

THE ELECTRON SPIN RESONANCE SPECTRA OF CELLULOSE CHARS TREATED WITH HALOGENS*

Evidence for Donor-Acceptor Complexes in Coals and Chars

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INTRODUCTION

Coals and low- and medium-temperature chars have been shown to be paramagnetic by bulk magnetic susceptibility measurements^{1,2,3} and by electron spin resonance studies^{4,5,6}. If due care is taken to eliminate errors, reasonable agreement in the estimate of the number of unpaired electrons present can be obtained⁷. While there is agreement on the existence of paramagnetic centres in these materials, the origin and nature of these free radicals is not understood^{8,9,10,11,12}. It is the purpose of this article to present new evidence to suggest that these unpaired electrons arise from donor-acceptor forces present in these materials.

One way of studying the nature of free radicals is by observing the behavior of the electron spin resonance signals when the substrate is treated with adsorbed gases and other reagents. Early workers in the field found that paramagnetic gases such as oxygen affected only the spin-lattice relaxation times of chars prepared at from 300° to 500°C. For chars prepared in the 550° to 800° temperature range, however, reversible line broadening occurred with an apparent decrease in free radical concentration at higher oxygen pressures. Removal of oxygen restored the original signal, which indicated that the phenomenon was due to physical and not chemical processes. Halogens were at first found to have no effect on coals and chars and the oxygen effect was attributed to spin broadening due to the paramagnetism of the oxygen molecules. Similar results to oxygen were obtained with nitric oxide.

In 1963 Wynne-Jones¹³ and co-workers found that e.s.r. signals in chars obtained by heating polyvinylidene chloride (saran) were affected by adsorption of halogens. These workers noted that IBr, ICl, I₂, Br₂, and Cl₂ caused partial or complete reduction in spin concentration at constant line width. The original signal was not restored by outgassing in vacuo at room temperature but could be partially restored by reheating the specimen at 100°C in vacuo. Since, as mentioned above, no halogen effect had been obtained on coals or more common chars, these authors attributed the susceptibility to halogens of these saran chars to a high degree of porosity. Reinvestigation of the interaction of a series of cellulose chars with iodine, bromine and hydrogen iodide in this laboratory has shown pronounced effects on the electron spin resonance of some of these materials.

EXPERIMENTAL

Cellulose chars were prepared by first charring cellulose powder (Whatman Cellulose Powder, Standard Grade) in an autoclave at 195°-200°C under nitrogen. Subsequently this char

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was heated under nitrogen in a Vycor tube to the desired temperature and held at temperature for one hour. Aliquots of the chars were then treated with a large excess of 0.1 M solutions of iodine or bromine in carbon tetrachloride. After standing in the solutions for twenty-four hours, the samples were washed once with carbon tetrachloride and dried. Samples for e.s.r. measurements were placed in 3 mm. o.d. glass tubes and evacuated.

Samples to be treated with hydrogen iodide were placed in open 3 mm. o.d. tubes placed in the cavity of the spectrometer and purged with purified nitrogen. Gaseous hydrogen iodide (Matheson) was passed directly over the sample in the cavity. Excess hydrogen iodide was removed after treatment by subsequent purging with nitrogen.

Electron spin resonance measurements were performed with a Varian Model 4500 electron spin resonance spectrometer fitted with a TE102 cavity and a 100 Kc modulation attachment. Saturation phenomena were avoided by working at 10 db attenuation and checks for saturation were made. Line widths and spin concentrations were measured from first derivative curves, generally by direct inspection but in the case of very wide and very narrow signals resort was made to graphical integration. A standard 500° cellulose char, used for calibration, was standardized against DPPH, CuSO_4 and a Varian Standard char. The amount of sample was always less than 10 mg. and asymmetric line shapes were not observed, indicating the absence of serious skin effects.

RESULTS

In Figures 1 and 2 are summarized the results of iodine and bromine treatment on line width and spin concentration as measured at room temperature. The untreated chars prepared at 625° and 650° show a marked decrease in line width as compared with those prepared at higher or lower temperature — an effect attributed to exchange⁴. It is seen that both iodine and bromine remove this intense narrowing in the 625° and 650° chars. Neither has a significant effect on the 300° to 500° chars but both broaden further the signal from the 700° char. The broadening due to bromine is not as great as that due to iodine and for the 600° char, in particular, the broadening effect of the bromine is minimal. The effect on spin concentration shows that line broadening is accompanied by a considerable drop in concentration in both the bromine and iodine treated chars.

Measurements made at 78°K showed that whereas the signals for the 300° to 500° chars were broadened somewhat, those from the iodine- and bromine-treated chars in the 600° to 700° range were narrowed. Washing the iodine-treated chars with cold 0.1 M sodium thiosulfate solution restored the original narrow signals. This showed that no chemical reaction had occurred to alter the signals.

Treatment of a series of chars with hydrogen iodide gas for sixty hours resulted in reduction of the signal strength and broadening of the signals as shown in Table I. The broadening for the 300°, 400° and 500° chars was moderate but that of the exchange narrowed chars (600° to 700°) was extensive. Cold 0.1 M sodium thiosulfate produced no further change in the signals but refluxing for twenty-four hours with thiosulfate restored the original signals^{1,4}. The restored signals of the 600°, 625°, 650° and 700° chars were sensitive to air whereas the restored signals of the 300°, 400° and 500° chars were not. The e.s.r. signals of the untreated chars refluxed with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ were unchanged.

TABLE I

Effect of Hydrogen Iodide on Free Radical Content of Chars

Electron Spin Resonance Signals

spins/g in vacuo and width in gauss*

Char Temperature	Untreated	HI Treatment 60 hours	Na ₂ S ₂ O ₃ 0.1 M Refluxed 24 hours
300	2.1 × 10 ¹⁸ 4.9	2.0 × 10 ¹⁷ 7.9	8.3 × 10 ¹⁷ 5.76
400	2.3 × 10 ¹⁹ 6.1	5.3 × 10 ¹⁸ 8.3	2.6 × 10 ¹⁹ 6.3
500	5.1 × 10 ¹⁹ 4.8	3.3 × 10 ¹⁹ 5.9	5.4 × 10 ¹⁹ 4.1
600	1.4 × 10 ²⁰ 0.45	1.3 × 10 ¹⁹ 19.1	1.4 × 10 ²⁰ 0.49
625	1.3 × 10 ²⁰ 0.40	1.7 × 10 ¹⁹ 22.4	9.8 × 10 ¹⁹ 0.49
650	1.0 × 10 ²⁰ 1.4	4.8 × 10 ¹⁹ 41.0	1.0 × 10 ²⁰ 1.2
700	7.4 × 10 ¹⁹ 1.4	1.2 × 10 ¹⁹ 43	7.2 × 10 ¹⁹ 2.0

* Width measured between points of maximum slope.

DISCUSSION

Two aspects of these results must be considered – the interaction with the halogens which are typical electron acceptors and the interactions with hydrogen iodide. In agreement with Wynne -Jones and co-workers, we are of the opinion that iodine, and to a lesser extent bromine, can form donor-acceptor complexes with the chars and in so doing affect the e.s.r. signals. Presumably the iodine and bromine act as acceptors and aromatic ring systems of the char act as donors in these complexes. The low-temperature chars, 300° to 500°, having few aromatic ring systems as large or larger than four or five rings¹⁵, are not affected by iodine or bromine. The 600° char apparently has a high enough donor ability – low enough ionization potential – to interact with iodine but not sufficient to react definitely with bromine, which is a much weaker acceptor. Both bromine and iodine readily form complexes with the 625°, 650° and 700° chars. The fact that the signals of the halogen affected chars are narrowed on cooling to 79°K is also indicative of donor-acceptor interaction between halogens and aromatic moieties¹⁶. It is possible that lack of porosity is sufficient explanation of the failure of the 300° to 500° chars to be affected by iodine¹³. However, the difference between iodine and bromine on the 600° char suggests that the electrophilicity and not the size of the adsorbed molecule is important.

The line broadening at 79°K of the 300°, 400° and 500° chars treated with halogens is not only indicative of no complex formation between halogen and the aromatic system but also suggests that the initial signals of these chars are due to complexes between quinonoid acceptors and carbocyclic donors¹⁶. This is further borne out by the effects of hydrogen iodide on these chars. Treatment of all the chars with hydrogen iodide causes a reversible reduction in the number of spins/g. Aromatic hydrocarbons would not be expected to show such reversible behavior^{17,18}, but electron acceptors such as quinones, which have been shown by Given and Peover¹⁹ to be present in coals and related materials, would interact with hydrogen iodide. A reasonable explanation is that the e.s.r. signals of these chars are associated with acceptor moieties. These acceptor or quinonoid moieties apparently exist in the 300° to 500° chars as well as the 600° to 700° chars, since the signals are all reduced reversibly by hydrogen iodide. Since the halogen treatments suggest that the free radicals of the 600° to 700° chars, and probably of the 300° to 500° chars as well, are associated with aromatic centres, the presence of both donor and acceptor moieties associated with free radicals in the untreated chars is indicated. Hence, we suggest that the free radicals in the 600° to 700° chars are due to donor-acceptor complexes between aromatic donors and quinonoid acceptors. It is likely that the signals in the 300° to 500° chars are similar in nature but the aromatic centres are too small to form complexes with iodine or bromine.

Russian workers²¹ reached similar conclusions, but only by a process of elimination, in order to account for the free radicals in a series of polyarylene polyacetylenes that had been heated to various temperatures. They concluded that complexes with charge-transfer were the only possible explanation after eliminating in turn the presence of paramagnetic ion impurities, radicals arising in the process of polymerization, and the existence of a triplet ground state. The first reference to charge-transfer complexes in coals or chars was made by Schuyer²² to explain why the molar increment of refractive index per gram of aromatic carbon (I_M/C_{ar}) decreases in the range between ninety per cent carbon and graphite. Some of the semiconductor properties of anthracites and chars were also explained on the basis of such a model.

In order to illustrate the relative importance of charge-transfer complexes in these chars a plot has been made in Figure 3 of the number of free radicals vs. carbon content. There has also been plotted the reciprocal of crystallite size in no./g. vs. carbon content calculated from the work of Hirsch¹⁵ and van Krevelen²³ assuming that there is an average crystallite height of three graphitic layers and that there is no unordered material. It should be noted that the average height of the crystallites would be somewhat less than three in the low temperature chars and possibly somewhat greater than three in the higher temperature chars. In any event, it is seen that in the 600° to 650° range the number of crystallites closely approximates the number of free radicals, accounting for the results of Schuyer²². In fact these latter chars are apparently composed of little but charge transfer complexes in close proximity to one another which explains the intensive exchange narrowing of the e.s.r. signals of these materials. The decrease in free radicals at higher temperatures is at least in part due to the decrease in number of crystallites at higher charring temperatures.

Extending the conclusions on cellulose chars to coal and related materials, suggests that e.s.r. signals in all these materials result from donor-acceptor complexes which, while reaching a maximum of importance in anthracites and 600° to 700° chars, may still be of significance in lower rank coals and humic acids. Such a conclusion finds support from a number of other aspects of the behavior of coal and humic acids. Charge-transfer forces between coal and solvent can be used to explain the order of effectiveness of coal solvents. Thus catechol and anthracene oils, which are donor molecules, are very effective in extracting or dispersing coal or humic materials. Charge-transfer equilibria can also rationalize the failure of coal extracts once dried to redissolve completely in the original solvent used for extraction. Free

radicals in coals and chars are physically affected by oxygen, as indicated by line broadening of the e.s.r. signal, but are stable to chemical attack. Such behavior could be explained as due either to spin-spin coupling of the oxygen molecule with the free electron of the charge-transfer complex or to formation of new donor-acceptor complexes between aromatic centres and oxygen²⁴.

The so-called molecular weight of humic acids and coal extracts should be re-examined in the light of the concept of donor-acceptor complexes. Thus molecular weight determinations of humic acids in catechol²⁵, a substance conceivably capable of breaking up donor-acceptor complexes of humic acids, resulted in a low molecular weight estimate. Determinations on apparently similar material in sulfolane, a poor complexing agent, produced very much higher estimates of molecular weight²⁶.

Finally, coals and related materials have a well-known broad absorption band at 1600 cm^{-1} in the infrared region which has defied interpretation. Donor-acceptor phenomena have been shown to produce strong and broad absorption in this region^{27,28} in aromatic systems, as shown in Figure 4, and hence may be the cause of this band in coal and chars.

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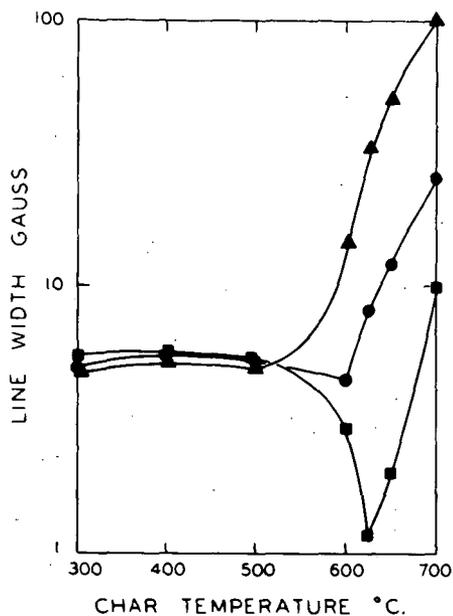


Figure 1.

Effect of I_2 and Br_2 on line widths of cellulose chars measured in vacuo at room temperature.

- no treatment
- ▲ treated with 0.1 M I_2 in CCl_4
- treated with 0.1 M Br_2 in CCl_4

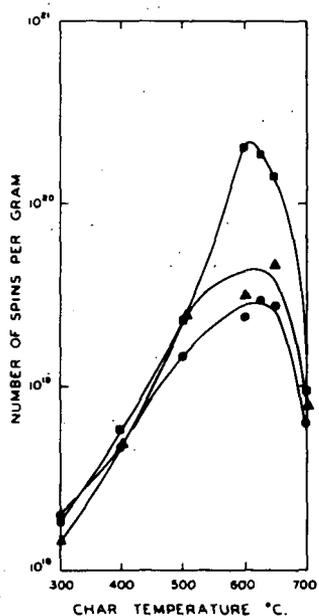


Figure 2.

Effect of I_2 and Br_2 on spin concentrations in cellulose chars measured in vacuo at room temperature

- no treatment
- ▲ treated with 0.1 M I_2 in CCl_4
- treated with 0.1 M Br_2 in CCl_4

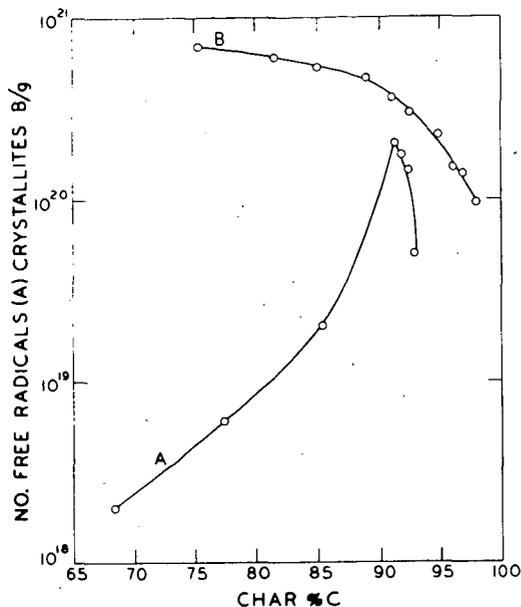


Figure 3.

Comparison of the number of free radicals with the size of crystallites in cellulose chars.

- A. number of free radicals per gram vs. Carbon content
- B. number of crystallites possible per gram vs. Carbon content

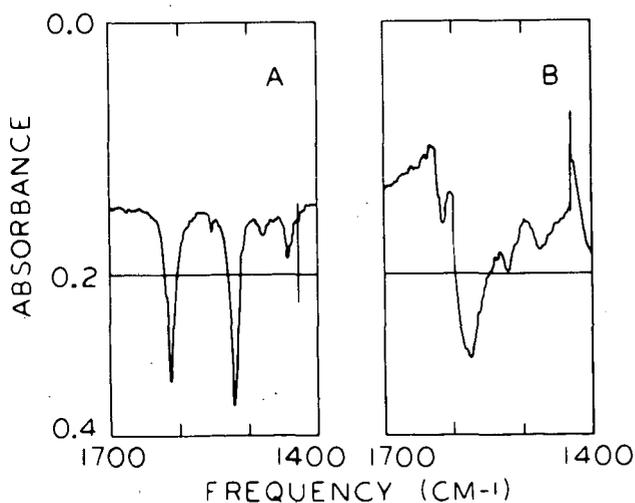


Figure 4.

The influence of charge transfer forces on infrared spectra.

- A. Tetrakis [p-dimethylaminophenyl] ethylene in fluorolube mull
- B. Iodine complex of tetrakis [p-dimethylaminophenyl] ethylene in fluorolube mull