

## Diffuse Reflectance Fourier-transform Infrared Spectroscopy: *in situ* Surface Oxidation of Carbon

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Diffuse reflectance Fourier-transform i.r. spectroscopy has been used to study surface groups on activated carbon during oxidative treatment *in situ* in an evacuable i.r. cell in which samples under spectroscopic examination can be heated to high temperature.

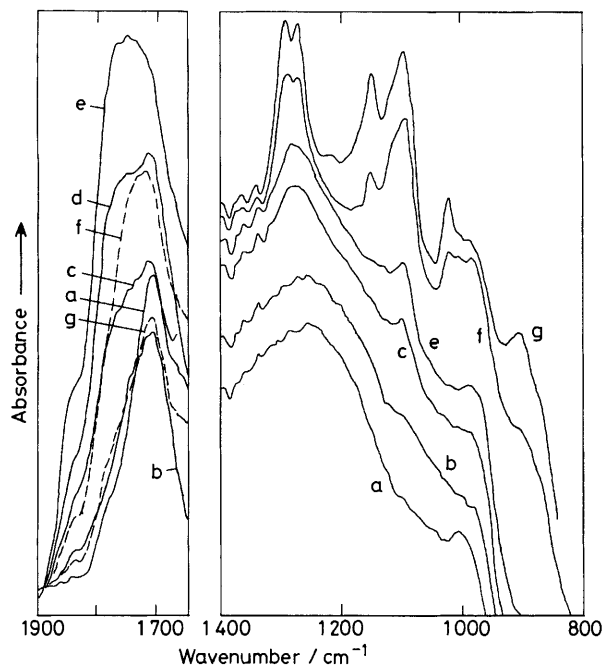
The advent of Fourier transform (F.t.) i.r. spectroscopy has improved the usefulness of i.r. techniques for the study of surface groups on carbons.<sup>1</sup> The commonest technique used so far has been to measure the transmission spectra of compacted discs of carbon dispersed in KBr after the carbon had been subjected to thermal or other pretreatment outside the i.r. apparatus.<sup>2-4</sup> A considerable advantage would be gained if the treatment of carbon samples could be carried out *in situ* in the i.r. cell. A suitable cell for transmission studies was described by Keifer *et al.*<sup>5</sup> who recorded spectra of samples of soot which were deposited on a fluorite disc and were subjected to heat treatment *in vacuo* and in gaseous atmospheres of nitrogen dioxide and sulphur dioxide. Use of the cell involved movement of the mounted sample from a position between optical windows to a furnace section where thermal treatment was carried out. Spectra of soot samples at elevated temperatures could not be recorded. The commercial availability of a vacuum chamber with a heated sample stage for use in conjunction with an i.r. diffuse reflectance accessory prompted the present investigation of the use of diffuse reflectance spectroscopy for the characterization of surface groups on carbon. The diffuse reflectance method has been briefly tested with some success<sup>1</sup> (although not with the sample *in situ* in a vacuum cell) but has not been well exploited. We here show that the combination of F.t. i.r., diffuse reflectance, and a vacuum cell with a heatable stage provides an extremely powerful method for the spectroscopic examination of carbon surfaces *in situ* under a variety of experimental conditions.

A homogeneous mixture of *ca.* 6 wt. % activated carbon (ref. 827/745, Sutcliffe, Speakman and Co., Leigh) and KBr

was evenly spread on the sample stage of a vacuum chamber (Harrick Scientific Corporation) mounted in a Harrick DRA-3SP diffuse reflectance accessory and linked *via* a flexible stainless steel tube (Swagelok; to allow movement of the sample shuttle) to a conventional glass vacuum apparatus fitted with grease-free taps. The average of 1000 scans at resolution 4 cm<sup>-1</sup> was recorded with a Perkin-Elmer 1710 Fourier transform i.r. spectrometer operating in conjunction with a Perkin-Elmer 7500 computer. Samples were subjected to heat treatment (15 min) in a flow of O<sub>2</sub> at 1 atm pressure and spectra were recorded either with the sample at elevated temperature or after cooling to ambient temperature. All the spectra presented here were after cooling, but other experiments showed that spectra recorded before and after cooling were identical in all the essential details. Spectra were recorded with reference to background spectra of either KBr alone in the i.r. cell or the initial KBr-carbon mixture in the cell before oxygen treatment. Repetition of experiments showed the results to be reproducible.

Spectra in Figure 1 are relative to KBr reference and were recorded with fluorite windows in the vacuum cell. The initial spectrum [Figure 1(a)] was similar to previous spectra of a variety of carbon blacks<sup>3</sup> with the addition of a band at 1000 cm<sup>-1</sup> ascribed to the C-O stretching vibrations of a surface species containing oxygen. Other bands were at 1710 cm<sup>-1</sup>, due to C=O stretching vibrations of surface species,<sup>3-5</sup> and 1570 cm<sup>-1</sup> (not illustrated because there were no changes in this region of the spectrum with thermal treatment of samples in oxygen) and 1260 cm<sup>-1</sup>. The latter two bands are probably due to vibrations of bulk carbon rather than surface groups.<sup>3</sup>

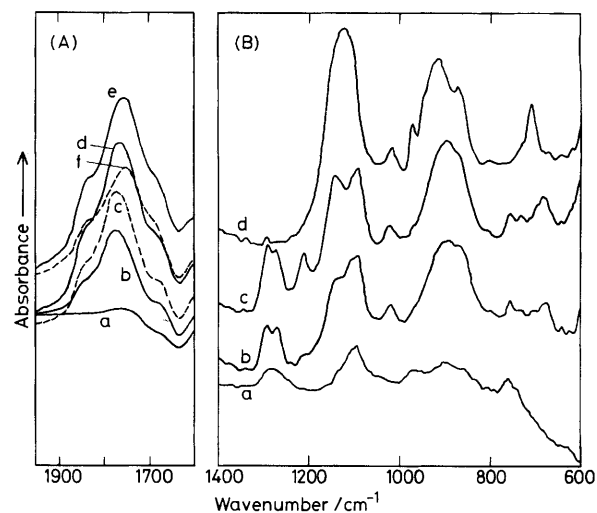
Progressive heat treatment of carbon in oxygen at increas-



**Figure 1.** I.r. spectra of carbon after treatment in oxygen at temperatures/K of (a) ca. 293, (b) 401, (c) 501, (d) 557, (e) 593, (f) 727, and (g) 785.

ing temperatures up to 593 K resulted in the growth of a maximum at  $1750\text{ cm}^{-1}$  with a shoulder at  $1830\text{ cm}^{-1}$  although treatment at higher temperatures led to decreases in the intensities of both bands which had almost disappeared at a sample temperature of 785 K. The maximum at  $1710\text{ cm}^{-1}$  was apparently unaffected by the series of treatments. Zawadzki<sup>6</sup> reported the appearance of bands at  $1760$  and  $1830\text{ cm}^{-1}$  in spectra of carbonized cellulose after heat treatment in oxygen at 573 K, and decreases in intensities of maxima at ca.  $1700$ – $1750\text{ cm}^{-1}$  have been observed after heat treatment of carbon samples at  $\geq$ ca.  $673\text{ K}$  *in vacuo* or nitrogen.<sup>3,5</sup> In one study the disappearance of a band at  $1725\text{ cm}^{-1}$  revealed an underlying maximum at  $1700\text{ cm}^{-1}$ .<sup>3</sup> The present bands are tentatively assigned to C=O stretching vibrations of cyclic acid anhydride<sup>3,5,6</sup> ( $1750$ ,  $1830\text{ cm}^{-1}$ ) or carboxylic acid<sup>2,3</sup> ( $1750\text{ cm}^{-1}$ ) and alkyl carbonyl<sup>5</sup> ( $1710\text{ cm}^{-1}$ ) groups on the carbon surface. Immersion of oxidised carbon in aqueous  $\text{NaHCO}_3$  (16 h) had no effect on the maximum at  $1710\text{ cm}^{-1}$  but caused the replacement of the other two bands by a maximum at  $1586\text{ cm}^{-1}$  due to a vibration of surface carboxylate ions.<sup>7</sup>

Bands in the lower spectral region (Figure 1) appeared at  $1290$ ,  $1272$ ,  $1210$ ,  $1150$ ,  $1097$ ,  $1020$ ,  $985$ , and  $908\text{ cm}^{-1}$  and may probably all be assigned to C–O vibrations of oxygen-containing surface groups.<sup>2,3,6–8</sup> Bands in this region were more clearly monitored by reference to a KBr–carbon blank and the spectral range studied was widened towards lower wavenumbers by fitting KBr windows to the cell (Figure 2B). Additional bands due to adsorbed products of surface oxidation appeared at  $870$ ,  $800$ ,  $759$ ,  $733$ ,  $710$ , and  $680\text{ cm}^{-1}$ . Previous assignments of maxima in this lower spectral region have involved attributions to furans,<sup>8</sup> anhydrides,<sup>6</sup> and aromatic CH-vibrations.<sup>9</sup> Spectra relative to a KBr–carbon



**Figure 2.** Changes in the i.r. spectrum of carbon induced by treatment in oxygen at temperatures/K of (A) (a) ca. 293, (b) 543, (c) 593, (d) 613, (e) 633, and (f) 653; (B) (a) 603, (b) 663, (c) 713, and (d) 813.

reference also confirmed the spectroscopic results in the  $1650$ – $1900\text{ cm}^{-1}$  spectral region (Figure 2A).

Detailed assignments of the bands observed here are not attempted at present as further work is desirable in order to characterize the behaviour of each band after treatment of samples thermally *in vacuo* and in the presence of a variety of gaseous reagents. A more detailed report will be published when the further work has been completed. However the spectra reported here illustrate the quality of data which can be gained from diffuse reflectance F.t. i.r. studies of surface groups on carbon maintained in the vacuum cell in which a wide variety of treatments can be carried out *in situ*. The technique enhances the rapidity with which experiments can be carried out and obviates ambiguities associated with the transfer of samples from reaction systems to the i.r. cell.

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