

ELECTRON SPIN RESONANCE STUDIES OF COALS AND COAL-DERIVED ASPHALTENES

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INTRODUCTION

The discovery of electron spin resonance (esr) absorption in natural carbons by Uebersfeld (1) and Ingram (2) prompted a number of investigators to apply the technique to coal and materials derived from coal. At least three excellent review articles describing the early esr studies of coals have been published (3-5). Although the exact nature of the species responsible for the esr absorption has not been established unambiguously, it is generally thought that the unpaired electrons, at least in non-anthracitic and possibly young anthracitic coals, are associated with organic free radical structures. One group of investigators, however, has proposed that charge-transfer complexes rather than stable free radicals may be responsible for the absorption (6).

During the present investigation, esr spectra were obtained for vitrains and fusains from a large number of coals. For most ranks of coal, samples of both lithotypes were studied. The objectives of the investigation were: 1) to better characterize the immediate chemical environment of the unpaired electrons; 2) to deduce information about the metamorphic changes that occur during vitrification and fusinization; and 3) to provide needed background information for future studies of the role of free radicals in coal liquefaction. To further pursue the latter objective, esr spectra of asphaltenes, which are considered by many coal researchers to be intermediates in the conversion of coal to liquid fuels, were also obtained. A secondary purpose for examining the asphaltenes was to explore the recent hypothesis (7) that charge-transfer interactions may be important binding forces between the acid/neutral and base components in these materials.

EXPERIMENTAL

Samples. Most of the vitrains and fusains studied were of high petrographic purity, although several of the vitrains are more appropriately described as vitrain-rich samples. Sixty-three vitrains, including samples from Antarctica, Austria, Canada, Germany, Japan, Pakistan, Peru, the United States, and Yugoslavia, and 30 fusains, most of which were separated from U. S. coals, were investigated. Petrographic characterization and other properties of many of these samples were published previously (8).

The asphaltene samples were derived from products from the Pittsburgh Energy Research Center's SYNTHOIL (9) coal liquefaction Process Development Unit using a recently described solvent separation method (10). The acid/neutral and base components of the asphaltenes were prepared according to published procedures (11).

Spectral Measurements. The esr measurements were made over a period of approximately ten years. The experimental techniques were essentially those published earlier (12) except for minor modifications that were made over the years to facilitate the measurements. All esr measurements were made on evacuated samples ($\sim 10^{-6}$ torr) to prevent line broadening by oxygen in the air. The electrical properties of many of the higher rank samples necessitated that the samples be dispersed in a non-conducting medium to avoid microwave skin effects.

RESULTS AND DISCUSSION

Vitrains and Fusains. ESR data obtained for vitrains and fusains during the present investigation are far too numerous to tabulate here; complete listings of the data are available from the authors upon request. The plots of Figures 1-6 show some of the more significant correlations of the data with coal composition or coal rank.

The concentrations of unpaired electrons in the vitrains, as estimated by comparing the esr intensity of each sample with that of a standard sample of diphenylpicrylhydrazyl, are shown as a function of the carbon contents of the samples in Figure 1. The relationship of Figure 1 is similar to those from earlier studies (3-5, 12), although the scatter of the data points is more pronounced in the present work. These data show that, in general, the concentrations of unpaired electrons increase with increasing coal rank up to a carbon content of approximately 94% after which the spin concentrations decrease rapidly. The initial, crudely exponential increase in spin concentration is generally attributed to the formation of organic free radicals during vitrification. The free radical electrons are thought to be delocalized over aromatic rings and thus stabilized by resonance. Resonance stabilization of the radicals is greater for the vitrains from higher rank coals since these presumably contain the larger polynuclear condensed aromatic ring systems. The precipitous decrease in spin concentration above 94% C results from the increased conductivity of the samples.

In contrast to the results for vitrains, the spin concentrations of the fusains (Figure 2) exhibit no readily discernable dependence on carbon content. The wide variation in thermal history experienced by fusains during their formation is the most likely explanation for this behavior (13).

The changes that occur in esr linewidths and g values during vitrification and fusinization are shown in Figures 3-6. The abscissa used in these figures is based on the coalification plots of Schopf (14) with slight modifications by Parks (15) and the present authors. The ranks shown on the plots are those of the parent coals as determined by standard procedures (16).

For the vitrains, an increase in esr linewidth with increasing rank is first observed (Figure 3); this trend is reversed at the low rank bituminous stage. The rate of decrease becomes larger as coalification progresses through the higher rank bituminous stages to the early anthracitic stages. Some of the anthracites and most of the meta-anthracites exhibit very broad lines (not shown in the figure); a linewidth in excess of 60 gauss was observed for one such coal. The linewidth results can be interpreted as follows: Nuclear broadening, i.e., unresolved proton-electron hyperfine interactions, plays an important role in the observed linewidths of peats, lignites, and bituminous coals. The relatively narrow lines observed in the spectra of some of the anthracites probably result from the smaller number of protons in the samples, although exchange narrowing of the esr resonances may also be occurring. The proton line broadening hypothesis is supported by a recent esr study of coals before and after catalytic dehydrogenation (17). The very large linewidths of the highest rank materials are undoubtedly due to the presence of graphite-like structures which form during the latter stages of coalification. The difficulty in differentiating between anthracites and meta-anthracites (18) may be responsible for the apparent lack of predictability of linewidths in vitrains from coals of these ranks.

The esr linewidths for the fusains (Figure 4) are very small, frequently less than one gauss, except for samples from the lowest rank coals. Unlike the results for the vitrains, no evidence was found for the formation of graphitic structures during the latter stages of fusinization. In addition, the gradual decrease in

linewidths of vitrains as coalification proceeds from the low rank bituminous stages to the early anthracitic stages (Figure 3) appears as a very rapid change in the fusinization plot (Figure 4). This is in accord with Schopf's (14) representation of fusinization as a process which has an early inception and progresses rapidly in the peat and lignitic stages, after which the metamorphic changes become nearly imperceptible. Vitrinization, on the other hand, involves a progressive change throughout all stages of rank development.

The relationship between the g values of the lithotypes and coal rank (Figures 5 and 6) also supports Schopf's theories of vitrinization and fusinization. The large g values found for the vitrains from meta-anthracites is in accord with the final step in vitrinization being the fusing of aromatic rings into graphite-like structures. The g value of each of the vitrains and fusains is higher than that of the free electron and lies in the spectral region expected for simple organic free radicals. The only exceptions are vitrains from the more highly metamorphized coals, one of which exhibited a g value of 2.011.

The fact that esr g values of organic free radicals are greatest for radicals in which the unpaired electron is localized or partially localized on atoms having high spin-orbit coupling constants can be used to explain the g value results for vitrains. Since the heteroatom contents of coals decrease with increasing rank, the high g values for peats and lignites can be interpreted in terms of aromatic radicals with some partial localization of the unpaired electrons on heteroatoms, particularly but not exclusively oxygen. As coalification progresses the g values decrease, suggesting that the radicals become more "hydrocarbon-like." The g values of many of the vitrains from bituminous and young anthracitic coals compare favorably with those exhibited by aromatic hydrocarbon radicals. During the final stages of coalification, the g values become quite large as one would expect if continued condensation of the aromatic rings into graphite structures occurs. The observation of a small, but reproducible, anisotropy in the g value of certain anthracites (Figure 7) suggests that some ordering of the polynuclear condensed aromatic rings is occurring.

Coal-Derived Asphaltenes. To better understand the chemistry of coal liquefaction, an esr investigation of coal-derived asphaltenes was initiated. Preliminary results are presented here. Of particular concern was the temperature variation of the esr intensities of asphaltenes and their acid/neutral and base components (Figure 8). The most significant finding to date is that the weighted average of the temperature dependencies of the two components reproduces the temperature dependence of the total asphaltene (before separation) exceptionally well. This suggests that charge transfer interactions, at least in the Mullikan sense, are relatively unimportant binding forces between the acid/neutral and base components of the asphaltenes.

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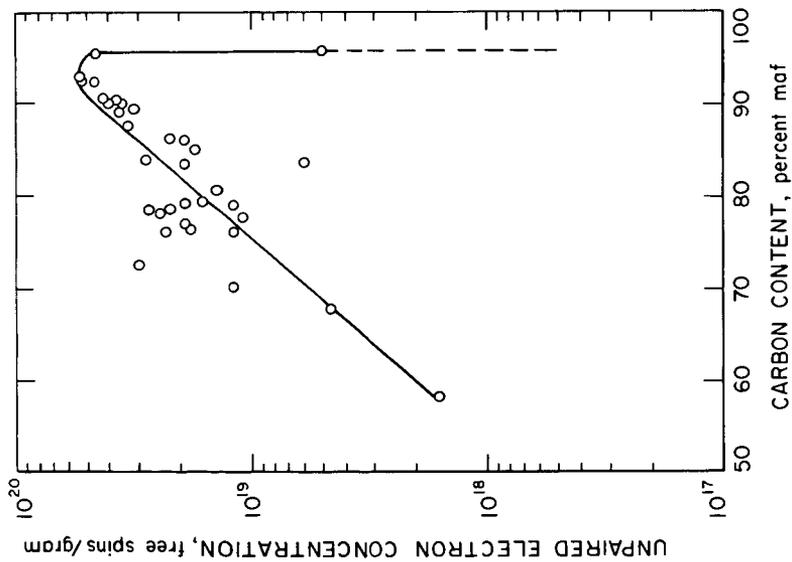


Figure 1—Concentrations of unpaired electrons as a function of carbon content for vitrains from selected coals.

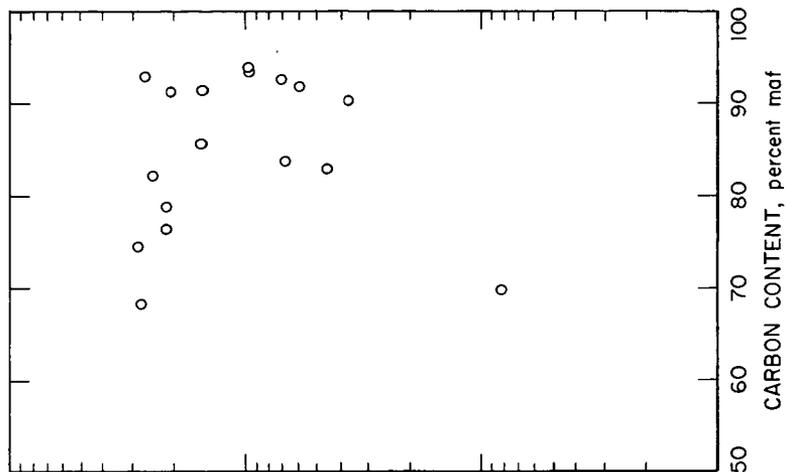


Figure 2—Concentrations of unpaired electrons as a function of carbon content for fusains from selected coals.

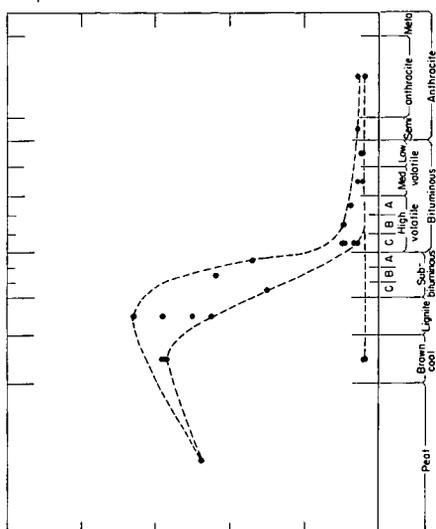


Figure 3—Electron spin resonance linewidths as a function of coal rank for vitrinite from selected coals.

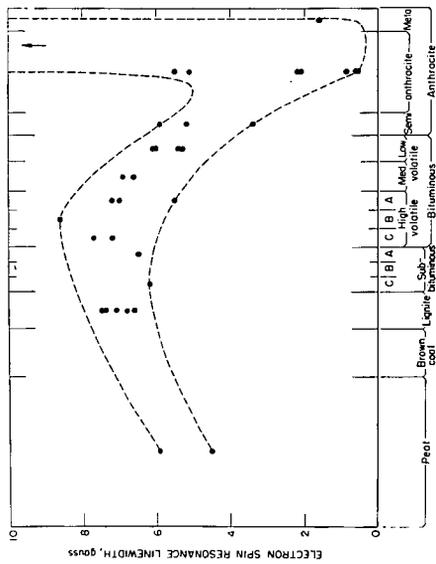


Figure 4—Electron spin resonance linewidths as a function of coal rank for fusinite from selected coals.

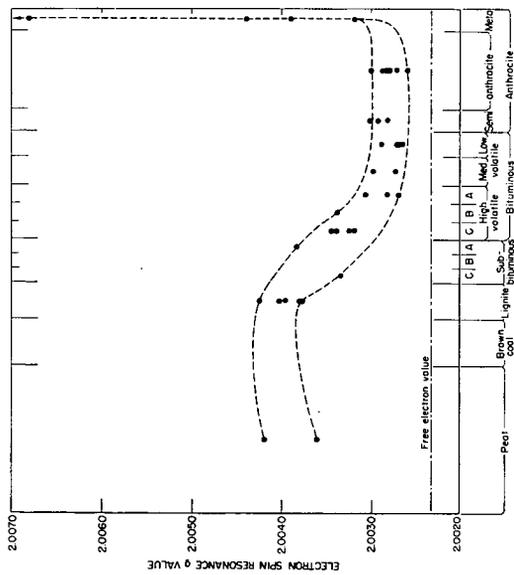


Figure 5—Electron spin resonance g values as a function of coal rank for vitrinite from selected coals

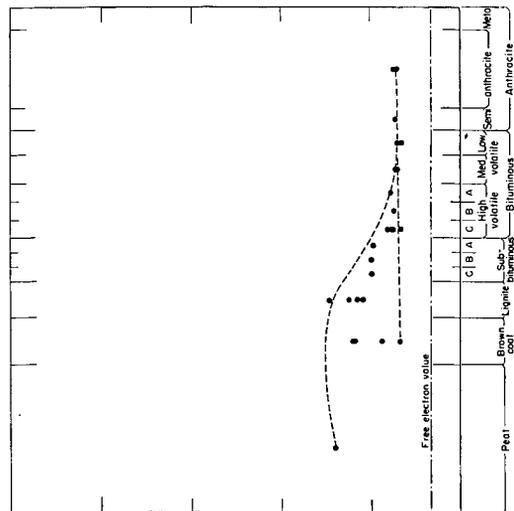


Figure 6—Electron spin resonance g values as a function of coal rank for fusinite from selected coals

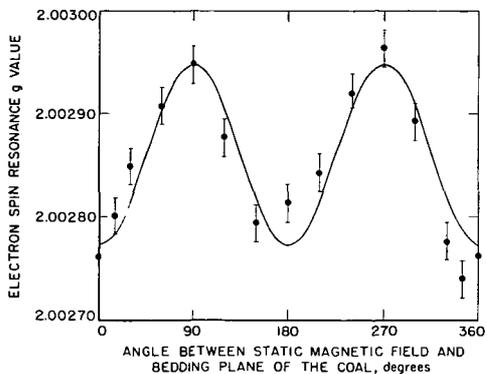


Figure 7-g Value anisotropy in Huber Mine anthracite

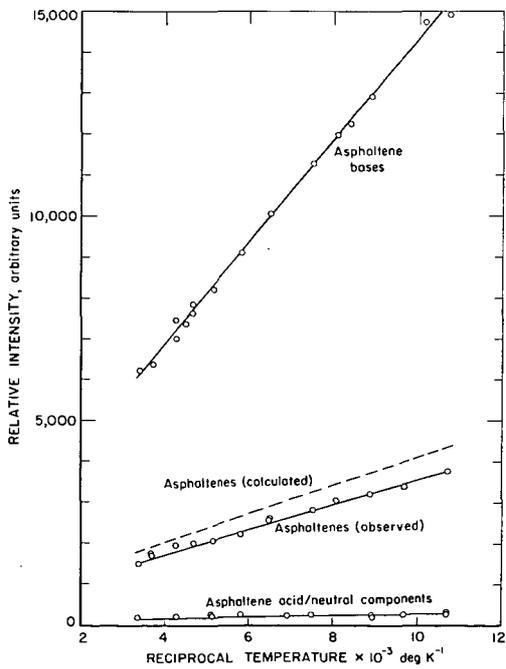


Figure 8-Variable temperature ESR data for asphaltenes and components.