

## ESR *g*-Shift Measures Pyrolytic Deoxygenation and the Effect of Flame Retardants

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### Synopsis

The theory of *g*-factors in aromatic radicals proposed by McConnell and Robertson and the statistical theory of Boltzmann were used to show that a small decrease in the *g*-factor of the ESR spectrum of the pyrolysis residue of cellulosic materials is proportional to a small decrease in the ratio of the bound oxygen atoms to that of the carbon atoms in the system. An average *g*-factor decrement was defined and used to evaluate the effect of a flame retardant on the rate of deoxygenation in the thermal decomposition of cellulosic materials at various temperatures.

### INTRODUCTION

The effect of flame retardants on the pyrolysis mechanism in cellulose has been investigated by several authors<sup>1,2,3</sup> using ESR technique. They reported that the flame retardant increased the unpaired spin concentration in the pyrolysis residue of a treated specimen relative to that in the pyrolysis residue of an untreated specimen; both specimens were pyrolyzed under the same conditions. Evaluation of the effects of various flame retardants on the pyrolysis mechanism requires, however, a quantitative relationship between the unpaired spin concentration and a parameter of the mechanism. Ingram et al.<sup>4</sup> found that the unpaired spin concentration in the pyrolysis residues of carbonaceous solids increased with an increase in the carbon content from 80% to 94%. It has been reported<sup>5</sup> that in the pyrolysis of wood, the formation of condensed benzene ring systems with broken bonds at the edges is an unpaired spin-producing mechanism, and the formation of graphitic sheets with bridging bonds in three-dimensional lattices is an unpaired spin concentration-reducing mechanism. It would be difficult, however, to establish a quantitative relationship between the unpaired spin concentration and the two mechanisms since its magnitude does not depend on the chemical constituents of the pyrolysis residue.<sup>6</sup> Moreover, the calculated value of the unpaired spin concentration is affected by the microwave power saturation of the spin states, the measured mass of the residue, and the mass loss of the flame retardant.<sup>7</sup> Consequently, the unpaired spin concentration is not a suitable ESR parameter to evaluate chemical changes and the effects of various flame retardants in the pyrolytic reaction of cellulosic materials. The *g*-factor depends on the chemical constituents of a pyrolysis residue, so it may be used for such evaluation.

In this article, a normalized  $g$ -factor decrement for the pyrolysis residue of cellulosic materials is defined, and it is shown that a small average rate of deoxygenation at a pyrolysis temperature of cellulosic material is proportional to the normalized  $g$ -factor decrement. It is also shown how a plot of the  $g$ -factor decrements against the pyrolysis temperatures may be used to evaluate the effectiveness of a flame retardant in cellulosic materials.

### THEORETICAL BACKGROUND

The qualitative theory of  $g$ -factors for aromatic radicals proposed by McConnell and Robertson<sup>8</sup> and the Boltzmann statistical theory of thermal excitation of molecules have been used. McConnell and Robertson explained the  $g$ -shift relative to the free electron  $g$ -factor (2.00229) as a result of second-order spin-orbit interaction through mixing of the excited  $\sigma$  and  $\pi$  configurations with the ground state. Blois et al.<sup>9</sup> have shown that there is a very little variation in the  $g$ -factor with a change in the temperature, the free-radical concentration, and the molecular size of the aromatic radicals. Consequently, the  $g$ -shift is proportional to the spin-orbit coupling constant of the bound atoms, and inversely proportional to the energy separation between the ground state and the particular excited level which mixes most effectively with the ground state. So the small  $g$ -shift (about 0.0002) for fully charred cellulosic materials is consistent with the small spin-orbit coupling constant ( $C_C = 28 \text{ cm}^{-1}$ ) of the carbon atom. Chemically bound oxygen with a much larger coupling constant ( $C_O = 152 \text{ cm}^{-1}$ ) produces a much larger  $g$ -shift. Chemically bound hydrogen with a very small coupling constant leads to a negligibly small  $g$ -shift.

The condensed ring system of the pyrolyzed residue has to have sufficient resonance energy to stabilize the unpaired spins to be detectable. Atoms or molecules bound to the edges of the ring system are called edge groups. The field of the edge groups with oxygen perturbs the resonance of the unpaired spins. The perturbation produces spin pockets (component lines) so that the spectrum of pyrolyzed cellulosic materials is the envelope of the spin pockets and inhomogeneously broadened.<sup>6,10</sup> The  $g$ -factor of the spectrum depends on the intensity of the various spin pockets and the perturbation of their spins. The perturbation depends on the edge groups with oxygen, i.e., in general, on the number density of oxygen atoms remained bound in the residue. The use of precise  $g$ -factors and their shift with temperature and time of pyrolysis of cellulosic materials is a sensitive method to determine the extent to which the unpaired spins are associated with the structure of the residue containing chemically bound oxygen. So,  $\Delta g$ , the  $g$ -shift for the pyrolysis residue relative to the  $g$ -factor (2.00255) for the fully charred material, may be related, in general, to the ratio  $Q$  of the number of oxygen atoms to that of the carbon atoms in the specimen by Boltzmann statistical theory as follows:

$$Q_r = Q_m \frac{\Delta g_r}{\Delta g_m} e^{-E/kT} \quad (1)$$

where  $Q_m$  and  $\Delta g_m$  are upper limits and initial values of  $Q$  and the  $g$ -shift available before pyrolysis of the material ground to 60 mesh. It is not required, however, that eq. (1) be valid for a specimen before the pyrolytic reac-

tion starts.  $Q_r$  is the  $Q$ -value, and  $\Delta g_r$  is the  $g$ -shift for the pyrolysis residue;  $E$  is the average bond energy of the edge groups with oxygen;  $T$  is the absolute temperature at which pyrolysis starts; and  $k$  is the Boltzmann constant.  $\Delta g_m$  and  $\Delta g_r$  are also the relative statistical weights for thermal cleavage of the edge groups with oxygen. Since  $Q_m$ ,  $\Delta g_m$  and  $E$  in eq. (1) are constants for a particular specimen, for a given pyrolysis temperature

$$Q_d \propto \Delta g_d \quad (2)$$

where  $Q_d$  is a very small decrease in  $Q$ , and  $\Delta g_d$  is a very small respective decrease in  $\Delta g$ . Since not all the edge groups with oxygen are cleaved simultaneously, the thermal energy  $B$  per second required to cleave  $Q_d$  per second of the edge groups may be given by

$$B = AEQ_d$$

where  $A$  is the probability of cleaving  $Q_d$  per second of the edge groups. Since  $Q_d$  and  $A$  vary during the pyrolysis process,  $\Delta g_d$  also has to vary. To measure accurately very small consecutive decreases in  $\Delta g$  is difficult and time consuming. It is more convenient to determine the average value of this spectral parameter over a longer period at a pyrolysis temperature. When a specimen is pyrolyzed for  $\tau$  seconds at  $t$  °C, and  $\Delta g_m$  is thereby decreased by  $\Delta g_\tau (= \Delta g_m - \Delta g_r)$ , and  $Q_m$  by  $Q_\tau (= Q_m - Q_r)$ , then the average decrease in the  $g$ -factor per second and degree Celsius over  $\tau$  seconds at  $t$  °C is given by

$$\eta(\tau, t) = \frac{\Delta g_\tau}{\tau t} \quad (3)$$

$\eta(\tau, t)$  may be called the normalized (to 1°C of the pyrolysis)  $g$ -factor decrement.  $Q_\tau/\tau$  is a measure for the average rate of deoxygenation at  $t$  °C. For a short  $\tau$  at  $t$  °C, it can be assumed that  $Q_\tau/\tau \simeq Q_d$ ; and  $\Delta g_\tau/\tau \simeq \Delta g_d$ . From relationship (2) and eq. (3),  $Q_\tau/\tau$  is proportional to  $\eta(\tau, t)$ , which was to be shown.

### EFFECT OF FLAME RETARDANT

Chemical analysis of the pyrolysis products and ESR studies on the pyrolysis residues of celluloses and wood both in the natural state and treated with flame retardants show that the flame retardant acts, in essence, as a deoxygenation and dehydrogenation agent during the pyrolysis process.<sup>11,12</sup> Since  $\eta(\tau, t)$  is a spectroscopic measure for such a deoxygenation, the plot of isochronic  $\eta(\tau, t)$  against the pyrolysis temperature for untreated and treated specimens gives information on the effect of flame retardant on the rate of deoxygenation at various pyrolysis temperatures. Figure 1 is such a plot for Douglas fir sawdust, natural and treated with ammonium dihydrogen orthophosphate. The greater the  $\eta(\tau, t)$  values and the larger the maximum of the curve and its shift to lower temperatures for the treated specimens, the more effective is the flame retardant as a deoxygenation agent.

The small decrease in the  $g$ -factor which has to be measured accurately may be considered as a practical difficulty. However, the advantages of using the  $g$ -factor decrement to evaluate the effect of flame retardants on the pyrolysis process of wood are that the  $g$ -factor does not depend on the ESR spectral intensity, the microwave power saturation, or the mass loss of the

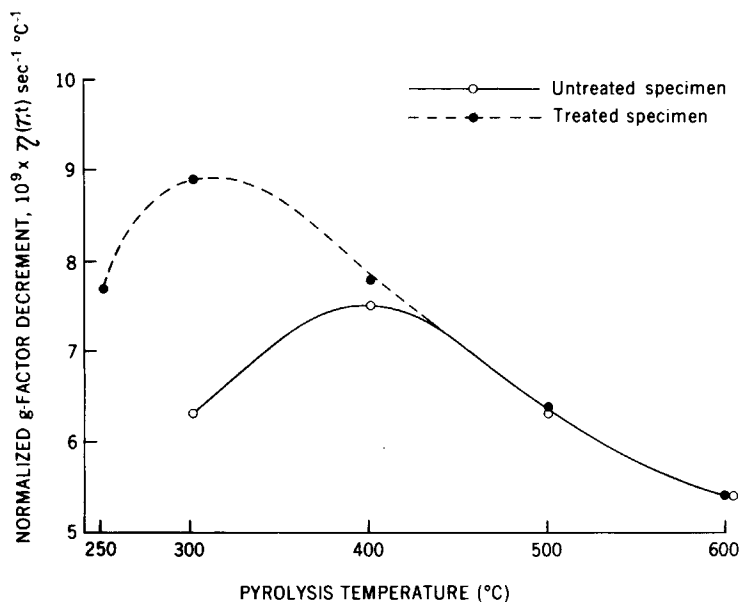


Fig. 1. Deoxygenation rate in the thermal decomposition of untreated Douglas fir sawdust and that treated with ammonium dihydrogen orthophosphate, as measured by the normalized  $g$ -factor decrement and shown as a function of temperature for 10-min pyrolysis.

specimen or the flame retardant. Blois et al.<sup>9</sup> and Segal et al.<sup>13</sup> developed experimental methods to measure  $g$ -factor very accurately. If their methods are considered to be complicated and time consuming, then the use of the method described previously may be used.<sup>5</sup> The latter method is simple, fast, and sufficiently accurate for the application of this theory.

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