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The nature and role of free radicals in coal conversion processes as revealed by e.s.r. studies

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Dr Ladner and Professor Pines in the previous two papers demonstrated how nuclear magnetic resonance can provide significant information on the structure of coals and coal extracts. We wish to provide evidence that electron spin resonance (e.s.r.) also can yield significant information on coal structure and coal conversion processes.

Free radicals in coal have been known for several years (Uebersfeld *et al.* 1954; Ingram *et al.* 1954). In our own research group, we have during the last several years carried out a systematic investigation of the nature and role of free radicals in coals, coal components and in coal conversion processes, with the use of e.s.r. techniques (Petrakis & Grandy 1978, 1980*a*, *b*; Grandy & Petrakis 1979; Petrakis *et al.* 1980). For the most part, we have studied residual free radicals, but very recently we have also constructed a special cavity that allows the study of free radicals under liquefaction and pyrolysis conditions. Professor Pines indicated in the previous paper that the very observation of the carbon-13 n.m.r. spectra of solid coal is possible because of the effects that free radicals in coal have on the relaxation times of the carbon-13 nuclei. E.s.r. allows the study of the free radicals in coal as they pre-exist in coals and during and after conversion. The significant e.s.r. parameters in these studies are spin concentrations, g values, line shapes and line widths.

Coals in their natural state have free radical concentrations and g values that are determined primarily by their rank. Pyrolysed coals show a marked increase in free radical concentrations, especially around 400 °C. This is due to thermal bond rupture and has been cited as a key to coal liquefaction. At higher temperatures, spin concentrations may diminish owing to recombination of the free radicals. Changes in the spectral line width and g value of the free radical signals after the coals have been pyrolysed have been noted and the results have been discussed in terms of the pyrolysis mechanism (Petrakis & Grandy 1978).

Free radical concentration is a very sensitive parameter, for spins in pure macerals can differ by five orders of magnitude (figure 1). Especially significant is the strong temperature dependence of the free radical concentration in vitrinite. From our work on Solvent Refined Coal (SRC-I) residues (Petrakis *et al.* 1980) there is evidence that the reaction pathways in the conversion of vitrinites are quite critical to good yields, since vitrinites can either be liquefied successfully or form coke.

In addition to pyrolysis studies of coals and macerals, we have carried out a large number of batch liquefaction runs. The efforts of solvent donor strength, heating rate, residence time, pressurizing gas and temperature on the e.s.r. spectral parameters have been examined in detail (Petrakis & Grandy 1980*a*). Figure 2 illustrates the results of free radical concentration measurements on Wyodak coal liquefied in seven different solvents. The structures of the

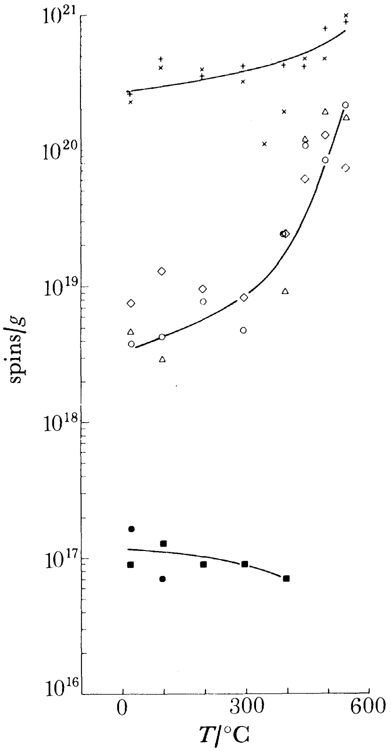

FIGURE 1. Radical concentration plotted against treatment temperature T. Evacuation was for 2 h. +, Fusinite HVA bituminous, West Virginia; ×, fusinite HV bituminous, Illinois; ◇, vitrinite sub-bituminous, Wyoming; ○, vitrinite HVA bituminous, West Virginia; △, vitrinite HVB bituminous, Ohio; ●, resinite sub-bituminous, Wyoming; ■, resinite HVC bituminous, Utah.

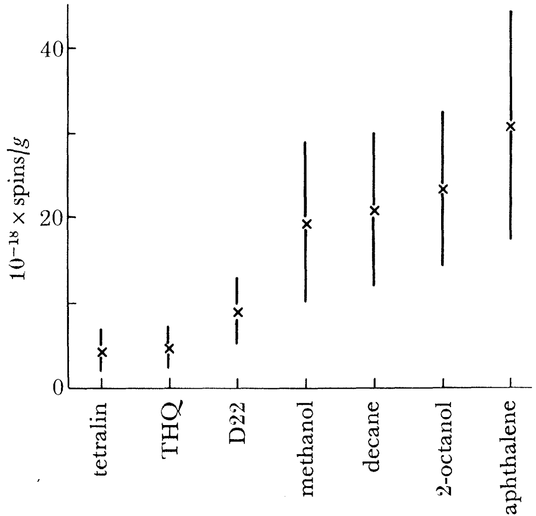

FIGURE 2. Radical concentration by solvent treatment, Wyodak sub-bituminous, all temperatures. THQ, tetrahydroquinoline; D22, N,N' di(*sec*-butyl)-*p*-phenylenediamine.

solvents determine their relative ability to quench the free radicals formed. Hydroaromatic heterocycles and hydrocarbons can lose 2 mol of hydrogen and form stable aromatic compounds. Removing 1 mol of hydrogen from naphthalene would be extremely difficult as the stable aromatic structure would be disrupted. The remaining solvents can lose 1 mol of hydrogen and form the appropriate alkene, aldehyde, imine or ketone. Thus, the relative order of effectiveness of solvents to quench free radicals is as follows: hydroaromatics > (compounds that can lose a mole of hydrogen and form stable unsaturated species) > aromatics.

Results obtained with a Waynesburg seam vitrinite are shown (figure 3) to illustrate the effectiveness of hydrogen donors (tetralin in this case) to quench the free radicals during liquefaction. At 425 °C, the radical concentration in the vitrinite is less than the natural free radical concentration in this material. The radical concentration appears to be independent of the pressurizing gas. However, rehydrogenation of the solvent is probably insignificant in that tetralin is in 100-fold excess on a molecule:radical basis at 400 °C, assuming the concentration of radicals measured in an evacuated heating experiment is the maximum number formed. At 450 °C and higher, this ratio of tetralin molecules to radicals formed is about 10:1, which may explain the higher radical concentration measured in the tetralin treated samples at these higher temperatures. A similar donor solvent effect on radical concentration has been observed in other high volatile bituminous vitrinites and coals (Petrakis & Grandy 1980*a*). Resinites and fusinites, as well as most other non-high volatile bituminous vitrinites and coals exhibit no solvent effect on free radical concentrations.

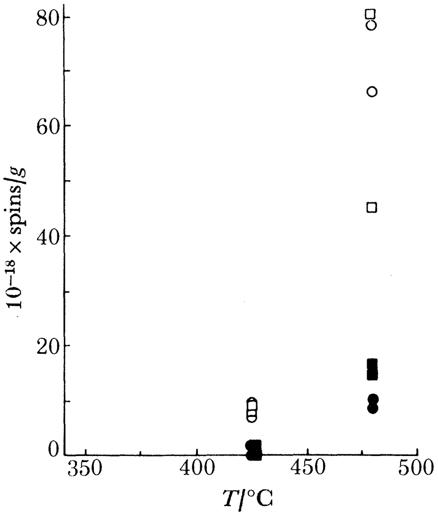

FIGURE 3. Radical concentration plotted against treatment temperature T. Vitrinite HVA bituminous, Waynesburg seam, West Virginia; residence time 10 min, heating rate *ca.* 32 K/min, pressure 12 MPa. ○, Naphthalene–N_2; □, naphthalene–H_2; ●, tetralin–N_2; ■, tetralin–H_2.

Owing to the wide range of free radical concentrations and the markedly different appearance of the liquefaction products, Soxhlet extractions were performed on a few select samples using toluene as an extraction solvent. Liquefaction conditions for the three maceral samples were 480 °C, 12.4 MPa of H_2, 10 min residence time and a tetralin:maceral ratio of 1:1 by mass. The Hiawatha resinite was essentially completely (98%) converted to toluene solubles. The Waynesburg vitrinite had a conversion level of 36% and the Illinois no. 6 fusinite had only a 5% conversion to toluene solids under these conditions. The donor solvent insensitivity of the free radical concentration in resinite and fusinite may be due to the propensity of resinite to undergo liquefaction and the refractory nature of the fusinites.

During the study of batch liquefaction experiments on coals and macerals, it became obvious that it would be desirable to study the formation and quenching of the free radicals in coal and coal macerals under high pressure and high temperature conditions similar to those used in the SRC-II or EDS liquefaction processes. This would enable (*a*) the collection of kinetic data and (*b*) the comparison of residual free radicals with those that exist during liquefaction. To this end, a high temperature (500 °C), high pressure (13.8 MPa) e.s.r. cavity has been constructed. This cavity allows the heating of coal and/or coal solvent slurries to temperatures in excess of 400 °C in about 2 min. E.s.r. data can be then obtained in about 3 min after the initiation of heating. Table 1 shows what we believe to be the first *in situ* e.s.r. measurements under liquefaction conditions. The results shown are from measurements made at 400 and 460 °C on Powhatan no. 5 coal and tetralin in a 1:1 ratio by mass. The heating time is less than 3 min and the gas is hydrogen at 11.03 MPa. Note that the spin concentration at 460 °C is much higher than at 400 °C and that the spin concentration increases by 30% over a 16 min time span at 460 °C. The spin concentrations measured at room temperature after the sample had been heated are not significantly different from those measured during heating. Extensive experimentation to study the effect of solvent, heating rate, residence time, pressure and gas on the free radicals formed during coal liquefaction is currently in progress.

Table 1. Time series spin concentration data for Powhatan no. 5 coal in tetralin

	$10^{-18} \times$ spins/g §	
time/min	400 °C	460 °C
0†	7.9	7.0
7	8.2	54.0
8	—	54.5
10	8.6	59.2
11	—	59.8
13	8.0	59.3
14	8.3	60.9
15	—	—
16	—	60.9
17	8.7	—
20	8.3	—
23	8.3	72.4
32	8.6	—
60	—	65.7
after‡	6.9	70.8

† Before heating: spectra obtained at 20 °C.
‡ After heating was complete, spectra obtained at 20 °C.
§ All spin concentration measurements at elevated temperature have been corrected to 20 °C.

Finally, significant information can be gained about structural aspects of coals as well as changes that take place upon conversion by monitoring other e.s.r. parameters. For example, g values depend both on rank and maceral content. Fusinites have g values that are characteristic of aromatic hydrocarbons, and they are not affected by thermal treatment. On the other hand, g values of vitrinites reflect the heteroatom (oxygen) content and for low ranked coals the g values are typical of quinones or methoxybenzenes (Petrakis & Grandy 1978). Removal of oxygen functionalities upon pyrolysis or liquefaction shifts the g values to those typical of fused aromatics. Other e.s.r. parameters (line widths, line shapes, multiple signals) can also be sensitive probes of the structure of coal and its changes upon liquefaction or pyrolysis.

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