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Electron Spin Resonance Studies of γ-Irradiated Cellulose. I. Free Radicals in Decrystallized Cellulose

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Synopsis

The types of free radicals formed in decrystallized cellulose prepared from cellulose I and II after γ-irradiation in nitrogen atmosphere at room temperature were studied by ESR spectroscopy. X-Ray diffraction revealed that decrystallized cellulose I and II have the same microstructure. The ESR spectra obtained with the γ-irradiated decrystallized samples are simple. By contacting the irradiated sample with moisture in nitrogen atmosphere, the ESR spectrum changed to a narrow singlet, which gradually decreased in intensity until the spectrum completely disappeared. It was found that the types of free radicals generated in the decrystallized cellulose by γ-irradiation consist of the overlap of singlet and doublet. The singlet spectrum is mainly attributed to alkoxyl radical formed by the rupture of glycosidic linkage at the C 1 or C 4 position, and the doublet spectrum is ascribed to radical formed by hydrogen abstraction from the C 1 position in cellulose molecule.

INTRODUCTION

Abraham and Whiffen[1] detected the presence of free radicals in γ-irradiated cellulose by electron spin resonance (ESR). Since that time, many workers have discussed the radical species and characters in irradiated cellulose. Florin and Wall[2] reported that the ESR spectrum consists of partially resolved five lines with overall width of about 50 G. They found no obvious effect of crystallinity on the yield or nature of free radicals. From the changes in spectral shape upon heating, they suggested that several different types of radical species are generated. Dilli, Ernst, and Garnet[3] also carried out an extensive study on the ESR spectra of free radicals in γ-irradiated cellulose. They examined factors affecting radical concentration, i.e., total dosage, dose rate, temperature, and pretreatment of cellulose, and kinetics of radical decay. They concluded that the observed ESR spectrum is composed of an overlap of singlet and triplet. Arthur and Hinojosa[4–6] reported that the spectra of irradiated cellulose I and II in the dry state are very similar, while the spectra obtained after wetting the irradiated cellulose with water or the spectra

after irradiation of cellulose which had been contacted with regain moisture consist of three lines for cellulose I and five lines for cellulose II. Using oriented cellulosic fibers, they suggested that the differences in the spectra for the irradiated celluloses are probably related to conformation of the trapped radicals which is dependent on differences in the types of crystal lattice between cellulose I and II. Worthington and Baugh[7] measured an ESR spectrum of amorphous cellulose and concluded that ESR method provides a sensitive technique of studying the accessibility of cellulose. Ahmed and Rapson[8] reported ESR spectra of the free radicals in various types of celluloses, viz., amorphous cellulose, recrystallized cellulose, regenerated cellulose, and cellulose crystallites treated with acetone. They concluded that the shape of ESR spectra depends on the fine structure of cellulose.

Although many papers have reported on the ESR studies of irradiated cellulose as described above, the radical species and the radical-trapping regions have not been sufficiently elucidated. In this report, in order to clarify the radical species and the radical-trapping regions in γ-irradiated cellulose, experimental data are presented and discussed based on ESR studies of the reaction of trapped radicals formed in irradiated decrystallized cellulose in nitrogen atmosphere containing moisture.

EXPERIMENTAL

Materials

Scoured cotton cellulose (cellulose I) of Mexican variety and commercial polynosic-type viscose rayon (cellulose II) fibers were purified by extracting with hot ethanol–benzene (1/1 volume ratio) for 24 hr and rinsed several times in distilled water prior to air drying.

Decrystallized cellulosic fibers were prepared as follows. Purified cellulose I and II were acetylated with acetic anhydride–benzene (1/3 volume ratio) for 48 hr at 40°C in the presence of a small amount of sulfuric acid as catalyst. After the celluloses were converted to triacetate, water was added to prepare secondary cellulose acetate with about a 2.6 degree of substitution, and the product was washed successively with benzene, ethanol, and water. The secondary cellulose acetate was dried under vacuum at room temperature, followed by saponifying with absolute ethanol containing 1% sodium hydroxide for 12 hr at 25°C. The product was washed with absolute ethanol for several days to remove the base completely and dried under vacuum at room temperature.

Methods

Decrystallized cellulosic fibers were combed so that fiber axes were mutually parallel and then dried under vacuum for 24 hr at 50°C by using a drybox. Subsequently, the samples were sealed in glass tubes under nitrogen atmosphere at room temperature and irradiated with ^{60}Co γ-rays at an exposure rate of 1.0×10^6 R/hr for 1 hr at room temperature. In the drybox under nitrogen atmosphere, the irradiated fibers were led into quartz

tubes so that the fiber axes were perpendicular to the magnetic field at room temperature for the ESR measurement. ESR spectra were taken with a JES-ME ESR spectrometer with 100 kHz modulation. The microwave power used was 1 mW, and in this condition no saturation effect was observed.

In order to determine the effects of orientations on the spectrum, the well-aligned fibers were cut in the dry-box under nitrogen atmosphere at room temperature and then led into a quartz tube so that the fiber axes were perpendicular to the tube axis.

The degree of crystallinity of cellulose I, cellulose II, and decrystallized fibers was estimated by the x-ray diffraction method.[9] X-Ray diagrams were also taken to check the orientation of the samples.

RESULTS AND DISCUSSION

Crystallinity and Orientation

The x-ray diagrams of cellulose I, cellulose II, and decrystallized cellulose I fibers are shown in Figure 1. The x-ray diagram of decrystallized cellulose II fibers was the same as that of the decrystallized cellulose I. The orientation of cellulose molecules in the decrystallized cellulosic fibers is not so clear as cellulose I and II fibers. The crystallinities of cellulose I, cellulose II, decrystallized cellulose I, and decrystallized cellulose II were 60%, 50%, 14%, and 7%, respectively. Obviously, the crystallinities of decrystallized celluloses were markedly decreased. From these results, it is concluded that the decrystallized cellulose thus obtained is almost amorphous and has random orientation of cellulose molecules and that the microstructure of decrystallized cellulose I is similar to that of decrystallized cellulose II.

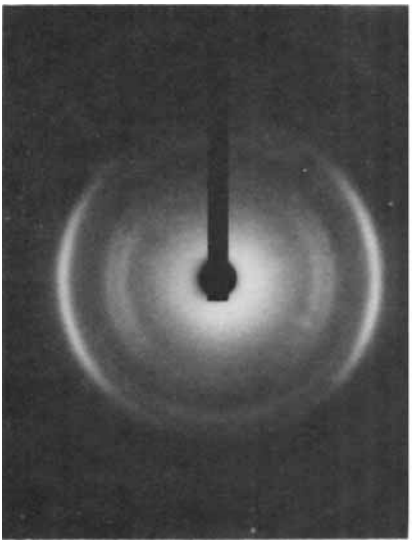
ESR Spectra Under Nitrogen Atmosphere

The ESR spectra of decrystallized cellulose I and II irradiated and measured under nitrogen atmosphere at room temperature are shown in Figure 2, where the fiber axes are perpendicular to the magnetic field. Both spectra are similar in shape. The ESR spectrum of decrystallized cellulose I with the fiber axes parallel to the magnetic field is shown in Figure 3. It is obvious that the spectral shape of the decrystallized cellulose is independent of the orientation of the fibers. The same result was also obtained with decrystallized cellulose II. This result is consistent with the x-ray results.

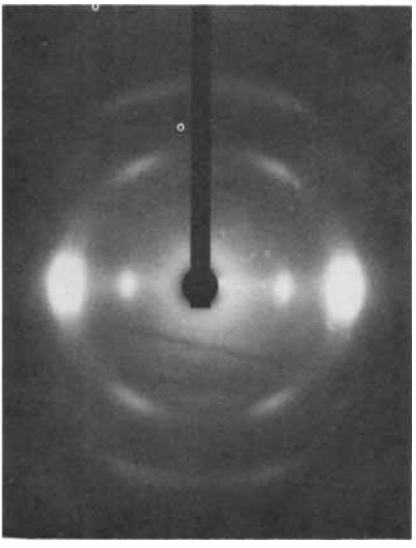
Effects of Moisture

When decrystallized cellulose irradiated under nitrogen atmosphere at room temperature is stored in nitrogen atmosphere with moisture at room temperature for one day, the ESR spectrum changes to that shown in Figure 4. After the storage of a few days, the spectrum changes to a fairly symmetrical singlet as shown in Figure 5. With the more prolonged contact of the sample with moisture, the radical concentration gradually

decreases without changes of the spectral shape until the spectrum completely disappears. Consequently, it is inferred that this spectrum is attributed to only one radical species scavenged by moisture. The line width of the symmetrical singlet spectrum is about 6 G. The narrow singlet spectrum is also independent of the orientation of the fibers.



(a)



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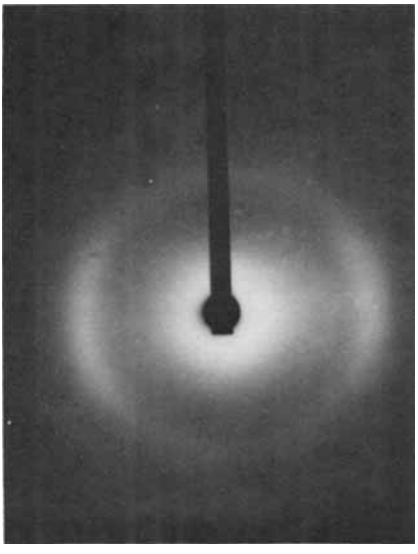

(c)

Fig. 1. X-ray diagrams of cellulosic fibers: (a) cellulose I; (b) cellulose II; (c) decrystallized cellulose I.

When the irradiated decrystallized cellulose was immersed in water for a few minutes at room temperature, the ESR spectrum was not observed. Therefore it can be said that the decrystallized cellulose prepared is almost amorphous and has no regions inaccessible to water.

The spectrum of free radicals scavenged by moisture at room temperature in the decrystallized cellulosic fibers irradiated in dry nitrogen is shown in Figure 6. This spectrum is obtained by subtracting the ESR spectrum of the sample treated under nitrogen atmosphere with moisture from the spectrum of decrystallized cellulose. The shape of this spectrum is similar to the spectrum (Fig. 2a) of the decrystallized cellulose irradiated under

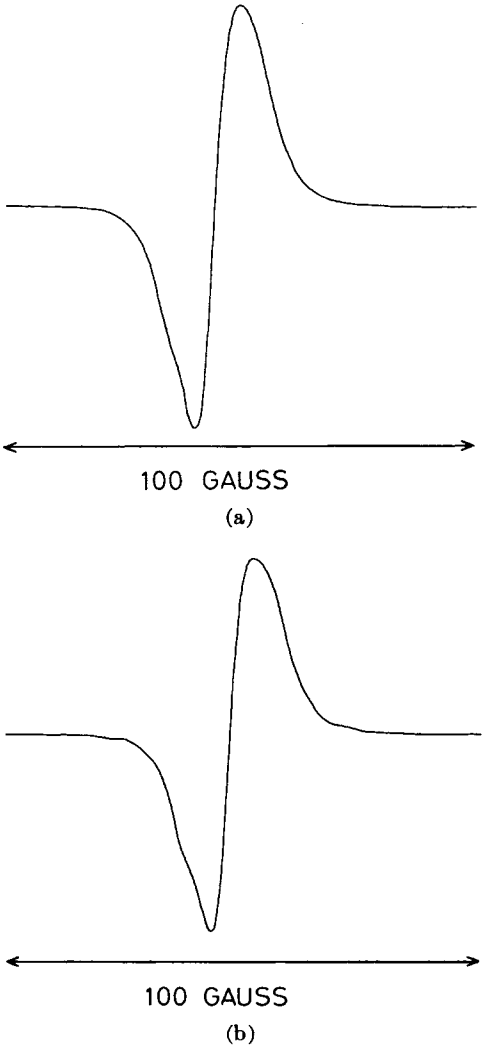

Fig. 2. ESR spectra of free radicals in decrystallized cellulose irradiated in dry nitrogen atmosphere, where fibers are perpendicular to magnetic field: (a) decrystallized cellulose I; (b) decrystallized cellulose II.

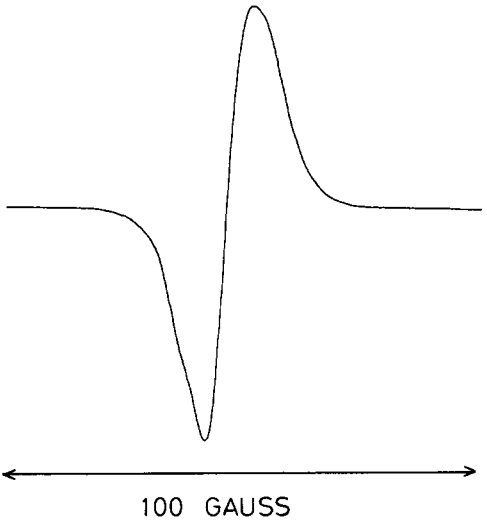

Fig. 3. ESR spectrum of free radicals in decrystallized cellulose I irradiated in nitrogen atmosphere. Fiber axes are parallel to magnetic field.

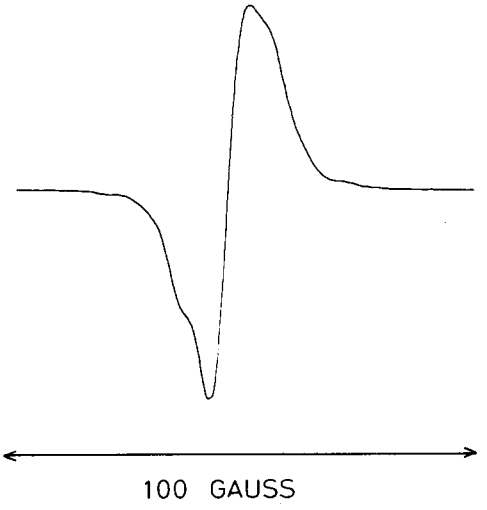

Fig. 4. ESR spectrum of free radicals remaining in decrystallized cellulose I after irradiation and storage in moist nitrogen for one day at room temperature. Fibers are oriented perpendicular to magnetic field.

nitrogen atmosphere without moisture. From the results of Figures 5 and 6, it is assumed that the spectrum of the decrystallized cellulose shown in Figure 2 consists of a singlet with a line width of 6 G and a component from other types of radicals.

A trial was made to obtain the spectrum attributed from other types of radicals. When substracting the singlet spectrum (Fig. 5) from the spectrum of decrystallized cellulose (Fig. 2a), the intensity of the singlet spectrum was multiplied by several times. The doublet spectrum shown in

Figure 7 was obtained by substracting the singlet spectrum (A) from the spectrum of decrystallized cellulose (B); the intensity ratio of spectrum A to spectrum B is 45:100. The hyperfine splitting of the doublet spectrum is about 10 G. It is estimated that this spectrum is also based on only one radical species. The g-values of the singlet and the doublet spectra are 2.0050 and 2.0045, respectively.

When the irradiated decrystallized cellulose was treated at 160°C for 5 min, the spectrum changed to a narrow singlet spectrum which has the same line width and g-value as that shown in Figure 5. A doublet spectrum, which decays during this treatment, was found by the substraction method.

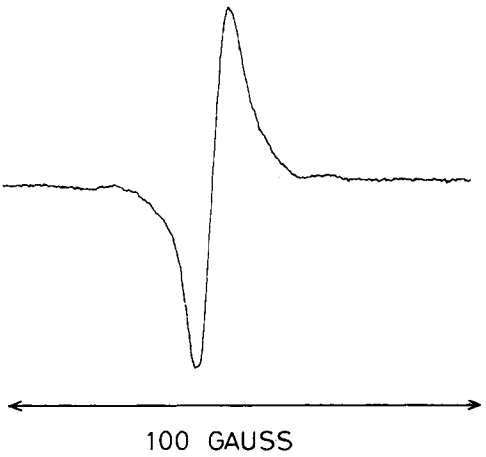

Fig. 5. ESR spectrum of free radicals remaining in decrystallized cellulose I after irradiation and storage in moist nitrogen for a few days at room temperature.

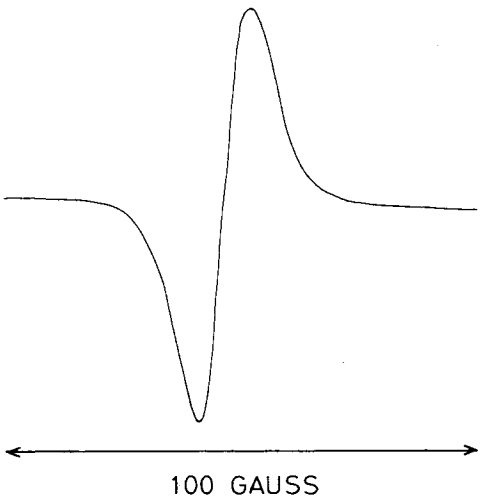

Fig. 6. ESR spectrum of free radicals scavenged by moisture at room temperature in decrystallized cellulose I irradiated in dry nitrogen; (Fig. 2a minus Fig. 5).

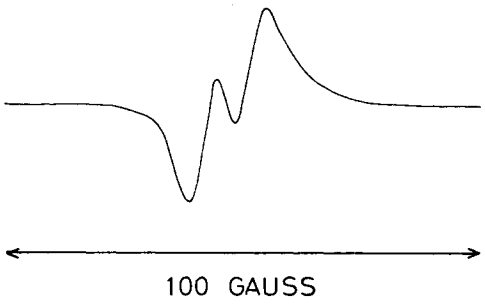

Fig. 7. ESR spectrum of free radicals obtained by subtracting spectrum (Fig. 5) from that (Fig. 2a); the intensity ratio of spectrum (Fig. 5) to spectrum (Fig. 2a) is 45:100.

Radical Species

It is inferred that the spectrum of free radicals generated by γ-irradiation in the decrystallized cellulose is composed of a singlet and a doublet.

The radicals which give the singlet spectrum are considered to be formed on the oxygen atom in the cellulose molecule. It is possible that such radicals originate from a few specific sites: (1) by hydrogen abstraction from a hydroxyl group, (2) by scission of the C—O bond in the glucose unit, or (3) by rupture of the glycosidic linkage at the C 1 or C 4 position. Meanwhile, we found a symmetrical singlet spectrum with a line width of about 7 G when cellulosic fibers were stretched under dry nitrogen atmosphere at room temperature. This spectrum is almost the same as the singlet spectrum (Fig. 5) detected after irradiation and contact with moist nitrogen, except for the difference in intensity. Generally, molecular weight of cellulosic fibers decreases on account of chain scission of the cellulose molecule after γ-irradiation from ^{60}Co. From these facts, the singlet spectrum found in the decrystallized cellulose after irradiation is considered to be due to alkoxyl radical produced by the rupture of glucosidic linkage at the C 1 or C 4 position in the cellulose molecule. Free radicals which give rise to the doublet spectrum with the hyperfine splitting of about 10 G must be caused by abstraction of hydrogen on carbon 1 of the glucose unit. The radical on C 1 should interact with the proton on C 2, and, consequently, the doublet spectrum is observed.

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