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Fourier Transform ir Spectroscopic Study of the Preparation of a Carbon-Coupled Porphyrin Catalyst Structure

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It has been demonstrated by means of Fourier Transform infrared spectroscopy, a specific sample preparation technique, and a background correction procedure, that the chemical coupling of tetra (*p*-carboxyl)porphyrin to an oxidized carbon surface is accomplished via an ethylenediamide bridge.

INTRODUCTION

For catalysis through molecular oxygen activation by sequential reduction (*1*) at an electrode it was necessary to bind a metallo(iron)porphyrin molecule covalently to a carbon surface, and for practicality to use both a simple porphyrin and an easily prepared carbon surface.

In this study the covalent attachment of a suitable porphyrin macrocycle to a derivatized carbon surface is examined by means of Fourier Transform infrared spectroscopy.

EXPERIMENTAL

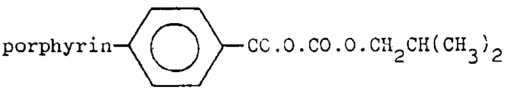
Preparation of the Porphyrin–Carbon Systems

Meso-tetra(*p*-carboxyphenyl)porphyrin was covalently attached to active carbon (Norit BRX with a surface area of 1800 m^2 g^{-1}) by the following steps:

(*i*) Oxidation of the carbon surface with a strong oxidant (potassium persulphate) (*2*); the extent of surface derivatization (to carboxyl groups) was estimated by titration to be of the order of 3 mmol/g.

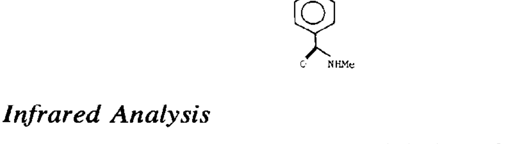
(*ii*) Formation of the intermediate acid chloride, by treatment with excess oxalyl chloride, and its reaction with ethylenediamine in large excess to give the derivatized (amide) amine surface.

(*iii*) Activation of the meso-tetraphenylporphyrin *p*-carboxylate group by formation of the isobutyl anhydride ester



and its administeration to the (amide)amine electrode surface.

(*iv*) Removal of the unreacted isobutyl anhydride ester groups with methylamine to give the final porphyrin–carbon conjugate.



Infrared Analysis

Spectra were recorded on a Digilab FTS-14 Fourier-Transform infrared spectrometer at a spectral resolution of 4 cm^{-1} by coaddition of 500 scans for each sample. Two specific procedures were employed in the elucidation of the ir spectra of carbonaceous systems, viz., a specific sample prep-

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aration technique and a certain background correction procedure.

The sample preparation technique used for preparing the carbonaceous samples for ir analysis allows the experimenter to study such systems in a free, unperturbed state (in contrast to the KBr and mull techniques). It comprises the following steps:

1. Milling approximately 10 mg of the carbon sample in a Perkin–Elmer vibrating mill with a pretreated stainless-steel capsule (length 20 mm; diameter 9 mm) and stainless-steel ball (diameter 5 mm). The pretreatment of the capsule consisted in roughening the inside surface by milling about 100 mg of carborundum (7–14 mesh) in it for 10^2 sec. Such a capsule, which is probably more effective in shearing the carbon particles than a nonpretreated capsule, was found to produce suitable carbon samples for analysis (particle size $\ll 1\ \mu m$) within very short milling times (10–100 sec). The advantage of such short milling times is that the sample is not notably affected by oxidation, as is often observed with the much longer milling times that are usually applied (*3*).

2. Applying the fine particles obtained in step 1 onto a noninteracting, solid, ir-transparent support (Ge-CaF_2, KBr single crystals) by painting or nebulizing them as a slurry in about 1 ml of a volatile, noninteracting carrier liquid (e.g., CCl_4, pentane).

This procedure gives a thin carbon film with a typical weight of 0.2–0.5 $mg \cdot cm^{-2}$ support surface area. The adhesive forces between the support and the particles are very weak, but sufficiently strong to allow the sample to be handled, e.g., to place it in a vertical position in the ir beam of the instrument.

The background correction procedure used to eliminate from the ir spectra the steep background absorbance inclining towards higher wave numbers (which is the result of scattering losses of the incident ir beam in the carbon sample) comprises the following steps:

1. Deriving the proper, 4-cm^{-1}-resolution spectrum from the interferogram (Fig. 1, top trace).

2. Deriving a second, 250-cm^{-1}-resolution spectrum from the same interferogram, now using only part of the interferogram with an apodization function (*4–7*) different from that employed in step 1 (Fig. 1, middle trace).

3. Using the low-resolution spectrum obtained in step 2 as reference (subtraction) spectrum for the high-resolution spectrum of step 1 (Fig. 1, bottom trace).

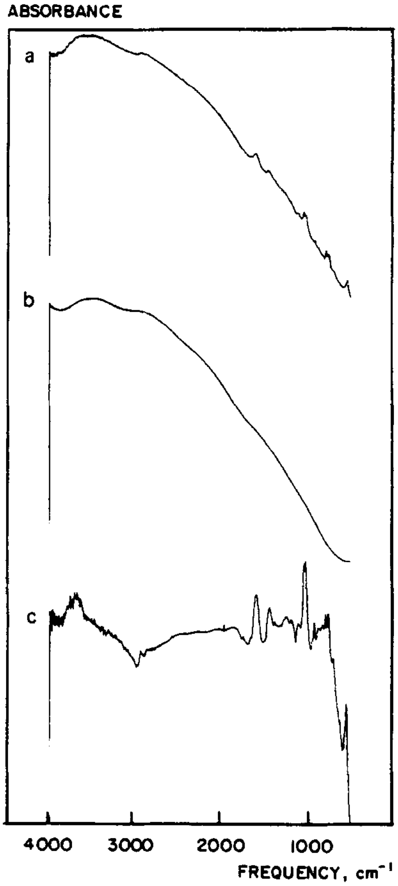


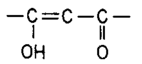
FIG. 1. Examples of the various types of spectra obtained from a solid carbonaceous sample (a mineral coal): (a) High-resolution spectrum; (b) Low-resolution spectrum; (c) Difference spectrum.

As a result of this procedure, much of the scattering background is eliminated and detailed spectral information of ir bands is maintained.

RESULTS AND DISCUSSION

The results of the oxidation of Norit BRX by means of $K_2S_2O_8$ (step (i) in the preparation described above) is shown in Fig. 2. The ir spectrum of Norit BRX is characterized by two relatively broad bands at 1580 cm^{-1} and approximately 1200 cm^{-1}.

The origin of the first band is still a subject of considerable dispute amongst scientists in the field (*8–12*). It is generally associated with aromatic C=C ring vibrations; for relatively pure carbon materials with low oxygen content it was proved (*13*) to be exclusively due to vibrations of the aromatic (hydro)carbon skeleton. However, greatly shifted carbonyl vibrations (e.g., in



$$-\underset{\text{OH}}{\underset{|}{C}}=C-\underset{\text{O}}{\underset{\|}{C}}-$$

groups) may also contribute to the 1580-cm^{-1} band. In view of the complex and unknown chemical nature of many carbonaceous systems it is therefore impossible as yet to arrive at an unambiguous assignment of this band.

The 1200-cm^{-1} band is also a common band of many carbonaceous solid materials, which is thought to originate from a variety of undefined, oxygen-containing structures, mainly C–O–C groups (*8, 9, 11, 14*).

For carbonaceous materials with a high carbon content, such as graphite and possibly also Norit, it seems attractive to use the 1580-cm^{-1} band as the internal (reference) standard if we want to estimate the extent of modification of the carbon in a qualitative or semiquantitative sense. Such an approach contains an element of speculation in that the 1580-cm^{-1} band is assumed to remain unaffected in the course of chemical modifications of the carbon. However, in the absence of a better alternative, we tend to consider the 1580-cm^{-1} band representative of the bulk of the carbon used.

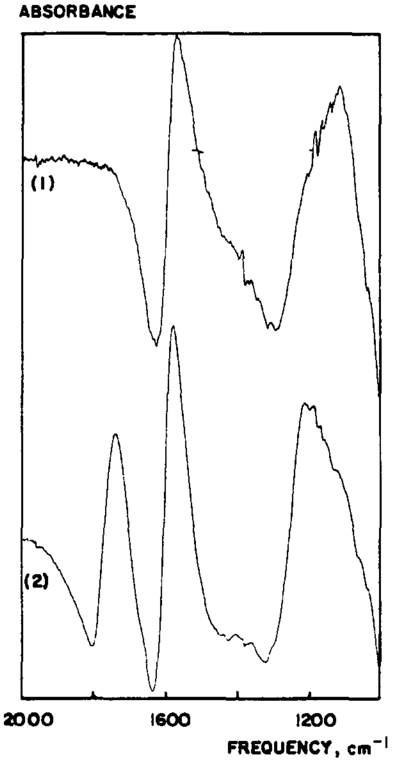


FIG. 2. Infrared spectra of (1) Untreated Norit BRX; (2) $K_2S_2O_8$-treated Norit BRX.

We will now consider the results. Treatment of the carbon with $K_2S_2O_8$ leads to the appearance of a pronounced band at 1735 cm^{-1}, which can be assigned to the CO stretch vibration of COOH groups. From this band we may conclude that surface carboxylate groups have been formed on the solid carbon.

The results of the reaction of the oxalyl chloride-treated acid carbon with ethylenediamine (step (ii) in the preparation described above) is shown in Fig. 3. Now a strong suppression of the intensity of the 1735-cm^{-1} band is observed, together with the formation of a small but significant band between 1670 and 1680 cm^{-1} and a low-frequency tailing of the 1580-cm^{-1} band. The latter is caused by the presence of bands at 1520–1530 cm^{-1} and 1440 cm^{-1}, as follows from the subtraction of the 1580-

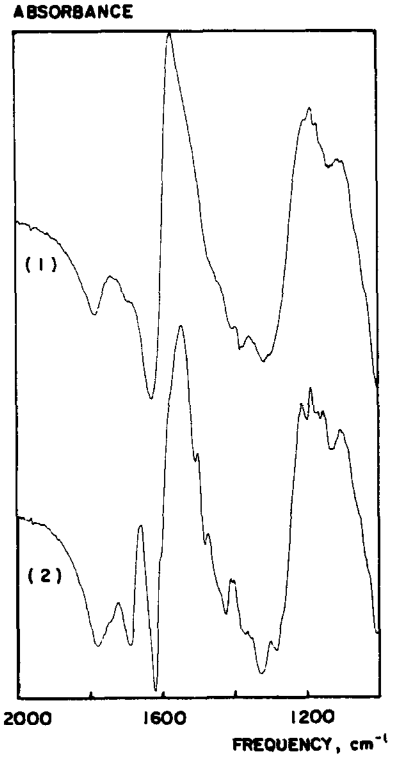
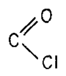


FIG. 3. Infrared spectra of (1) the reaction production of Norit BRX treated successively with $K_2S_2O_8$ $(COCl)_2$ and ethlenediamine; (2) the reaction product of the product of trace (1) and the porphyrin molecule (i.e., steps (iii) and (iv) under Experimental).

cm^{-1} band of the acidic carbon from the tailed 1580-cm^{-1} band of the amidated carbon. The bands at 1680 and 1520 cm^{-1} can be assigned to the vibration of CO and to the NH and CN groups of a free secondary amide, respectively. The band at 1440 cm^{-1} can be assigned to ethylene groups. These spectral changes with respect to the acid carbon strongly suggest that the ethylenediamine has coupled with a large proportion of the surface



groups to form amide groups.

The results of the reaction of tetra(*p*-carboxyphenyl)porphyrin with the amidated carbon (second part of step (iii) above) is shown in Fig. 4. The spectrum features

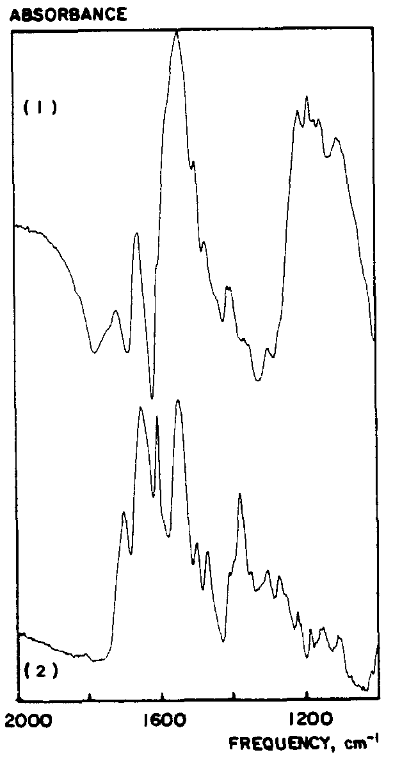
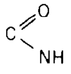


FIG. 4. Infrared Spectra of (1) the carbon/porphyrin system (trace (2) of Fig. 3) (2) the porphyrin used.

bands at 1655, 1550, and 1300 cm^{-1}, which are all absent in the pure porphyrin material and which can be assigned to bands of associated secondary amides. The other bands, superimposed onto the spectrum of Norit BRX, coincide well with those of the spectrum of the pure porphyrin compound, shown in the same figure.

From the results it follows that coupling of the porphyrin molecule to carbon has taken place via an (ethylene)diamide bridge. The amide bands found in the product of the first coupling step point to the formation of free amides. This could be explained by the surface coverage of carbon with COCl groups (and hence



groups) being low enough to prevent mutual interaction between adjacent amide groups. The situation is different with the final product, which seems to be largely composed of associated amides. Such a situation is likely to occur in view of the many amide groups now present.

Our results, which prove the coupling between the porphyrin and the carbon surface, are in line with those reported by Lennox and Murray (*15*, *16*). These workers immobilized *p*- and *m*-isomers of tetra(aminophenyl)porphyrin on glassy carbon electrodes and employed X-ray photoelectron spectroscopy and cyclic voltammetry (and differential pulse polarography) to characterize the state of the electrode. In our opinion, the present ir evidence has provided more direct proof of such a coupling.

An important difference between the electrode materials prepared in this work and those employed by Lennox and Murray (*15*, *16*) is that our electrode materials have been derivatized with nucleophiles. Most workers in this field follow the so-called Miller procedure (*7*) meticulously; i.e., they first form the acid chloride and then add reactant nucleophiles. In the electrode preparation followed in the present study, this procedure was reversed. The advantage of such an approach is, in general, that *any* carboxylic acid-containing material can be coupled to such carbons. More specifically, in our case, the method allowed a more easily accessible porphyrin (tetra(*p*-carboxyphenyl)porphyrin) to be used instead of the *meta*- and *para*-aminophenylporphyrins, which were used by Lennox and Murray and are difficult to prepare in appreciable quantity.

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