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ESR Studies of Photoirradiated Cellulose on Radical Formation and Decay

YOSHITAKA OGIWARA, NYOK-SAI HON, and HITOSHI KUBOTA,
Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

Synopsis

The ESR spectra of untreated samples and photosensitized samples of rayon cellulose, amorphous cellulose, and wood cellulose irradiated with ultraviolet light were studied. Generally, several kinds of spectra were established, and ferric ion photosensitizer increased the yield of free radicals in celluloses on irradiation. The observed five-line spectrum was resolved to be a superposition of single-line, two-line, and three-line spectra. The decay of free radicals of celluloses at ambient temperature was also examined for changes of the pattern and the intensities of ESR spectra. Based on the changes of spectra induced by a warm-up process, three kinds of radicals which gave three components of the five-line spectrum were identified. During the warm-up process, phenomena of radical migration and formation of new radicals synchronized with the decay of radicals were recognized on photosensitized samples of rayon cellulose and amorphous cellulose.

INTRODUCTION

The fact that cellulose is degraded by ultraviolet light has been known since 1883.[1] In general, ultraviolet light brings about a decrease in strength[2–6] and degree of polymerization[4,7–11] of cellulose, and an increase in alkali solubility[2,12,13] and copper number.[14–16] Furthermore, ultraviolet light causes yellowing and browning[17,18] and formation of carbonyl and carboxyl groups[4,8,10,19–23] along the cellulose chain, and a fragmentation of molecules to diversities of neutral and acidic nonvolatile, volatile, and gaseous products.[9,10,24–27] Despite the published data, not enough information is available yet to lead to the acceptance of a mechanism of photodegradation that can account for all the facts. In order to elucidate the mechanism of photodegradation of cellulose, some investigators carried out examinations of free radicals initiated by ultraviolet light with the use of electron spin resonance (ESR) methods. Phillips et al.[28] obtained a narrow singlet ESR spectrum of purified cotton cellulose, and Baugh et al.[29] also obtained a singlet spectrum for dyed cotton cellulose. Although Nanassy et al.[30] suggested that three components were formed in their experiment, they could not demonstrate concrete ESR spectra instead of a singlet-like spectrum. Despite their research effort, the observed singlet spectrum was inadequate to illustrate the mechanism of

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photodegradation of cellulose. The aim of the present work is to gather more information on the formation of radicals by ultraviolet light based on the results of ESR measurement. Furthermore, as no detailed study has been reported about the postirradiation behavior of free radicals, the decaying behavior of the free radicals was also taken into consideration in this article.

EXPERIMENTAL

Materials

Commercial dissolving pulp from softwood was used as wood cellulose sample. Amorphous cellulose was prepared by deacetylating cellulose triacetate under anhydrous conditions by immersing it in a mixture of 75% ethanol and 1*N* NaOH for 20 hr. The sample was then neutralized with glacial acetic acid, washed with 75% ethanol, and dried in a vacuum oven at room temperature.[31] Commercial rayon cellulose was boiled in water for 4 hr only, without any further purification. Photosensitized celluloses were prepared by treating samples with different concentrations of ferric chloride aqueous solution having a liquid:material ratio of 100 ml:1 g, at 45°C for 60 min, then filtering on a glass filter, and air-drying at room temperature.[32]

Methods

For the ESR measurements, the cellulose samples were packed uniformly into a screw-cap quartz tube fitted with rubber gaskets. The tubes containing samples were filled with nitrogen and were rotated at certain times during the irradiation to ensure uniform irradiation. The sources of the ultraviolet irradiation were a superhigh-pressure mercury lamp (Ushio Denki 250D) and a high-pressure mercury lamp (Toshiba Denki H-400P). The former lamp was used with a lamp house having a Pyrex window eliminating wavelengths shorter than 3000–3300 Å. The latter lamp provided predominant wavelengths of 4358 Å, 3650 Å (strongest), 3132 Å, and a trace of 2537 Å. In all cases of ultraviolet irradiation, the distance between light source and sample was about 10 cm, and the sample was kept in liquid nitrogen. ESR spectra were measured with an X-band ESR spectrometer (Japan Electron Optics Lab. Co., Model JES, 3BS-X, 100 kc field modulation). To avoid distortion of the spectra by power saturation, the ESR measurements were carried out at a microwave power of 2 mW. All spectra were recorded at liquid nitrogen temperature (77°K) by inserting a Dewar flask with a quartz finger into the cavity.

RESULTS AND DISCUSSION

Formation of Radical

Typical ESR spectra are shown in Figures 1, 2, and 3, and numerical parameters, in Table I.

TABLE I
Comparison of ESR Spectra of Photoirradiated Celluloses

Sample	Spectrum line	Spacing, gauss		
		Inner peaks	Center peaks	Outer peaks
Rayon cellulose				
Untreated	3	—	24	68
Photosensitized[a]	5	10	30	66
Photosensitized[b]	5	10	32	68
Amorphous cellulose				
Untreated	5	13	27	63
Photosensitized[a]	5	7	30	65
Photosensitized[b]	5	9	31	68
Wood cellulose				
Untreated	3	—	24	64
Photosensitized[a]	5	7	27	65
Photosensitized[b]	5	14	26	66

[a] Irradiated with the high-pressure mercury lamp, 77°K, 60 min.
[b] Irradiated with the superhigh-pressure mercury lamp, 77°K, 90 min.

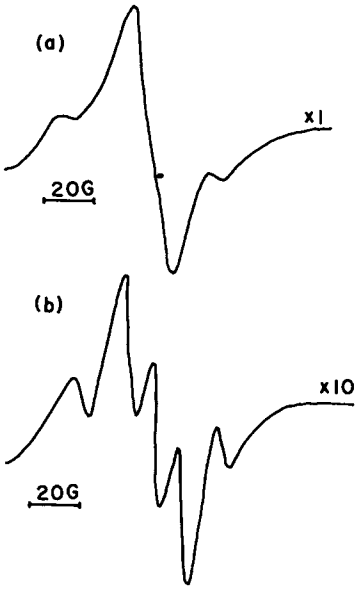

Fig. 1. ESR spectra of untreated sample (a) and photosensitized sample (b) of rayon cellulose, irradiated with the high-pressure mercury lamp for 60 min at 77°K and recorded at 77°K. Number represents relative intensity of the spectrum.

The ESR spectra of untreated and photosensitized samples of rayon cellulose observed at 77°K after irradiation with the high-pressure mercury lamp at 77°K for 60 min are shown in Figure 1. The untreated sample yielded a poorly resolved three-line spectrum of approximately 24 gauss splitting with a g-value of 2.003. When the photosensitized sample, with

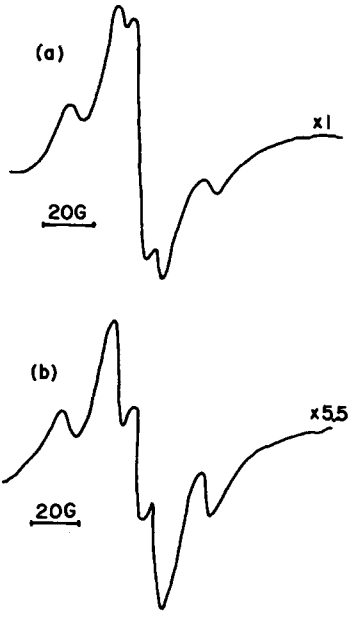

Fig. 2. ESR spectra of untreated sample (a) and photosensitized sample (b) of amorphous cellulose, irradiated with the high-pressure mercury lamp for 60 min at 77°K and recorded at 77°K. Number represents relative intensity of the spectrum.

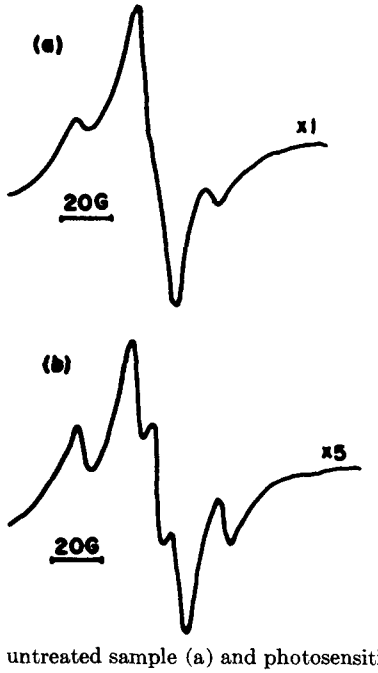

Fig. 3. ESR spectra of untreated sample (a) and photosensitized sample (b) of wood cellulose, irradiated with the high-pressure mercury lamp for 60 min at 77°K and recorded at 77°K. Number represents relative intensity of the spectrum.

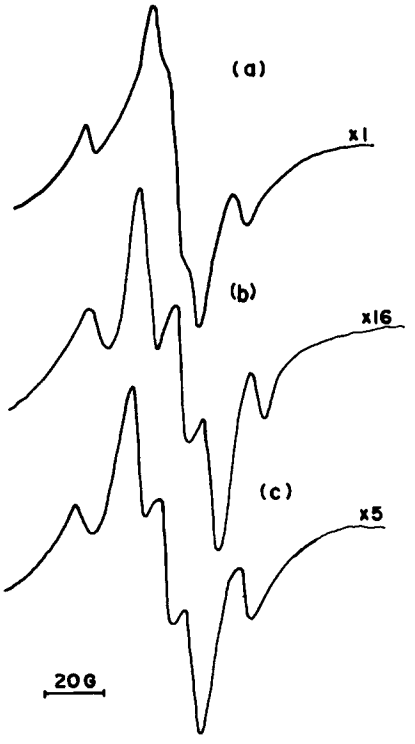

Fig. 4. ESR spectra of photosensitized samples of wood cellulose (a), rayon cellulose (b), and amorphous cellulose (c), irradiated with the superhigh-pressure mercury lamp for 90 min at 77°K and recorded at 77°K. Number represents relative intensity of the spectrum.

5 mmoles/l. ferric ion, was irradiated under the same experimental conditions, five prominent ESR lines was observed, as shown in Figure 1b. It is obvious that, by using the photosensitizer, the ESR spectrum was increased in its intensity and changed from the three-line spectrum to a five-line spectrum with derivative peaks at 10, 30, and 66 gauss (see Table I). The ESR spectra of untreated and photosensitized samples of amorphous cellulose and wood cellulose, irradiated with the high-pressure mercury lamp at 77°K for 60 min, are very similar to the spectra of irradiated rayon cellulose, as shown in Figures 2 and 3. Simply, the untreated samples of cellulose show a three-line spectrum of 24–27 gauss splitting, with the g-value of a free-spin electron, and the photosensitized samples of cellulose show a five-line spectrum with derivative peaks at 7, 27–30, and 65 gauss (see also Table I). The spectrum of untreated sample of amorphous cellulose (Fig. 2a) differ from the other untreated samples, at the center portion, and rather resemble the spectra of photosensitized samples, likely to be a five-line spectrum, which might be due to the differences of the nature and of the lower crystallinity of the sample.

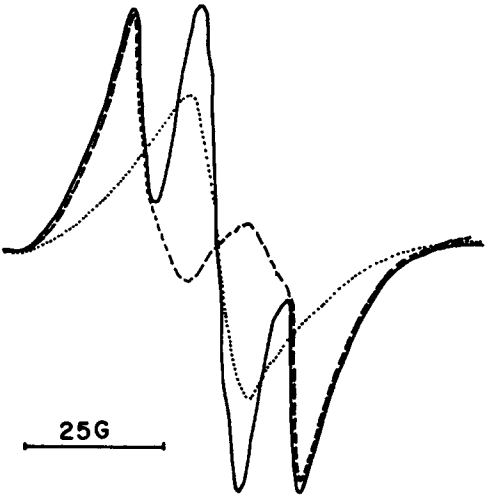

Fig. 5. ESR spectrum of wood cellulose photosensitized with ferric ion (0.1 mmol/l.), irradiated with the superhigh-pressure mercury lamp for 90 min at 77°K and recorded at 77°K. Dashed curve shows a two-line spectrum of hydroxy radicals. Dotted curve shows spectrum after warming at ambient temperature for 2 min.

The photosensitized samples of rayon cellulose, amorphous cellulose as well as wood cellulose, irradiated with the superhigh-pressure mercury lamp at 77°K for 90 min, yielded ESR spectra resembling those observed in the case of irradiation with the high-pressure mercury lamp, as shown in Figure 4. However, it can be noticed that no ESR signal was detected on the untreated samples of rayon cellulose, amorphous cellulose, as well as wood cellulose with the irradiation by the superhigh-pressure mercury lamp. Obviously, the ferric ion photosensitizer plays an important role in radical formation, especially in the wavelength region longer than 3000 Å. When a low concentration of ferric ion such as 0.1 mmole/l. was applied on wood cellulose, irradiation with the superhigh-pressure mercury lamp resulted in a spectrum which had a three-line form with an intensity ratio of approximately 1:1:1, which has not been reported and is given in Figure 5. Since there is no position in the anhydroglucose unit which could by itself yield a 1:1:1 three-line spectrum, it is believed that the spectrum shown in Figure 5 is not a single spectrum originating from a single radical species, but is the superposition of spectra which should be attributed to several radical species. In order to scrutinize whether or not the spectrum shown in Figure 5 is a superposition of spectra, the irradiated sample was subjected to heat treatment, which will be described in details in a subsequent section. Upon heat treatment, the three-line spectrum was changed remarkably to a single-line spectrum, as shown by the dotted curve in Figure 5. In an attempt to trace the short-lived disappearing radicals, a photosensitized sample of pure ice, with 0.1 mmole/l. ferric ion, was irradiated with the high-pressure mercury lamp for 60 min

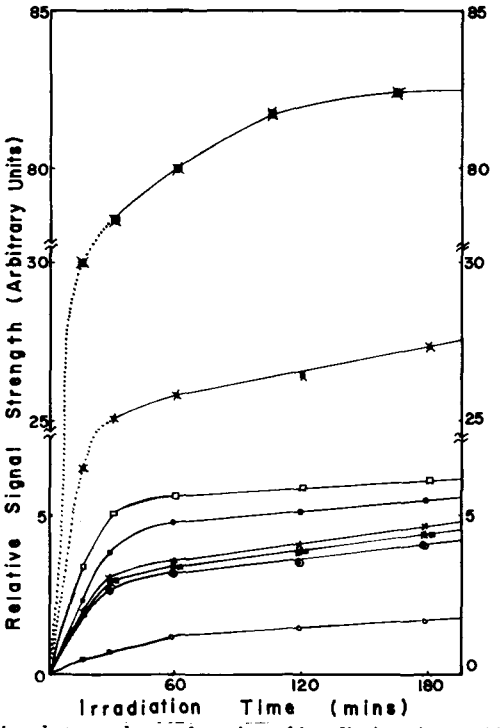

Fig. 6. Relative signal strength as a function of irradiation time at 77°K. Untreated samples irradiated with the high-pressure mercury lamp: (○) wood cellulose; (×) amorphous cellulose; (□) rayon cellulose. Photosensitized samples irradiated with the high-pressure mercury lamp: (●) wood cellulose; (⊠) amorphous cellulose; (⊠) rayon cellulose, and irradiated with superhigh-pressure mercury lamp: (⊙) wood cellulose; (⊠) amorphous cellulose; (■) rayon cellulose.

at 77°K. A two-line spectrum with hyperfine splitting of approximately 43 gauss was observed, which has been assigned to the hydroxyl radical.[33-36] In view of the similarities in hyperfine splitting and g-value and the spectrum which disappeared upon heat treatment of the irradiated sample, as shown in the figure by the dashed curve, the two-line spectrum is proposed to be due to free radicals produced by the photolysis of C—OH at the C_2, C_3, or C_6 positions of the anhydroglucose unit.

Effects of irradiation time on the ESR signal strength generated by the free radicals in irradiated cellulose are shown in Figure 6. It leads us to assume that the differences among the samples, the effects of photosensitizer and wavelength region upon irradiation, greatly affect the formation of free radicals on cellulose, which will be discussed in details in a separate paper.[37] Simply, the free radicals are being formed more easily in the order of rayon cellulose > amorphous cellulose > wood cellulose, which might be partly due to differences in nature. The ESR signal strength observed from the samples irradiated with the high-pressure mercury lamp is greater than that irradiated with the superhigh-pressure mercury lamp due to the

difference in wavelength of the light sources. The intensities of the ESR signal strength increased with irradiation time, whereas, at the initial period of the irradiation, the build-up of radicals was considerable and then decreased monotonically. Generally, when ferric ion was applied as a photosensitizer to the samples, the intensities of the spectra increased markedly. It implies that ferric ion greatly promotes the radical formation on photo-irradiated celluloses.

ESR Spectra with Decay at 77°K

All of the observations of ESR spectra in our experiment were conducted at 77°K. It is necessary to pinpoint the behavior of free radicals at this temperature. For this purpose, the sample was inserted in a Dewar flask with liquid nitrogen and placed into the ESR cavity for measurement without any warming after irradiation at the same temperature. The intensities of the ESR spectra were checked for a long time after the start of the first observation immediately after irradiation. There was practically no change in intensities of ESR spectra for any sample. The shapes of the spectra also did not change throughout this experiment. Therefore, it is clear that radicals are very stable at 77°K.

Changes in Hyperfine Structure of ESR Spectra with Decay at Ambient Temperature

If the samples are treated repeatedly for a certain duration at ambient temperature from 77°K, an array of spectra observed at 77°K can be accumulated, showing the change in hyperfine structure as the resonance signal decays with time. A number of features are of interest. The array of spectra in Figure 7 shows the changes in hyperfine structure as a function of warming time of wood cellulose at ambient temperature. For the sample which was warmed for 2 min and recorded at 77°K, the intensity of the spectrum decreased but still remained a three-line spectrum. When the sample was warmed for 20 min, the intensities of the 1,4-peaks were almost reduced, and a single-line spectrum with very weak intensity was observed (Fig. 7a). The wood cellulose photosensitized with ferric ion, irradiated with the high-pressure mercury lamp upon warming-up process, decreased the spectrum intensity similarly and changed the line shape from the five-line spectrum as shown in Figure 7b. Photosensitized cellulose irradiated with the superhigh-pressure mercury lamp also gave indications of similar changes by warming at ambient temperature, as shown in Figure 7c.

Besides, the three-line spectrum of wood cellulose treated with a concentration of ferric ion as low as 0.1 mmole/l., irradiated with the superhigh-pressure mercury lamp and warmed to ambient temperature, was changed markedly to a single-line spectrum and is shown in Figure 5 by the dotted curve.

With the above findings, it is apparent that the intensity ratio of 1:1:1 three-line spectrum is a superposition made up of a single-line and a two-line

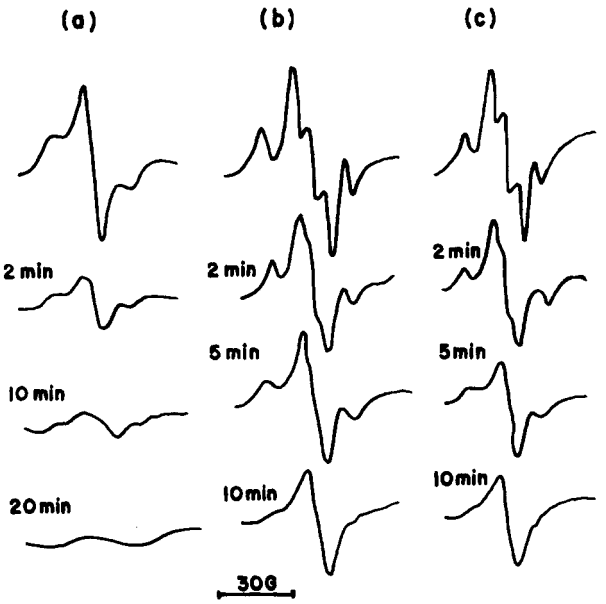

Fig. 7. Change and decay of ESR spectra by warming samples to ambient temperature and recorded at 77°K: (a) wood cellulose irradiated with the high-pressure mercury lamp for 60 min at 77°K; (b) ferric ion-sensitized wood cellulose irradiated with the high-pressure mercury lamp for 60 min at 77°K; (c) ferric ion-sensitized wood cellulose irradiated with the superhigh-pressure mercury lamp for 90 min at 77°K.

spectrum, and the general three-line spectrum is made up of a single-line and a three-line spectrum, which probably consists of a two-line spectrum of small intensity. These three kinds of spectra, namely, a single-line, a two-line, and a three-line spectrum, are probably superimposed to form the observed five-line spectrum. Therefore, it is clear that more than two kinds of radical species are produced with ultraviolet irradiation on cellulose.

Photosensitized samples of amorphous cellulose and rayon cellulose irradiated with the superhigh-pressure mercury lamp at 77°K for 90 min showed a distinctive behavior during the warm-up process, as shown in Figure 8. The aspect of the change of spectra pattern was found to be quite different from that of wood cellulose. The line shape of the spectrum of amorphous cellulose (Fig. 8a) can be divided into two steps. That is, the overall intensity once increased on warming the sample to a warming time of 2 min and thereafter decreases slowly. Rayon cellulose also showed a similar behavior, however, the intensities of the 1,6-peaks, which are marked with arrows in the figure, decreased while the other peaks were increased at the initial step at the beginning of 2 min of warm-up process (Fig. 8b). Decay of the relative intensity of the resonance signal in terms of the height of principal line plotted as function of warming time at ambient temperature is shown in Figure 9. It is clear that the spectrum strengths of photosensitized samples of amorphous cellulose and rayon cellulose which were irra-

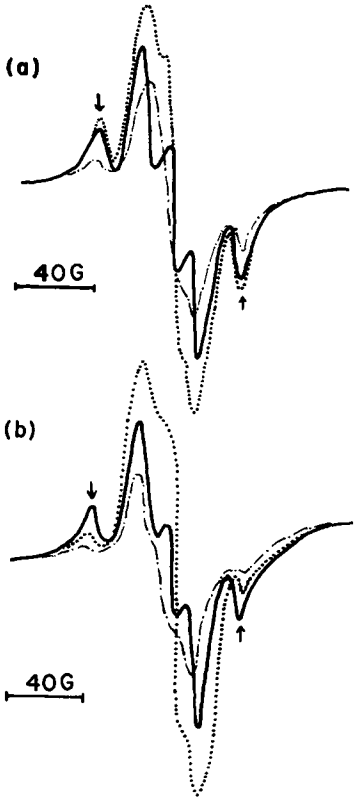

Fig. 8. Change of ESR spectra of ferric ion-sensitized samples of amorphous cellulose (a) and rayon cellulose (b) by warming to ambient temperature and recorded at 77°K. Warming time: (·····) 2 min; (-·—·—·—·-) 5 min.

diated with the superhigh-pressure mercury lamp initially increase and then decrease, while that of the photosensitized wood cellulose shows radical decay at the initial step during the first 4 min, accounting for 50% of all the radicals formed at 77°K. The mobilities or the torsional oscillation of molecular chains of amorphous cellulose and rayon cellulose, which have rather low crystallinity, would reasonably be much more activated than those of wood cellulose with higher crystallinity at the warm-up process, due to the heat energy, so that the cellulose radicals can more easily migrate to form other new radicals in the sample upon warming. The intensities of the ESR spectra seem to be increased in this way, being transformed into radicals with stronger intensities. The decay curves of the photoirradiated samples of treated and untreated celluloses with the high-pressure mercury lamp are shown in Figure 10. At the initial step of the warming, the intensities of the spectra decreased to some extent from the initial value and then decreased slowly upon further warming. Therefore, it is clear that the radicals generated by irradiation with the superhigh-pressure mercury lamp and with the high-pressure mercury lamp are quite

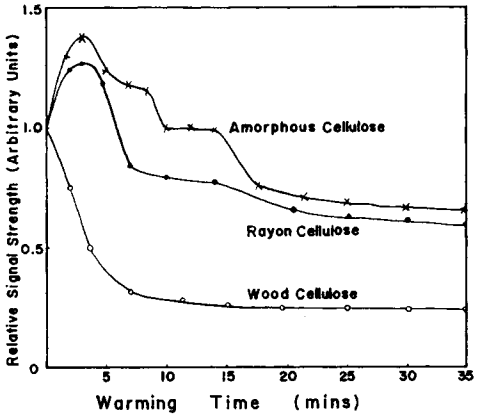

Fig. 9. Decay at ambient temperature of free radicals in various kinds of celluloses irradiated with the superhigh-pressure mercury lamp for 90 min at 77°K.

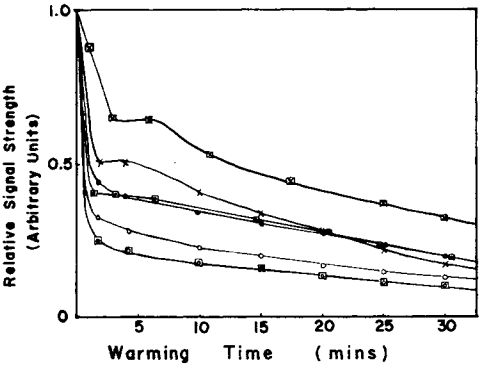

Fig. 10. Decay at ambient temperature of free radicals in various kinds of celluloses irradiated with the high-pressure mercury lamp for 60 min at 77°K. Untreated samples: (×) amorphous cellulose; (●) rayon cellulose; (○) wood cellulose. Treated samples: (⊠) amorphous cellulose; (⊡) rayon cellulose; (◘) wood cellulose.

different in nature, and that the radicals generated by the former light source have a different characteristic showing the phenomena of radical migration and formation of new radicals by warming. On the whole, in either treated or untreated states, the radicals produced on amorphous cellulose and rayon cellulose were rather more stable than wood cellulose toward the warm-up process.

It should be concluded that free radicals of cellulose induced by ultraviolet irradiation all are very stable at liquid nitrogen temperature. Through the changes in the line shape of the ESR spectra with decay at ambient temperature, it was found that the five-line spectrum generated by the free radicals on cellulose is really a superposition of the single-line, two-line, and three-line spectra. It implies that more than two kinds of radicals are produced on cellulose by ultraviolet irradiation.

A more detailed study[37] of the photoinduced radicals on cellulose has been undertaken based on this preliminary investigation.

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