

ESR Studies on the Effect of Lignin and Gases on UV Photodegradation of Cellulose

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Synopsis

Aspen wood pulp and aspen dioxane-lignin were irradiated by ultraviolet light under vacuum employing a special technique for uniform irradiation of the powdered samples. Examination of the effect of various gases and lignin contents of the pulps on the ESR spectra showed that the spin concentration was reduced by oxygen and lignin content, while atomic hydrogen reduced it to zero. The width and shape of the line were unaffected by oxygen, while lignin content reduced the width. A resolution for the hyperfine component of the spectrum yields an average distance of 1.3 Å between the free spin at C-5 and the protons at C-6 of the cellulose.

INTRODUCTION

The photochemical degradation of cellulosic materials has been the subject of numerous investigations. Although considerable work has been done on the electron spin resonance (ESR) spectra of gamma-irradiated cellulose, very few investigations have been carried out to examine free radicals produced by ultraviolet light (UV) in cellulosic materials. Kleinert¹ studied the ESR spectra of cellulose irradiated with UV, in the presence of air, nitrogen, oxygen, and under vacuum and found that free radicals were formed in all cases. Further, chain cleavage through free-radical formations was suggested to be the primary action of UV in photodegradation of cellulose. Phillips et al.² found that there was no specific chromophore responsible for UV absorption by cellulose, but that a broad region from about 3250 to 4000 Å was active in the process. The formation of free radicals in wood resulting from exposure to fluorescent light has been recently reported by Kalnins et al.³

It seems that the ESR technique has not yet been used to study the effect of lignin on the UV photodegradation of cellulose. Further, measurement of saturation power and examination of line shape and hyperfine splitting of ESR spectra of UV-irradiated woodpulp have received little attention in previous studies. In this paper, some effects of the presence of lignin and several gases on the UV photodegradation of cellulose have been examined by the ESR technique. A possible resolution for the

hyperfine components of the spectrum has been proposed on the basis of the observed results.

EXPERIMENTAL

Materials

Bleached Aspen Pulp. A₁. The pulp was prepared by treating aspen chips with a 50:50 mixture of sulfolane and water. The ratio of wood to liquor was 3:2. The treatment was carried out at an initial pH of 7 with 1 hr of cooking at 175°C. The resulting pulp was first treated with chlorine dioxide, then aqueous alkali, and again chlorine dioxide. The pulp obtained was practically free from lignin and contained about 87% α -cellulose.

Bleached Aspen Pulp. A₂. The pulp was prepared in a manner similar to that for pulp A₁, except that the sulfolane-to-water ratio was 30:70 and the cooking time 4 hr. The pulp obtained was practically free from lignin and contained about 94% α -cellulose.

Filter Paper. A₃. Whatman No. 1 filter paper, chromatography grade, was ground in air to 40 mesh. The α -cellulose content of the paper was about 99%.

Bleached Black Spruce Pulp. A₄. Spruce chips were impregnated with 0.5% sulfur dioxide (w/v) solution in a 70:30 mixture of sulfolane and water under 200 psi nitrogen for 1/2 hr and then cooked for 5 hr. The resulting pulp was bleached with chlorine dioxide as in the treatment of pulp A₁. The pulp obtained was practically free from lignin and contained about 86% α -cellulose.

Unbleached Aspen Pulp. B. This was pulp (A₂) without bleaching with chlorine dioxide, and contained about 4% lignin.

Unbleached Aspen Pulp. C. This was pulp (A₁) without bleaching with chlorine dioxide and contained about 10% lignin.

Ground Wood. D. Aspen chips, in natural state, were ground in air to 40 mesh.

Aspen Dioxane Lignin. E. The lignin was extracted from aspen saw-wood by the procedure described by Pepper et al.^{4,5}

Irradiation Chamber

When powdered cellulose, lignin, or wood was close-packed in a quartz sample tube, a UV light beam irradiated only a thin outer layer of the material. A special chamber and a method for uniform irradiation of material were developed. Figure 1 shows a cross section of the irradiation chamber in schematic form. A 550-W Hanovia high-pressure mercury lamp, A₁, with a transformer, A₂, produced 47% radiation in the UV region, of which 50% was in the 3130–3660 Å range. The balance of the radiation comprised 43% in the visible, and the remainder, in the infrared region. The mercury lamp and a quartz sample tube, B, were supported

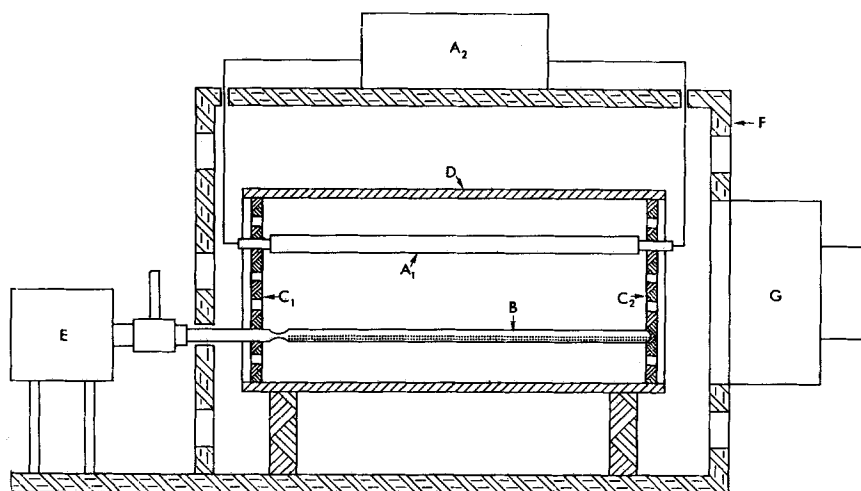


Fig. 1. Cross section of the irradiation chamber (see text for key).

by two Teflon disks, C_1 and C_2 , inside an aluminum tube, D , 4 in. in diameter. The internal surface of the aluminum tubing was polished to a mirror finish to act as two cylindrical mirrors facing each other. The mercury lamp and the sample tube were placed horizontal and parallel to each other, about 2 in. apart, in the focal lines of the two cylindrical mirrors. The powdered specimen was uniformly spread out in the sample tube which was rotated by a Rincó evaporator, E , at 1 rps and connected to a vacuum pump. The aluminum tube was placed in a housing, F , which was furnished with a fan, G , to cool the chamber by air circulating through the openings in the walls of the housing and the Teflon disks.

Preparation of Specimens

Each of the materials was packed in a high-quality quartz sample tube, 4 mm inside diameter, to a length of about 1 cm. A constriction in the sample tube and quartz wool were used to block the open end of the tube, to prevent any loss of the specimen by vacuum pumping. The specimen was dried in a Rincó evaporator under a vacuum of about 5×10^{-5} torr at 110°C for 18 hr. Preliminary NMR measurement showed that strongly bound water molecules could not be removed by vacuum pumping at temperatures less than 110°C . The identical ESR signal intensities measured before and after heating indicated that no thermal decomposition occurred at this temperature. The dried specimen was uniformly spread out in the sample tube and irradiated for 1 hr under a vacuum of about 5×10^{-5} torr. Preliminary ESR measurements showed that 1 hr was optimum; longer irradiation did not increase the free spin concentration. After irradiation, the sample tube was sealed under vacuum at the constriction. The mass of each specimen was determined from the weights

of the sample tube with and without the specimen. The UV irradiation produced a detectable number of free spins in the quartz sample tube, too; this was removed by heat annealing.

Saturation Measurement

The ESR spectra were recorded by an X-band spectrometer⁶ constructed in the laboratory. With each specimen, a series of spectra were recorded at several microwave powers, P , in the range from $1 \mu\text{W}$ to 1 mW , in the cavity. The detectors were operated at the square-law conversion region⁶ and all other electronic conditions were fixed. In every case, the first derivative of the ESR absorption curve was recorded at a sweep of 2.6 gauss/min of the dc magnetic field. The area under the absorption curve was calculated from the recorded spectral intensities by graphic double integration. The ratio D of the area A under the absorption curve of a particular signal to the power P , i.e., $D = A/P$, was calculated. According to the theory for the static susceptibility, D remains constant with an increase in P until saturation of the energy levels is absent; after that, D decreases. The values of D obtained for a specimen at powers up to $P_0 = 10 \mu\text{W}$ showed a random error of less than 5%. The average of these values was used as a reference, D_0 , of nonsaturation, and from the remaining values of D the ratio D/D_0 was calculated. The plot of D/D_0 versus P gives the saturation curve for a specimen.

Measurement of Free Spin Concentration

The sample tube was set on the top of a fixed quartz tube, which ensured that every specimen occupied the same place in the cavity. As skin effect is absent in powdered dry wood, lignin, and cellulose, it is reasonable to assume that the Curie law is valid for the relation between static susceptibility and free spin concentration. Since a microwave power higher than about $10 \mu\text{W}$ caused saturation in the energy levels and a better signal-to-noise ratio was attainable at 1 mW , the free spin concentration was calculated from spectra recorded at 1 mW . The difference A in the areas of the two absorption spectra recorded at the same microwave power, before and after irradiation, was converted to its nonsaturation value A_0 at $10 \mu\text{W}$, employing the relationship $A_0 = A/(100D/D_0)$, derived from the result of the saturation experiment. The method also increased the accuracy of measuring the spectral intensities in the wings of a spectrum, which were very weak at $10 \mu\text{W}$. The free spin concentration due to irradiation was then calculated from the comparison of this area (A_0) with that under the absorption curve of a standard DPPH signal recorded at $10 \mu\text{W}$, with all the other electronic and field conditions fixed. DPPH starts to saturate at about 3 mW .

Determination of the g -Factor

The g -factor was determined in reference to the lines of dilute Fremy's salt solution⁷ using the technique referred to earlier.⁶

Determination of the Line Shape

The method developed by Tikhomirova and Voevodskii⁸ was used to analyze the line shape. The method involves plotting $\log_{10} (Y/J')$ against Y^2 for a Gaussian curve and $(Y/J')^{1/2}$ against Y^2 for a Lorentzian curve, where J' is the height of the derivative of the specimen line at any point and Y is the field interval from the crossover point to a particular value of J' . The plot is linear for the section of a spectral line which is either Gaussian or Lorentzian. From the linear portions of a plot and the maximum value of the derivative curve, three independent field parameters may be calculated by the use of eqs. (5) and (6) in the above reference.⁸ The type of interaction responsible for the broadening of a line was defined by increasing the microwave power to saturation and changing the microwave frequency by 1 GHz about 9.37 GHz. In both cases, the width of a line was measured and its shape was defined using the above method.

Effects of Gases

When the spectral study on a specimen under vacuum was completed, the effects of gases A, N₂, O₂, and H on the spin concentration and the width and shape of the spectral lines were investigated. The seal of a sample tube was broken under vacuum and a gas at 1 atm and room temperature was introduced.

RESULTS

Saturation

In Figure 2, the values of D/D_0 for all the samples are plotted against the microwave power P fed into the cavity. Plot A represents the saturation curves for all the pulp specimens, and plot B, that for the wood and lignin samples. The curves show that all the specimens start to saturate at an input power of about 10 μ W and that the rate of saturation in the pulp specimens is slightly smaller than that in the wood and lignin specimens.

Free Spin Concentration

In Table I, the values show that the irradiation has produced a free spin concentration N in the pulp specimens about four times larger than that in the wood and lignin specimens. The pulp specimens had insignificant free spin concentration N_0 before irradiation, whereas N_0 for the wood and lignin specimens was relatively large.

g -Factor, Width, and Shape of the Lines

The g -factors were the same, within 2.0045 ± 0.0003 , for all the specimens.

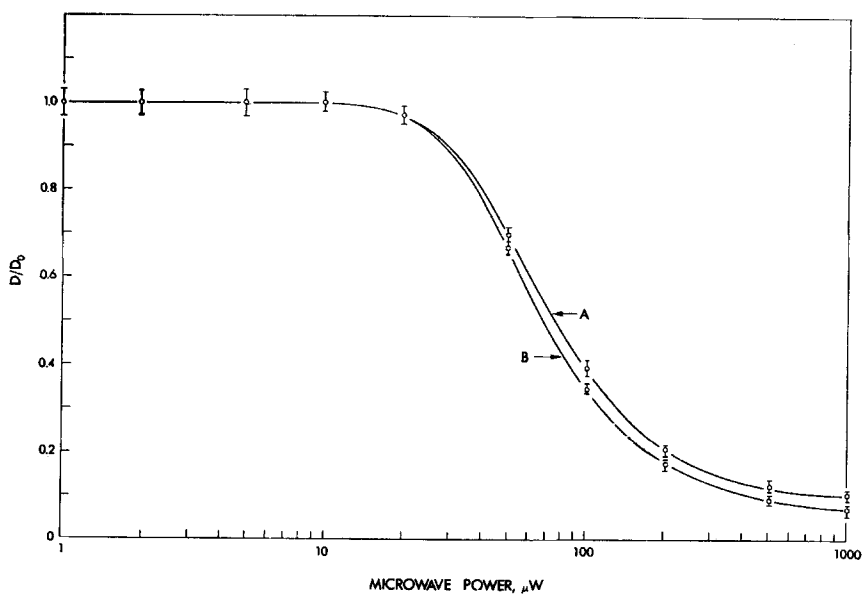


Fig. 2. Saturation curves for specimens: (A) pulps; (B) wood and lignin.

The preirradiation spectrum of the pulp specimens shown in Figure 3 was a single line without hyperfine structure. The postirradiation spectra, however, shown in Figure 4 for the pulp specimen with 0, 4%, and 10% lignin contents, A, B, and C, respectively, comprised hyperfine structure, and those for the wood and lignin specimens, D and E, respectively, were single lines. All the spectra appeared symmetric with respect to the crossover point. The lines shown in Figures 3 and 4 were recorded at 1 mW, but the amplifier gain for Figure 3 was higher than that for Figure 4.

The width ΔH of the lines was measured between maximum slopes (Table I). The line width is appreciably larger for the pulps than for the

TABLE I
Line Width and Spin Concentration of Specimens

Material used (specimen)	Line width ΔH , gauss	(Number of spins/gram) 10^{-17}	
		After irradiation	Before irradiation
A ₁ aspen pulp (0% lignin)	23	7.8	0.1
A ₂ aspen pulp (0% lignin)	23	8.0	0.1
A ₃ Whatman filter paper	23	7.8	0.1
A ₄ black spruce pulp	23	7.9	0.1
B aspen pulp (4% lignin)	22	7.4	0.1
C aspen pulp (10% lignin)	20	6.2	0.2
D aspen ground wood	11	2.3	0.3
E aspen lignin (dioxane)	8	1.8	0.6

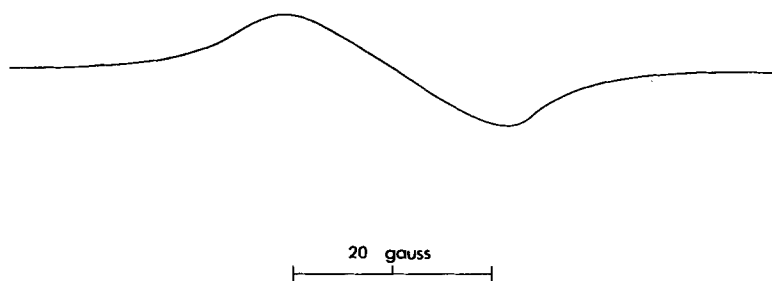


Fig. 3. Preirradiation spectrum of pulp specimens.

lignin, and the larger the lignin content, the smaller the line width. The microwave power saturation of a specimen, or a change in the frequency by 1 GHz about 9.37 GHz, produced no change in the line width.

Figures 5 and 6 show the plots of the linear forms of the spectral lines for the pulps with 0% lignin content and for the lignin specimen, respectively, at microwave powers of 10 and 100 μW and 1 mW. Plots were similar for the remaining specimens and are not presented. As the plots indicate, the lines are neither Gaussian nor Lorentzian for the pulps, are Lorentzian in the center and Gaussian in the wings for the lignin specimen, and do not change shape by saturation.

For the pulp with 0% lignin content, the spectrum was resolved by trial and error for hyperfine components, as shown in Figure 7. Curve (a) is the spectrum recorded, and (b), (c₁), (c₂), and (c₃) are the hyperfine components. The resolution could be made such that the sum of the component intensities for a particular field was equal to the intensity of the spectral record and that the integrated absorption for curve (c₂) was about twice as large as that for curve (c₁) or (c₃). The maximum-slope line width for curve (b) is 23 gauss and 8.5 gauss for (c₁), (c₂) and (c₃). The hyperfine splitting ΔH_{hsp} between curves (c₂) and (c₁) or (c₃) is 25 gauss. The plots of the linear forms of the hyperfine components shown in Figure 8 indicate a Gaussian shape.

For the lignin specimen, three field parameters of the two standard-line components could be calculated. The values are given in Table II, where ΔH_G and ΔH_L are the half-width at half-power point for the Gaussian and the Lorentzian portions of the line, respectively; ΔH_e is the field

TABLE II
Field Parameters for Lignin Specimen at Three Microwave Powers

Microwave power, μW	ΔH_G , gauss	ΔH_L , gauss	ΔH_e , gauss	$(\Delta H_G^2)/(\Delta H_L \Delta H_e)$
10	10.5	6.3	17	1.02
100	10.0	5.7	17	1.03
1000	10.3	6.0	17	1.04

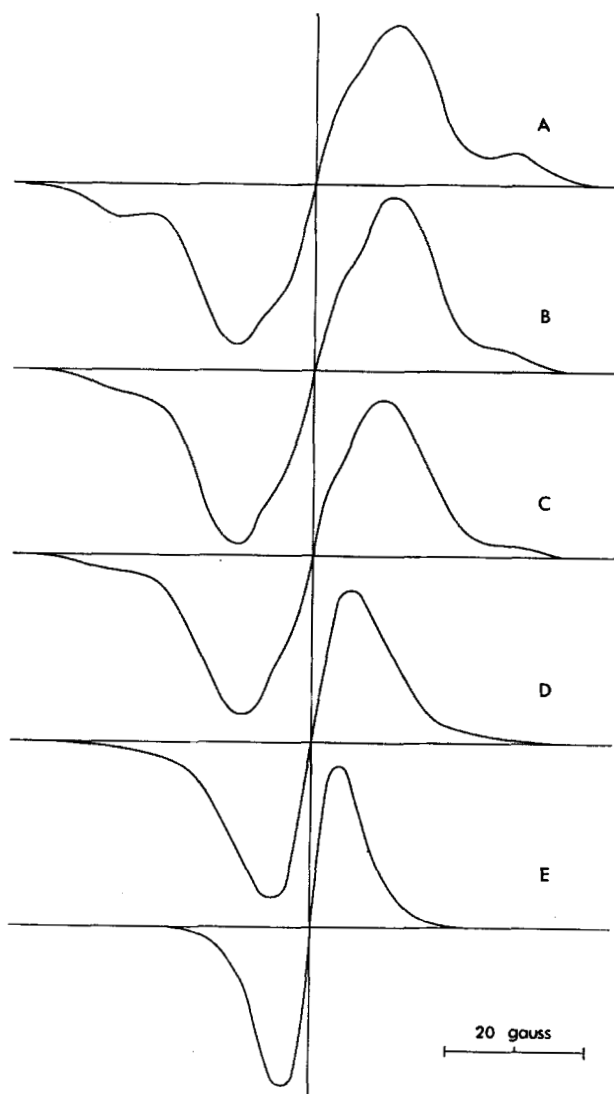


Fig. 4. ESR spectra of the specimens at 1 mW: (A) pulps, A₁, A₂, A₃, and A₄ (Table I) with 0% lignin; (B) and (C) pulps with 4% and 10% lignin, respectively; (D) ground wood; (E) lignin.

region where the line changes from one standard shape to the other. The values in the fifth column are approximately equal to unity, which confirms the validity of the analysis.

Effects of Gases

No change in the spin concentration or the shape and width of the spectral lines was observed with gases A and N₂. Oxygen reduced the

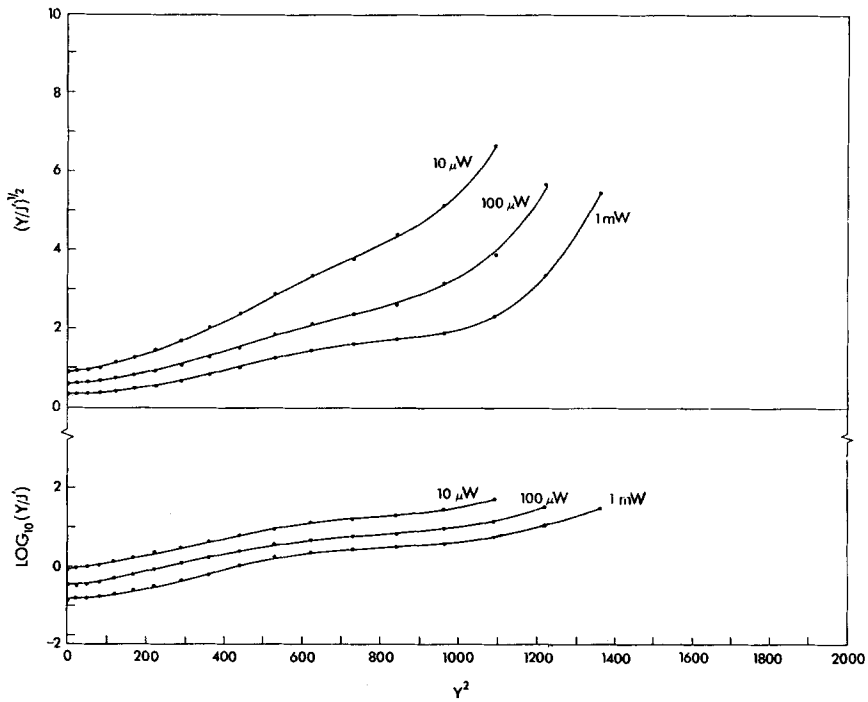


Fig. 5. Line shape curves (plots of linear forms) of spectra for pulps with 0% lignin, at 10 and 100 μ W and 1 mW (curve A, Fig. 4).

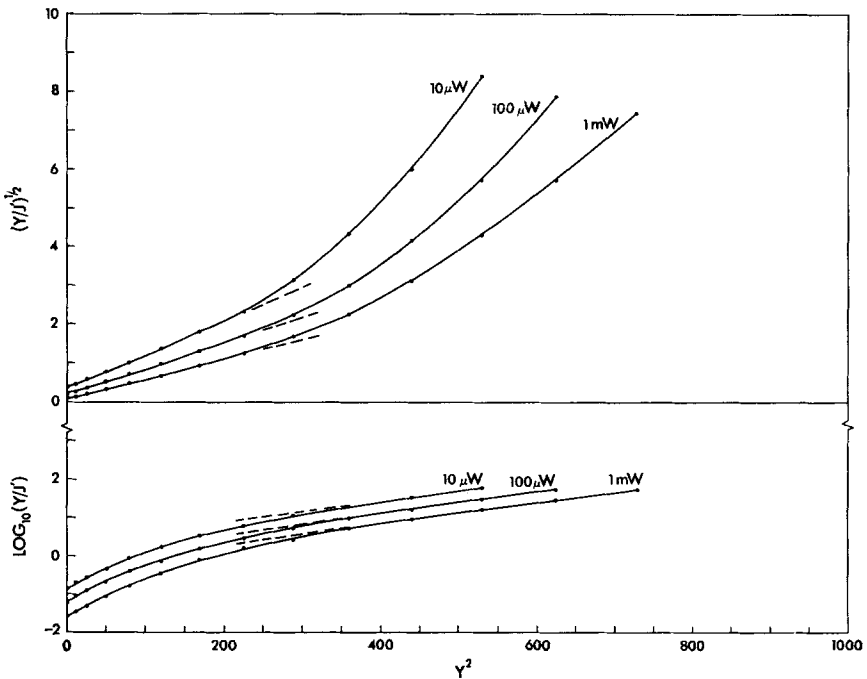


Fig. 6. Line shape curves (plots of linear forms) of spectra for lignin specimen at 10 and 100 μ W and 1 mW (curve D, Fig. 4).

spin concentration in the pulp specimens but produced no change in the width or shape of the line. The lines for the lignin and the wood specimens were unaffected in the presence of O_2 . Atomic hydrogen reduced the spin

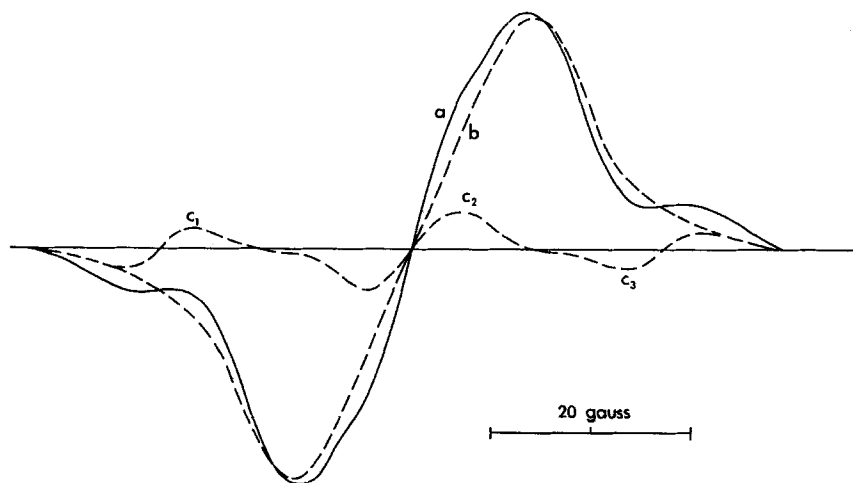


Fig. 7. Resolution for the hyperfine components of spectrum A (Fig. 4): (a) spectrum recorded; (b), (c_1), (c_2), and (c_3) hyperfine components.

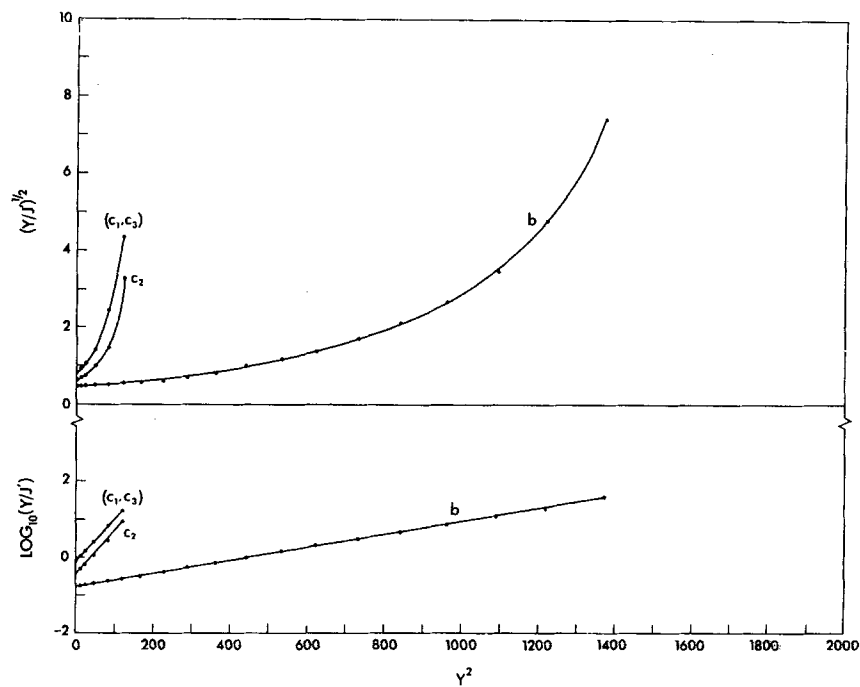


Fig. 8. Line shape curves (plots of linear forms) of hyperfine components of spectrum A, Fig. 7.

concentration to zero in the pulp specimens but did not produce any change in the lines for the lignin and the wood specimens. Vacuum pumping of O₂ or H at room temperature or at 100°C could not restore the original line intensity.

DISCUSSION

Portis⁹ dealt with the saturation behavior of various broadenings in ESR spectra. He pointed out that the relaxation times could be calculated from saturation measurements in the case of homogeneous broadening, but such a calculation would be difficult for inhomogeneous broadening. It was found that the line shape was independent of the extent of saturation (Figs. 5 and 6) and that the line width was unaffected by a change in the microwave frequency. Hence inhomogeneous broadening is involved in the hyperfine interaction of spins with protons in the system,⁹ and it is difficult to calculate the relaxation times from the saturation curves. However, as relatively low microwave power (about 10 μW) caused saturation of the energy levels (Fig. 2), long relaxation times were indicated.

Phillips et al.² and Arthur et al.^{10,11} have shown that the line shape and width and the hyperfine splitting of the ESR spectra of UV- and γ-irradiated cellulose are dependent on the type of cellulose, the moisture content, the temperature, the frequency distribution and intensity of the irradiation energy, and the spin concentration. At low temperatures, or at low spin concentrations, single-line spectra were obtained. With increased temperature and with the presence of moisture, spectra with hyperfine splitting to three and five lines were obtained. According to Arthur et al.,¹⁰ free spin formation may be expected at C-1, C-4, or C-5 through the cleavage of H or OH. With C-1 or C-4, a single Gaussian-line component will result, whereas the cleavage of H at C-5, or the OH group at C-6, or H from the OH group at C-6 would result in three Gaussian-line components with intensity ratio 1:2:1.¹¹ The spectrum with hyperfine structure (Fig. 4) could be resolved for hyperfine components as shown in Figure 7. Curve (b) represents the single Gaussian-line component due to a free spin site on either C-1 or C-4, or both, while the three Gaussian-line components, (c₁), (c₂), and (c₃), can be attributed to the free spin site at C-5 or C-6. The most likely site of the free spin is C-5, because of the delocalization effect of the adjacent oxygen atom to which it is attached.¹⁰ Hence the three Gaussian-line components can be assigned to the anisotropic dipolar interaction of the free spin at C-5 with the two identical H atoms at C-6. From the hyperfine splitting, $\Delta H_{\text{hsp}} = 25$ gauss, an average distance of 1.3 Å between the free spin at C-5 and either of the two protons at C-6 was found by eq. (4.23) reported by Ingram.¹² (The C-C and C-H bond lengths are about 1.5 and 1.1 Å, respectively.)

Chain scission is considered to be the primary process in photochemical degradation of cellulose,^{1,13} which may indicate that the free spin concentration from sites C-1 and C-4 can be greater than that from any other

sites. Isotropic interaction of either of these free spins with the nearest proton produces a doublet. Since each of these spins is situated in similar solid structure, the g -factors for the doublets are approximately equal. A resolved pattern of these doublets, however, is smeared out and broadened by considerable anisotropic dipolar interaction due to the random orientation of the molecules in the polycrystalline and amorphous solid structures. In addition, any resolved pattern of these doublets is further reduced by the anisotropic interaction of these free spins with protons attached to C-2 and C-3, respectively. So it is conceivable that the anisotropic dipolar interaction of these free spins with several protons has produced the strong single-line component, b , of the hyperfine structure¹² (Fig. 7). This is supported by the line width (23 gauss) which corresponds to the separation expected for the doublets.

The ESR spectrum of lignin was a single narrow line (Fig. 4). When lignin was present in the pulp, a narrowing of the line for the pulp occurred, the effect increasing with lignin content. Hence, the narrowing in the line for the pulp can be the result of superposition of the lines due to the cellulose and lignin contents of the pulp.

The spin concentration of a pulp was reduced with an increase in the lignin content (Table I). Sandermann et al.,¹⁴ Kleinert,¹⁵ and Lin et al.¹⁶ reported that the high absorption of UV photons by lignin resulted in a preferential lignin degradation. Hence, it can be concluded that the strongly UV-absorbing lignin has a screening effect which results in a reduction in free spin concentration of the pulp.

The ESR line shape of lignin is Lorentzian in the center and Gaussian in the wings (Fig. 6), which indicates the operation of line-narrowing mechanism, exchange, or delocalization in a frequency interval corresponding to $\Delta H_e = 17$ gauss (Table II) about the crossover point.

Free radicals trapped in γ -irradiated polymers with extensive hydrogen bonding, e.g., cellulose and starch, were found to be resistant to reactions with SO_2 and O_2 , which was attributed to the impermeability of the substrate to these gases.¹⁷ Kleinert¹ found that oxygen slightly reduced the ESR signal intensity of UV-irradiated cellulose. A similar effect of oxygen was observed in the present study. Subsequent evacuation of the oxygen at room temperature and at 100°C did not restore the original signal intensity, indicating chemisorption of oxygen.

When atomic hydrogen, produced by the sodium amalgam method, was introduced into the sample tube, the signal disappeared completely. Subsequent evacuation at room temperature or at 100°C did not restore the original signal, indicating chemisorption of hydrogen. A similar effect of atomic hydrogen on the free spin concentration in γ -irradiated polymers has already been reported.¹⁸ The difference in behavior of oxygen and hydrogen (both paramagnetic) can be attributed to the greater reactivity of the atomic hydrogen as compared to molecular oxygen and to the difference in permeability of the substrate to the individual gases.

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