Effect of Crystalline Structure on the Trapped Radical Spectra of Irradiated Cellulose*

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Synopsis

The effects of crystalline modification of cellulose and of water on the ESR spectra generated by the trapped free radicals in gamma-irradiated celluloses were investigated for cotton cellulose I, II, III, and IV, partially decrystallized cotton cellulose, ball-milled cotton cellulose, hydrocelluloses of cellulose III and IV, and ramie.   On irradiation of the celluloses, free radicals were formed on the cellulose molecule, probably following dehydrogenation or chain cleavage.   The free radicals located within the less ordered or amorphous regions of the cellulose reacted readily with water and were terminated.   The radicals located within the more ordered regions of the celluloses could be made accessible to reaction with water by the interaction of the celluloses with solvents which caused dimensional changes in the cellulosic structure.   In the highly ordered regions of the celluloses, even after long periods of time in solvents which caused large dimensional changes in the cellulosic structure, the trapped free radicals were not terminated by reaction with solvent or water.   The ESR spectra of the irradiated, dried celluloses were determined at −160°C, the single-line spectra recorded had line widths of about 18–24 gauss.   On the absorption of water by the irradiated celluloses, the ESR spectra changed and were dependent on the crystalline structure of the irradiated celluloses.   The effects of different arrangements of the inter- and intramolecular bonding forces in the different polymorphic forms of the irradiated celluloses, as shown by their trapped radical spectra, particularly after interaction with water, were discussed.

INTRODUCTION

The chemical reactivity of cotton cellulose has been related to the degree of order in the cellulosic fiber and the type of crystalline lattice. Physical methods, including x-ray diffraction, infrared spectroscopy, and density, and chemical methods, including measurement of the extent and rate of selected reactions and of sorption of chemicals, particularly moisture, have been used to determine the effects of chemical and/or physical modifications of cotton cellulose on its chemical reactivity.[1]   During the investigation of radiation-initiated graft copolymerization reactions of cotton cellulose with vinyl monomers, it was observed that the ESR

spectra of trapped radicals in irradiated cellulose I and II, recorded at
25°C and containing regain moisture, were three-line and five-line spectra,
respectively.[2]   It was also noted that even when solvents, which were used
for the monomers, caused large dimensional changes in the macrostructure
of the cellulose, about thirty percent of the trapped radicals in the irradiated
cellulose were not terminated.[3]

Experimental data are presented in this report, based on an ESR spec-
troscopy study, of the reactions of the trapped radicals, formed in irradiated
cellulose, with water vapor as related to the type of crystalline lattice of
the cellulosic structure.   The effects of lattice modification on the degree
of order and the inter- and intramolecular bonds in the cellulosic structure,
as indicated by the trapped radical spectra, are discussed.

EXPERIMENTAL

Preparation of Samples

Purified cotton cellulose was prepared as previously described by extrac-
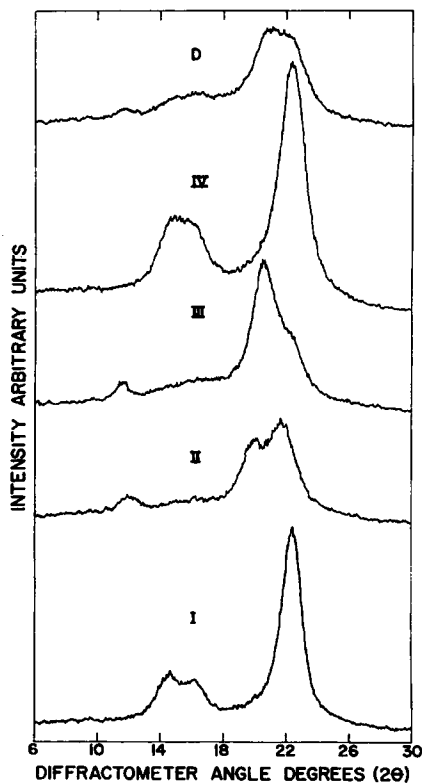tion with hot ethanol followed by boiling in dilute sodium hydroxide then

Fig. 1. X-ray diffractograms of celluloses I, II, III, IV, and partially decrystallized (D)
cellulose.

washing with water and neutralization.[4]   The cellulose was conditioned at 21°C and 65% R.H. to a moisture content of about 7% and had lattice type I and a viscosity-average molecular weight of about 700,000.[5] Cellulose II was prepared by immersing samples of cotton cellulose I in 23% sodium hydroxide solution at 25°C for 10 min, then washing with distilled water to remove the base, and air-drying at 25°C.[6]   Cellulose III was prepared by immersing cotton cellulose I in ethylamine, in the absence of oxygen, for 4 hr at 16°C; then the ethylamine was removed by evaporation.[7,8]   Cellulose IV was prepared by forming an ethylenediamine complex with cotton cellulose I, then heating the complex at reflux in N,N-dimethylformamide for 4 hr and finally washing with water and air-drying at 25°C.[9-11]   Partially decrystallized cellulose was prepared by immersing cotton cellulose I in ethylamine, in the absence of oxygen, for 4 hr at 16°C; then the ethylamine was removed by extraction with hexane, followed by air-drying at 25°C.[12]

Hydrocelluloses were prepared by acid hydrolysis of the selected celluloses in 1 N hydrochloric acid at 80°C for 4 hr to the leveling-off degree of polymerization.[13]   Ramie hydrocellulose II was obtained by ten consecutive treatments of purified ramie fiber with 23% sodium hydroxide solution at 25°C, washing with water after each treatment, and finally air-drying at 25°C, and then hydrolyzing with hydrochloric acid.   The ball-milled cellulose was prepared by grinding 5 g portions of cotton cellulose I for about 4 hr in a vibratory mill.

Typical x-ray diffractograms (Cu Kα radiation)[14] of the samples used, with the exception of the ball-milled cellulose, are shown in Figure 1.   The diffractogram for the ball-milled cellulose showed low intensity of scattering characteristic of this type of material.

Methods

Samples of the cellulose were irradiated in sealed quartz tubes (3 mm diameter) in the SRRL ^{60}Co radiation source[15] at a dose rate of about 6 × 10^{19} ev/g - hr to the desired dosage.   The samples were irradiated at ambient temperature in vacuo or in air and either dry or containing equilibrium moisture after exposure to air at 21°C and 65% R.H.   The samples of cellulose with low moisture content (estimated to be less than 0.5% moisture) were obtained by drying the cellulose at 25°C in vacuo over phosphorus pentoxide to constant weight.   The samples were irradiated near one end of the sealed quartz tube.   After irradiation the end of the tube containing the irradiated sample was cooled, and the other end was heat-annealed to dissipate any unpaired electron sites induced in the quartz by the irradiation.   After the tube returned to ambient temperature, the irradiated sample was moved to the heat-annealed end of the tube.   Then this end of the quartz tube was cooled, and the remainder of the tube was heat-annealed.   The unirradiated celluloses, including the ball-milled cellulose, did not generate ESR spectra.

The ESR spectra of the irradiated celluloses, in the heat-annealed, sealed quartz tubes, were determined in a Varian 4502-15 EPR spectrometer system. The system was equipped with a variable temperature accessory which allowed operation from about -185 to $300°C$.

RESULTS AND DISCUSSION

Trapped Radical ESR Spectra at $-160°C$

Celluloses, with moisture contents of less than 0.5% were irradiated in vacuo at $25°C$ to a dosage of about 1×10^{19} ev/g. About one chain cleavage per molecule occurred, so that the viscosity-average molecular weight of the irradiated cotton celluloses was about 350,000. Trapped radical ESR spectra of the irradiated celluloses, recorded at $-160°C$, are shown in Figure 2, and later in Figures 6b and 7a. Except for cellulose I, the ESR spectra generated by the irradiated celluloses were fairly sym-
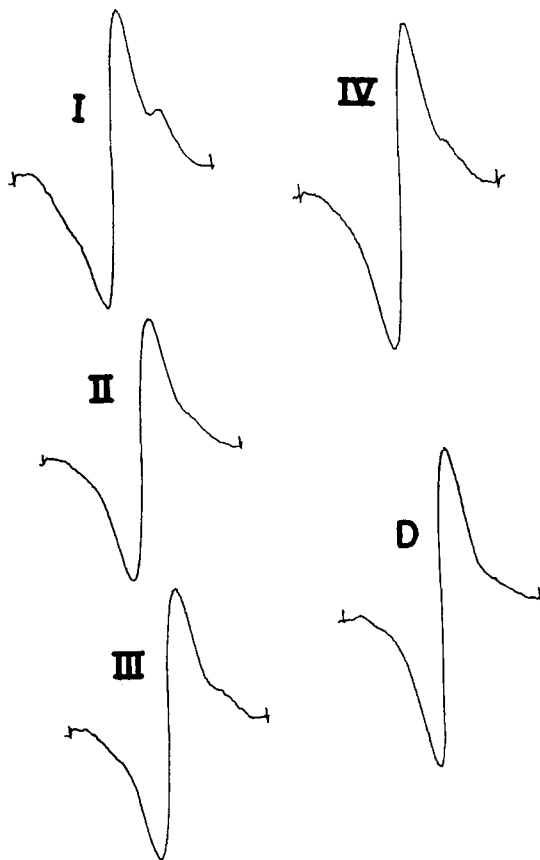

Fig. 2. ESR spectra of celluloses irradiated dry and in vacuo recorded at $-160°C$. Magnetic field increasing left to right; sweep, 100 gauss.

metrical singlet spectra with g-values near the free electron value and line widths of 18–24 gauss.   In the case of cellulose I, the principal line had a g-value near the free electron value and a width of about 17 gauss. However, in this case there was some indication of hyperfine splitting, probably due to traces of hydrogen-bonded or "nonfreezing" water which was not completely removed during the drying process.   Cellulose I had the highest degree of order of the celluloses irradiated and for this reason may bind water more tenaciously than the less ordered samples.

The ESR spectra indicate that the free radical sites formed on any of the irradiated celluloses were similar.   The removal of moisture and the low temperature at which the spectra were recorded would tend to minimize the effects of "freezing" water and electronic environment on hyperfine splitting of the spectra.   Any spin-spin interactions of the free radical sites through dipole interaction as a result of hydrogen-bonded water would be minimized.   The widths of the ESR lines were about the same for all of the irradiated celluloses; the spectra indicated that at $-160°C$ interactions of the spin of the free radical sites on the irradiated celluloses with the crystalline lattices of the celluloses were also minimized.

Effect of Temperature

The effects of trace amounts of water present in the irradiated celluloses on their ESR spectra recorded at $25°C$ are shown in Figure 3 and later in Figure 6a.   The hyperfine splitting of the ESR spectra of irradiated cellulose I recorded at $25°C$ was more pronounced than the splitting when

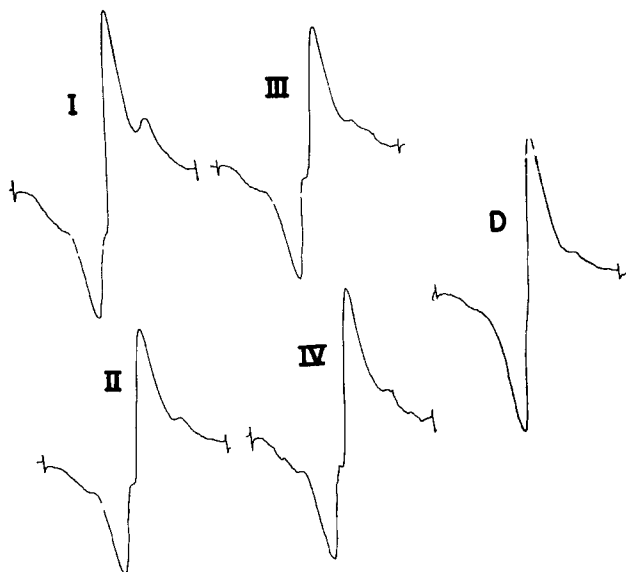Fig. 3. ESR spectra of celluloses irradiated dry and in vacuo recorded at 25°C. Magnetic field increasing left to right; sweep, 100 gauss.
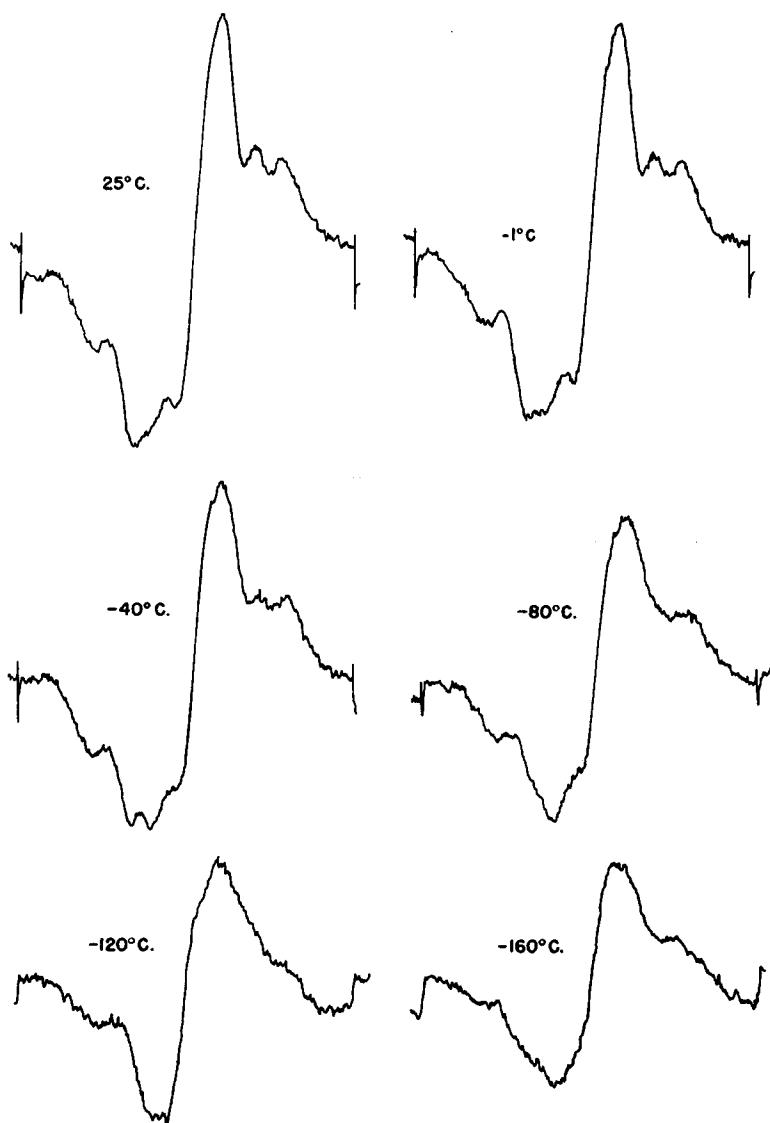
Fig. 4. Effect of recording temperature on ESR spectra of cellulose II irradiated containing regain moisture and in air. Magnetic field increasing left to right; sweep, 100 gauss.

the spectra were recorded at −160°C (compare with Fig. 2). The ESR spectra of the other irradiated celluloses, recorded at 25°C, also showed hyperfine splitting, although not as pronounced as that for cellulose I.

Cellulose II, containing regain moisture (about 7%), was irradiated in air. The effects of the temperature of recording on the ESR spectra of the irradiated cellulose are shown in Figure 4. As the temperature of recording

of the spectra was decreased, the hyperfine splitting of the spectra decreased. At $-160°C$ the spectrum was almost a singlet. These changes indicated that most of the water absorbed by the celluloses was probably "freezing" water.

Effect of Water

When the celluloses, containing regain moisture, were irradiated in air, the ESR spectra recorded at 25°C are shown in Figure 5. The spectrum for irradiated cellulose I was a fairly symmetrical triplet. The spectra for irradiated celluloses II, III, and IV consisted of five lines. The spectrum of irradiated cellulose, partially decrystallized with ethylamine, also appeared to consist of five lines. The hyperfine splitting was much weaker for decrystallized cellulose than for celluloses I, II, III, and IV.

When ball-milled cellulose, with less than 0.5% moisture, was irradiated in vacuo, the ESR spectra, recorded at 25° and $-160°C$, are shown in Figures 6A and 6B, respectively. When the irradiated cellulose was conditioned in air at 25°C and 70% R.H., the water vapor reacted with the
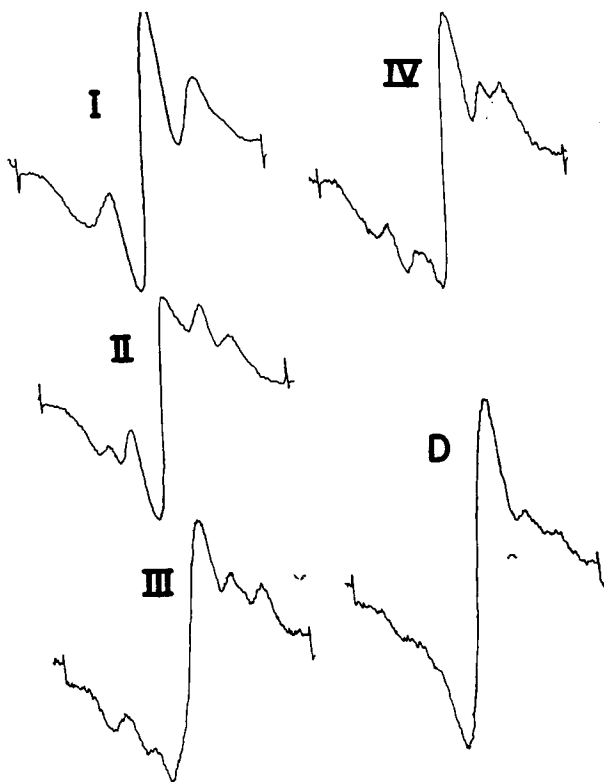

Fig. 5. ESR spectra of celluloses irradiated containing regain moisture and in air recorded at 25°C. Magnetic field increasing left to right; sweep, 100 gauss.
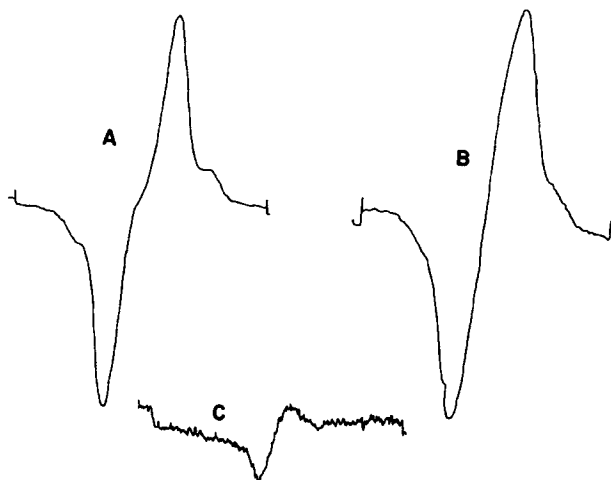
Fig. 6. ESR spectra of ball-milled cellulose irradiated dry and in vacuo. (a) recorded at 25°C; (b) recorded at −160°C; (c) irradiated cellulose conditioned for 36 hr in air at 25°C and 70% R.H.; then recorded at 25°C.   Magnetic field increasing left to right; sweep, 100 gauss.

accessible free radical sites to terminate them, as shown by comparing the ESR spectra shown in Figures 6a and 6c.   Since all of the free radicals were not terminated, the ball-milled cellulose apparently retained some ordered regions.   Similarly, it was also observed that the concentrations of free radicals in the other irradiated celluloses decreased on interaction with water vapor.   The concentration of free radicals in irradiated cellulose, decrystallized by ethylamine, decreased to a greater extent on absorption of water vapor than the concentrations of free radicals in irradiated celluloses I, II, III, and IV but to a lesser extent than in irradiated, ball-milled cellulose.

Hydrocelluloses

Samples of the hydrocelluloses were dried to less than 0.5% moisture and irradiated in vacuo at 25°C to a dosage of about 1×10^{19} ev/g.   The ESR spectrum of the irradiated ramie hydrocellulose II, recorded at −160°C, was a singlet with a line width of about 22 gauss, as shown in Figure 7a.   When the irradiated hydrocellulose was conditioned in air at 25°C and 70% R.H., the ESR spectrum decreased in intensity and changed from a single-line to a five-line spectrum, as shown in Figure 7b.   The line widths were about 11 gauss for the principal line and 38 and 59 gauss for the other lines.   If the hydrocellulose, containing regain moisture, was irradiated, a similar ESR spectrum was obtained.   Results obtained with hydrocelluloses I, III, and IV were similar to those obtained for the corresponding cellulose.   This indicated that the hyperfine splittings of the ESR spectra, observed for the irradiated celluloses after interaction with
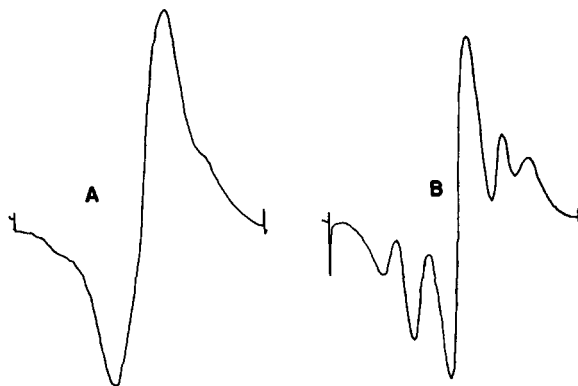
Fig. 7. ESR spectra of ramie hydrocellulose II irradiated dry and in vacuo. (*a*) recorded at −160°C; (*b*) irradiated hydrocellulose conditioned for 36 hr in air at 25°C and 70% R.H.; then recorded at 25°C. Magnetic field increasing left to right; sweep, 100 gauss.

water, were dependent on changes in molecular forces in the more ordered regions of the celluloses.

Conclusions

The interaction, transfer, and localization of high energy in cellulose have been shown to initiate dehydrogenation reactions of cellulose which result in oxidative degradation, depolymerization, and formation of trapped free radicals.[16] When fibrous celluloses I and II were dried and irradiated in vacuo, higher initial concentrations of free radicals were obtained than when samples, containing regain moisture, were irradiated to the same dosage. Some of the trapped radicals formed in irradiated, dried cellulose were readily accessible to and were terminated by water vapor. Additional trapped radicals were terminated when irradiated fibrous cellulose was immersed in solutions of zinc chloride which caused large dimensional changes in the fibers. However, even under these conditions about 30% of the initially formed free radicals were not terminated. The ESR spectra, generated by trapped radicals, in irradiated celluloses I and II after absorption of water vapor were three-line and five-line spectra, respectively.[16]

When irradiated dry and in vacuo and the ESR spectra of the trapped radicals in irradiated celluloses were recorded at −160°C, similar spectra were obtained for irradiated celluloses which had different crystalline structures and degrees of order. This indicated that the localization of energy and formation of the free radical site, either by dehydrogenation and/or depolymerization, were independent of the structure of the cellulose. At −160°C the effects of any trace amounts of "freezing water" on hyperfine splitting of the ESR spectra would be minimized. When the celluloses containing regain moisture, were irradiated, the ESR spectra of the trapped

TABLE I
Comparison of the ESR Spectra of Irradiated Celluloses[a]

Property	Cellulose lattice type					
	I	II	III	IV	Partially decrystal- lized	Ball- milled
Dried and irradiated in vacuo						
Spectrum, lines	3	3	3	3	3	3
Line width, gauss	23	23	22	22	23	26
major line[b]	(2.6)	(4.1)	(4.1)	(3.9)	(6.4)	(5.0)
other line[c]	50	56	55	55	57	52
	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
Containing regain moisture and irradiated in air						
Spectrum, lines	3	5	5	5	5	1
Line width, gauss	12	11	20	10	21	12
major line	(2.0)	(2.1)	(1.8)	(1.9)	(4.6)	
nearest to	47	38	39	36	52	—
major line	(1.0)	(1.4)	(1.2)	(1.3)	(1.4)	
other line	—	55	65	55	80	—
		(1.0)	(1.0)	(1.0)	(1.0)	

[a] ^{60}Co *gamma*-radiation dosage at 25°C: 1×10^{19} ev/g; spectra recorded at 25°C.
[b] Relative intensity of line given in ().
[c] Hyperfine splitting weak.

radicals were dependent on the crystalline structure and degree of order of the celluloses. Comparisons of the ESR spectra of the irradiated celluloses, recorded at 25°C, are made in Table I. The line widths of the major lines of the ESR spectra of the celluloses, irradiated dry in vacuo and recorded at 25°C, ranged from 22–26 gauss as compared with 18–22 gauss when the ESR spectra of these celluloses were recorded at −160°C. Also, weak hyperfine splittings of the spectra of the irradiated celluloses, recorded at 25°C, occurred to give three lines. The principal differences in the spectra of the irradiated celluloses were in the relative intensity of the major line to the other lines, which tended to increase with decrease in order in the cellulose.

Irradiated cellulose I generated an ESR spectra with three lines. Celluloses II, III, IV, and partially decrystallized cellulose generated ESR spectra with five lines. The ESR spectra generated by irradiated ball-milled cellulose were very weak, indicating that absorption of water had terminated most of the free radicals. The line widths of the major lines for irradiated celluloses I, II, and IV ranged from 10–12 gauss and for irradiated cellulose III and decrystallized cellulose, 20–21 gauss. These effects were dependent on interaction of water vapor in the more ordered regions of the cellulosic structure, since similar results were observed with hydrocelluloses.

The principal differences in the celluloses are: degree of order, lattice

type, and inter- and intramolecular bonding forces, particularly hydrogen bonding. The reaction of water vapor with trapped radicals, in the less ordered regions of the irradiated celluloses, to terminate them would explain observed decreases in the intensities of the ESR spectra. It has been suggested that the three-line spectrum was generated by a trapped radical on carbon C-5 by its interaction with the equivalent protons on carbon C-6. Also, it was previously suggested that changes in molecular forces resulted in trapped radicals being formed on both carbons C-5 and C-6 and that the five-line spectrum resulted from the superposition of two three-line spectra.[2]

From the ESR spectra of irradiated celluloses, containing regain moisture, irradiated celluloses II and IV apparently have a similiar distribution of molecular bonding. Cellulose III and ethylamine decrystallized cellulose apparently have similar distributions of molecular forces which contribute to the hyperfine splittings of the spectra. However, the intensity of the major line of the spectra for the irradiated, decrystallized cellulose relative to that of the minor line was greater than the similar value for irradiated cellulose III. As additional information is developed concerning the inter- and intramolecular forces in the cellulose lattice, the technique explored in this report could become a useful tool for investigating the fine structure and reactions of cellulose.

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