95.9	3.7	0.4	Powder

1/ O^{18}-labeled chars were not analyzed.
2/ Very small sample; oxygen analysis dubious.
3/ Ash, 3.5 percent, apparently due to a trace of glass from vial opening.

Table 2.- Negative spectral shifts of oxygen-18 labeled chars

	Spectral shift, cm^{-1} 1/
Linoleic acid-O^{18} (22 and 36 percent)	< 5
Phenol-O^{18} (86 percent)	< 5
Benzoic acid-O^{18} (95.6 percent)	< 5
Sodium benzoate-O^{18}	< 5

1/ Bands were broad. Small shifts were difficult to measure accurately.

The phenol chars also showed no shift from 1600 cm^{-1}, even though one char contains 20 percent oxygen. It is not surprising if the pyrolysis of phenol at 550° C does not produce carbonyl groups. The 1600 cm^{-1} band observed in the spectrum of the phenol char must be due to aromatic absorption enhanced by oxygen-containing substituents on the aromatic rings (ethers and phenols).

The char of sodium benzoate also shows a negligible shift. It was the most likely possibility for producing an isotope shift, as the elimination of oxygen encountered in the chars of linoleic and benzoic acid does not occur for the char of sodium benzoate. The sizeable percentage of oxygen present in the char, 4 percent, is likely to exist in the char as carbonyl groups of some sort; even so, no appreciable shift is observed.

The lack of appreciable shift in the spectra of O^{18}-labeled chars may be attributable to extremely strong association (chelation, or other). With the sizeable oxygen content of some of these chars there are presumably some carbonyl groups present. Unfortunately no O^{18}-labeled pure compounds having very strong hydrogen-bonding have been investigated. As mentioned above, the spectrum of benzoic acid-O^{18} shows a smaller shift for the associated dimer acid (-20 cm^{-1}) than for the free monomer (-32 cm^{-1}).[10] These results are for a rather weakly associated acid dimer; the vibration of the C=O group in the dimer obviously involves participation of other groups in the molecule. For a more strongly hydrogen-bonded chelate, as acetylacetone, the participation of other groups in the molecule would be greater and the shift probably would be less. On this basis the small shifts in chars are explainable. Certainly the negligible shift observed for chars does not exclude the presence of C=O groups in structures producing the 1600 cm^{-1} band. In order to investigate the effect of strong chelation on the $C{=}O^{18}$ shift preparation of dibenzoylmethane, $H_5C_6\text{-}CO^{18}\text{-}CH_2\text{-}CO^{18}\text{-}C_6H_5$, is being carried out at the CSIRO laboratories. Little or no $C{=}O^{18}$ shift is expected. If an appreciable shift is observed for this compound it will be necessary to conclude that chars do not contain strongly chelated carbonyls.

Further studies will be carried out on labeled chars as other O^{18}-containing compounds become available. It is expected that prices of these compounds will decrease greatly, for cheaper methods of preparation are being developed.[18]

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