## STRUCTURE OF THE RESIDUAL CARBON MADE BY

## FLUOROCARBON PYROLYSIS

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Fluorocarbon defluorination products show an unusual temperature dependence for the paramagnetic susceptibility in the range 77-300 K after pyrolysis at 650-1000°C, which is explained from dynamic equilibrium between the formation and dissociation of free radicals involving a bond energy of 11.22 kJ/mole. The ESR line width initially increases with temperature but then decreases. The width of the inhomogeneously broadened line has been calculated as a function of the frequencies of the static and dynamic spin exchange, which shows that at low temperatures there is a local increase in the radical concentration, but at higher temperatures, the dynamic exchange averages out this dipole spin-spin interaction. A suggestion confirmed by x-ray structure analysis is that the products contain a linear form of carbon.

Recently, research on carbon-material fluorination [1, 2] has been accompanied by that on the converse: defluorination [3-6]. Defluorination studies by means of DTA have shown [3] that the decomposition temperatures for  $(CF)_n$  vary widely (from 320 to 610°C). A detailed analysis has also been performed on the fluorocarbon decomposition products produced under vacuum, and it has been found that thermal defluorination is described by

$$2(CF)_n \rightarrow nC^* + xCF_2 + yC_2F_4 + \dots$$

where x + 2y = n and C\* is amorphous carbon. Then these gaseous products form various compounds such as CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub>.

Kamorchik and Margrave [4] found that the decomposition occurs in a plane containing an active center, but they were unable to establish why the  $(CF)_n$  decomposition rate is dependent on the formation conditions. It has been found [5] that this rate is determined by the number of stressed centers having high potential energies. The carbon phase is formed initially at the boundary between two small fluorocarbon crystallites. The decomposition in a low-crystallinity specimen begins at a lower temperature. The defluorination by  $\gamma$  rays [6] indicates that the decomposition is initiated in the  $CF_2$  and  $CF_3$  at the surface of  $(CF)_n$  crystals or at points on them that are deformed because of high stresses at the grain boundaries.

We have applied electron spin resonance (ESR) to those products.

The fluorocarbon was made by fluorinating viscose fiber after heat treatment at 2500°C; the fluorination conditions have been described [1, 2]. The pyrolysis was in an electric oven at 650-1000°C, which contained the tube previously evacuated to 0.1 Pa containing the fluorocarbon. The defluorination was explosive.

The ESR spectra were recorded with an ER-200 radio spectrometer. The modulation amplitude and UHF power were chosen such as to avoid distorting the line shape [7]. A JSM-35CF scanning electron microscope was also used at 25 kV. The x-ray diffraction patterns were recorded with a DRON-2 diffractometer and Cu K<sub> $\alpha$ </sub> radiation filtered with nickel to remove the  $\beta$  lines.

The residual carbon had properties dependent on the defluorination rate and differed substantially from those of the initial carbon material.

The photomicrographs showed that the initial integral filamentary carbon was partially dispersed by the fluorination and almost completely lost its integrity on subsequent pyrolysis.

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Material	d002, <b>nm</b>	20, <b>deg</b>	L <sub>c</sub> , nm	
TTO carbon fiber, 2500°C Fluorocarbon (CF) <sub>n</sub>	0,3628 0,6827	24°54′ 12°58′	1,4 2,0	
Pesidual carbon	0 4040	22°00'	0.9	

TABLE 1. X-Ray Structure Parameters



Fig. 1. Absorption-curve area as a function of temperature: crosses from experiment,  $(\times \times \times)$ , solid line from theory, (---).

The x-ray structure parameters in the same sequence (Table 1) show a transition from a turbostatic structure in the fiber to an amorphized one in the residual carbon, which has  $d_{002} = 0.404$  nm.

The residual carbon gives a line having d = 0.404 nm at small angles, which is due to the carbon formed. The (002) diffraction profile for the carbon is skewed, with a gentle fall towards large angles, which shows that the material is heterogeneous. The  $d_{002}$  calculated from the (002) peak with crystalline silicon as standard is  $d_{002}$  = 0.404 nm, which is much greater than the  $d_{002}$  = 0.344-0.380 nm for aromatic turbosatic carbon. That large distance, which exceeds 0.400 nm, characterizes linearly organized aliphatic carbon with sp hybridization, which is commonly encountered in hard coals [8]. The (002) line shape and spacing for that carbon suggest that it is a mixture of sp<sup>2</sup> and sp carbon components.

The ESR line shape alters considerably on thermal defluorination, with complete loss of the hyperfine structure and intensity increase in the central singlet, which arises [9] from the paramagnetic carbon centers.

The completely defluorinated carbon shows a symmetrical ESR line sensitive to atmospheric oxygen, which is characteristic of amorphous carbons made by heat treatment of organic compounds at 550-750°C.

The oxygen broadens the line without affecting the susceptibility; the width between the turning points in the first derivative is 30-60 G in air, but 5-0.5 G under vacuum correspondingly (0.1 Pa). The paramagnetic susceptibility is dependent on the decomposition temperature and time and attains a maximum of about  $10^{-6}$  CGSM units/g, which corresponds to  $5 \times 10^{20}$  spin/g.

The absorption-curve area varies in accordance with Curie's law in the range 300-125 K (Fig. 1) and decreases by a factor 2-3 in the range 125-90 K. In some specimens, the intensity fell to an unobservable level. At 130-120 K, some specimens showed a narrow line, which had a negative temperature coefficient, whereas the intensity of the broad line decreased as the temperature fell. The narrow line is probably present also at room temprature but is inappreciable because of low intensity. The two lines show that the residual carbon consists of two phases. The lines showing all the above changes is due to a carbon phase in the sp state, while the narrow one is due to the sp<sup>2</sup> state.

The signal sensitive to oxygen gradually vanishes at treatment temperatures of 900-1600°C and is replaced by an insensitive one [10]. The effects of oxygen on the spectra for carbon made by defluorination persist on heat treatment under vacuum for 10 min at 2000°C.

## DISCUSSION

The temperature dependence of the paramagnetic-center concentration is described by dynamic equilibrium throughout the range:

$$\dot{R_1} + \dot{R_2} \rightleftharpoons R_1 R_2$$

in which  $R_1$  and  $R_2$  are paramagnetic centers with equal concentrations x, while  $R_1R_2$  is the non-paramagnetic recombination product having concentration  $C_0 - 2x$ ;  $C_0$  is the limiting concentration of the latter at low temperatures.

The absorption-curve area is proportional to 2x. The relation between the concentrations of the three species is related to the equilibrium constant:

$$Ae^{\frac{\Delta E}{RT}} = \frac{\left[R_{1}^{*}\right]\left[R_{2}^{*}\right]}{\left[R_{1}R_{2}\right]} = \frac{x^{2}}{C_{0}-2x} = k(T)$$

and the area under the curve from Curie's law is proportional to 2x/T, i.e.,

$$S = \frac{2\alpha x}{T} = \frac{2\alpha C_0 k(T)}{T \left[ k(T) + \sqrt{k^2(T) + k(T) C_0} \right]}$$

in which  $\alpha$  is a coefficient of proportionality. Figure 1 shows the observed and theoretical temperature dependence for the area, with the theoretical one corresponding to a  $R_1-R_2$  bond energy of  $\Delta E = 11.22 \text{ kJ/mole}$ .

There is satisfactory agreement at all temperatures. When  $R_1$  and  $R_2$  have been formed, they continue to interact. There are dipole-dipole and exchange interactions at short distances, which affect the line shape and in particular govern the temperature dependence of the width.

The local radical concentration  $C_{loc}$  increases with temperature, and so does the Lorentz line width  $\Delta_{\rm L} = \Delta_{\rm L}^{0} + \kappa C_{\rm loc}$ , in which  $\kappa = 5.1 \cdot 10^{-20}$  Oe·cm<sup>3</sup> [11]. There are two limiting types of exchange interaction [12]. The first broadens the lines, which then merge, and the subsequent single line narrows. This is dynamic exchange, which corresponds to double spin transfer. The second type leads to line splitting, which increases with the exchange rate but is not accompanied by broadening. In the first case, one gets only broadening and shape change. These types of exchange are readily observed with biradicals.

Interest attaches to the shape and width of the inhomogeneously broadened line as affected by exchange. We write the line shapes for the two radicals  $R_1$  and  $R_2$  having resonant fields  $H_1$  and  $H_2$  [12] for the case of spin exchange coupling  $\delta \pm = 1/\tau \pm iJ$ , inwhich  $1/\tau$  is the dynamic-exchange frequency and J the exchange integral, which corresponds to static exchange.

In the case of a Gaussian distribution with parameter  $\Delta_g$ , the line shape A(H) = A<sub>+</sub>(H) + A<sub>-</sub>(H) is described by

$$A_{+}(H) = \frac{2}{\pi^{2}} \int_{-\infty}^{\infty} \frac{\exp(-2x^{2}-2y^{2}) \left[z - \frac{i\Delta g}{2}(x+y) + \delta^{+}\right] dx dy}{\left[z + \delta^{+} - \frac{i\Delta g}{2}(x+y)\right] \left[z - \frac{i\Delta g}{2}(x+y)\right] + \frac{\Delta^{2} g}{4}(x-y)^{2}};$$

the  $z = \frac{1/3}{2}\Delta_g + iH$ ;  $x = \frac{H_1}{\Delta_g}$ ;  $y = \frac{H_2}{\Delta_L}$  dimensionless local resonant fields for the Gaussian distribution, with  $\Delta_g$  the parameter characterizing the spread in the local fields, with the observed width equal to  $\Delta_g$  in the absence of exchange and Lorentz broadening ( $\Delta_L \rightarrow 0$ ), while  $\Delta_L$  is determined by the relaxation width and the local dipole-dipole interaction ( $\Delta_L = \Delta_L^0 + \kappa C_{loc}$ ).

The measured absorption spectrum is proportional to the first derivative of the real part of A(H), while the line width is defined by the conditions Re(A''/H) = 0.

To establish how the inhomogeneously broadened width is dependent on the spin exchange rate, we calculated the relative width  $\Delta/\Delta_0$  as a function of the relative exchange  $\delta/\Delta_0$  for various fixed  $\Delta_L/\Delta_0$  and  $\Delta_g/\Delta_0$  in which  $\Delta_0$  is the line width in the absence of exchange, which is given by  $\Delta_0\Delta_L + \Delta_L^2 = \Delta_0^2$ , and  $\Delta$  is that observed with exchange. The relative width

TABLE 2. Relative Line Width  $\eta = \Delta/\Delta_0$  as a Function of Relative Magnitude of Dynamic and Static Exchange with Various Relations for the Lorentz and Gaussian Widths

$\Delta g^{\Delta_0}$	0,500		0,707		0,866	
	0,	750	0,500		0,250	
	Exchange					
$\delta/\Delta_0$	static	dynamic	static	dynamic	static	dynamic
0,0100 0,0316	1,006 1,005	1,001 0,996	1,007 1,005	0,998 0,988	1,007 1,006	0,997 0,977
$0,1000 \\ 0,3160 \\ 1,0000 \\ 10,0000$	$\begin{array}{c} 1,001 \\ 0,970 \\ 0,893 \\ 0.891 \end{array}$	0,983 0,950 0,902 0,896	$0,995 \\ 0,934 \\ 0,819 \\ 0.812$	$\begin{array}{c} 0,960 \\ 0,904 \\ 0,829 \\ 0.819 \end{array}$	0,993 0,897 0,759 0.758	0,931 0,857 0,770 0,759

 $\eta = \Delta/\Delta_0$  as a function of  $\varepsilon = \delta/\Delta_0$  was calculated for two limiting cases: static exchange  $J/\Delta_0$  and dynamic  $1/(\tau \cdot \Delta_0)$ , which are given in Table 2.

Table 2 shows that always the width begins to decrease as the exchange rate increases. With the maximal exchange, the Gaussian width does not average to zero, as might be supposed, but is merely reduced by a factor  $1/\sqrt{2}$ .

The essential difference between static and dynamic spin exchange has no marked effect on the width, and from the width and shape, it is therefore difficult to determine the type of exchange, i.e., to determine whether there is dynamic electron transfer between the two radicals or whether spin-spin coupling occurs along a conjugation chain. The two types can be distinguished from the temperature dependence of the width. An Arrhenius relation applies for the width with dynamic exchange.

In static exchange, which is due to spin delocalization along the conjugation chain, the width should be largely independent of temperature. The local spin concentration increases with temperature, which raises the dipole width.

The equilibrium reversible temperature dependence of the observed width can thus be very complicated and requires special analysis in each particular case.

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