

## Formation of Free Radicals in Photo-irradiated Cellulose. IV. Effect of Ferric Ions

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### Synopsis

The effects of wavelength and concentration of ferric-ion photosensitizer on radical formation in cellulose irradiated with ultraviolet light were studied by means of electron spin resonance spectroscopy. Irradiations were carried out at 77°K. The absorption spectra of ferric complexes with cellulose model compounds, namely, glucose, lactose, and cellobiose, indicate that light absorption of iron-cellulose complex takes place at 365 nm, to initiate free-radical formation. A three-line electron spin resonance spectrum with a relative signal intensity 1:1:1 was observed when the sample was treated with 0.1-mmole/l. ferric ion and irradiated with light  $\lambda > 3400 \text{ \AA}$ . Five-line spectra with different signal intensities were observed when the sample was irradiated with light  $\lambda > 2800 \text{ \AA}$  and  $\lambda > 2537 \text{ \AA}$ , respectively. Further, the 1:1:1 three-line spectrum was immediately changed to a five-line spectrum when the sample was re-irradiated with light  $\lambda > 2537 \text{ \AA}$ . The concentration of ferric ion strikingly affected the radical formation in cellulose and caused changes of the line-shape and of the relative signal intensities of the spectra. The sample with 0.1-mmole/l. ferric ion exhibited the 1:1:1 three-line spectrum; however, when the concentration was increased to 20 mmoles/l., a prominent five-line spectrum with relative signal intensity 1:2:0.8:2:1 was observed, when the sample was irradiated with light  $\lambda > 3400 \text{ \AA}$ . On the basis of these findings, it is apparent that several kinds of radical species can be formed by employing suitable wavelengths and varying concentrations of ferric ion.

### INTRODUCTION

It is well known that the photodegradation of cellulose occurs via free-radical routes. However, knowledge of the nature and mechanism of free-radical formation in photo-irradiated cellulose is still meager. Photo-induced graft-copolymerization of cellulose has received considerable attention in recent years, especially in the area of using metal salts (or inorganic ions) as initiators of the reaction.<sup>1-9</sup> Unfortunately, the radical species produced after photo-irradiation—as well as the mechanism of radical formation in cellulose, leading to graft-copolymerization—are still not completely clear.

In view of this, we have carried out electron spin resonance (ESR) studies of radical formation in cellulose irradiated with ultraviolet light. Some factors influencing the radical formation—namely, wavelength,<sup>10</sup> moisture content,<sup>11</sup> and photosensitizers<sup>12</sup>—have been described.

In previous studies,<sup>12</sup> we have confirmed the effect of various photosensitizers on radical formation in cellulose irradiated with ultraviolet light by means of ESR spectroscopy. We found that metal salts (especially the ferric ion) greatly affected radical formation. In spite of the important effect of the metal salts on the photochemical behavior of radical formation, no information is yet available in the literature, regarding ESR studies.

In order to elucidate in more detail the effect of metal salts on free-radical formation in sensitized cellulose irradiated with ultraviolet light, ferric ion was conveniently chosen as a model sensitizer. The present work is primarily concerned with the effects of wavelength and of the concentration of ferric ion on the radical formation in sensitized cellulose.

## EXPERIMENTAL

### Materials

Commercial dissolving pulp from softwood was used as the cellulose sample. The air-dried pulp was beaten in a mixer: the portions passing through a net of 40-mesh screen were discarded, and the remaining parts were used. The ferric chloride employed as a photosensitizer in this study was reagent grade and was used without further purification.

Photosensitized samples were prepared in different concentrations by treating cellulose in ferric chloride aqueous solution having a liquid:material ratio of 100 ml:1 g at 45°C for 60 min, then filtering the treated samples through a glass filter, and air-drying at room temperature.<sup>12,13</sup>

### Methods

Details of the ESR experimental procedures employed have been given elsewhere.<sup>10</sup> ESR spectra were measured at liquid nitrogen temperature (77°K). The first- and second-derivative spectra were recorded on most samples in order to obtain the maximum amount of information about the radical species present. Conventional 100-kHz detection was used, the first-derivative signal being obtained by modulation at 100 kHz and the second-derivative by modulation at 100 kHz and at 80 Hz. The sources of 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 quartz window emitting a spectrum ranging from 2800 Å to 6000 Å, or having a pyrex window eliminating wavelengths shorter than 3400 Å. The latter lamp provided predominant wavelengths of 4358 Å, 3650 Å (strongest), and 3132 Å, and a trace of 2537 Å. In all cases of ultraviolet light irradiation, the samples were kept at the temperature of liquid nitrogen.

Ultraviolet absorption spectra were recorded on a Cary 15 Recording Spectrophotometer. A reference solution of ferric chloride was used. The reading of the absorption spectrum was made 3 min after the solutions had been mixed.

## RESULTS AND DISCUSSION

## Effect of Wavelength

When cellulose was irradiated with light  $\lambda > 2537 \text{ \AA}$ , an intricate seven-line spectrum with two doublet signals at either side was observed; when cellulose was irradiated with light  $\lambda > 2800 \text{ \AA}$  only the seven-line spectrum was observed, whereas, no ESR signal was detected when the sample was irradiated with light  $\lambda > 3400 \text{ \AA}$ , as described in Part I.<sup>10</sup>

The formation of free radicals in cellulose sensitized with ferric ion (0.1-mmole/l.), irradiated with three different light sources emitting different wavelengths—i.e.,  $\lambda > 3400 \text{ \AA}$  from the superhigh-pressure mercury lamp through its pyrex window,  $\lambda > 2800 \text{ \AA}$  from the superhigh-pressure mercury lamp through its quartz window; and  $\lambda > 2537 \text{ \AA}$  from the high-pressure mercury lamp—at 77°K, is shown in Figures 1, 2, and 3. Although no ESR signal was detected from the nonsensitized cellulose irradiated with light  $\lambda > 3400 \text{ \AA}$ ,<sup>10,13</sup> when ferric ion was applied as a sensitizer an ESR spectrum was detected, as shown in Figure 1. This indicates that ferric ion affected the radical formation in cellulose even at the wavelength longer than 3400  $\text{\AA}$ . According to the Photochemical Law, light absorption is characteristic of a particular structure. Only the light that is absorbed by a molecule can be effective in producing photochemical change in the molecule.<sup>14</sup> Free radicals were formed in cellulose when irradiation was carried out with light longer than 3400  $\text{\AA}$ ; this implied that some chromophoric groups must be present in the system. In order to elucidate the new absorbing center in photosensi-

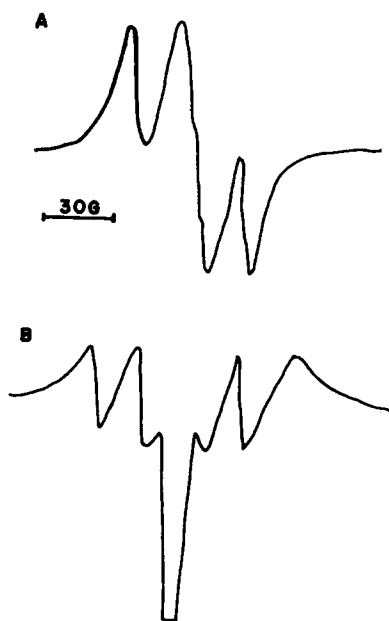


Fig. 1. ESR spectra of cellulose sensitized with 0.1-mmole/l. ferric ion, irradiated with superhigh-pressure mercury lamp through pyrex window at 77°K for 90 min, and recorded at 77°K. A shows the first- and B shows the second-derivative ESR spectrum.

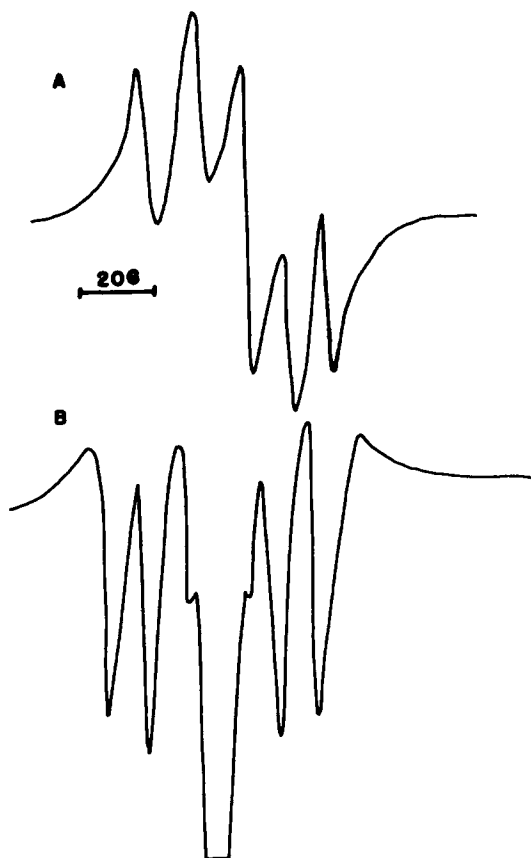


Fig. 2. ESR spectra of cellulose sensitized with 0.1-mmole/l. ferric ion, irradiated with superhigh-pressure mercury lamp through quartz window at 77°K for 60 min. A shows the first- and B shows the second-derivative ESR spectrum.

tized cellulose, the absorption spectra of the ferric complexes were studied. Since no suitable method is currently known which will allow a direct determination of absorption spectra of fiber cellulose, the absorption spectra of ferric complexes with model compounds, namely glucose, lactose, and cellobiose, were examined, as shown in Figure 4. It is generally agreed that carbohydrate is transparent beyond the region of 3000 Å.<sup>15</sup> In this study, however, all complexes show significant absorption curves with maximum at 365 nm. From this, it can be presumed that cellulose formed a stable complex with ferric ion, absorbing light at 3650 Å, to initiate free-radical formation. The ESR spectrum of cellulose-iron complex irradiated with the light longer than 3400 Å is shown in Figure 1. It is clear that a three-line spectrum with an intensity ratio of approximately 1:1:1 was formed. Since the intensity ratio is not the expected ratio for interaction of an electron with two equivalent protons (theoretical intensity ratio 1:2:1), and 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 1 is not a single spectrum originating from a single radical species, but is the superposition of spectra that should be attributed to several radical species. A result that supports this assumption was obtained by measurement of the second-derivative ESR ab-

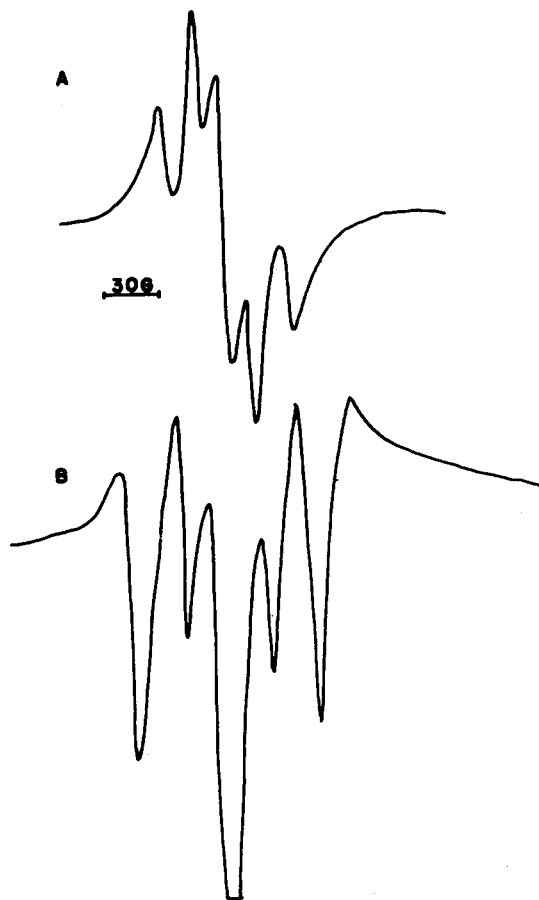


Fig. 3. ESR spectra of cellulose sensitized with 0.1-mM/l. ferric ion, irradiated with high-pressure mercury lamp at 77°K for 60 min. A shows the first- and B shows the second-derivative ESR spectrum.

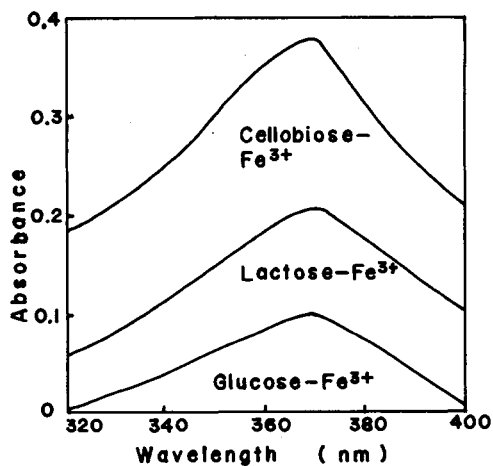


Fig. 4. Absorption spectra of cellulose-ferrous ion complexes. Concentrations of cellulose model compounds and ferric ion are 100 mM/l. and 1 mM/l., respectively.

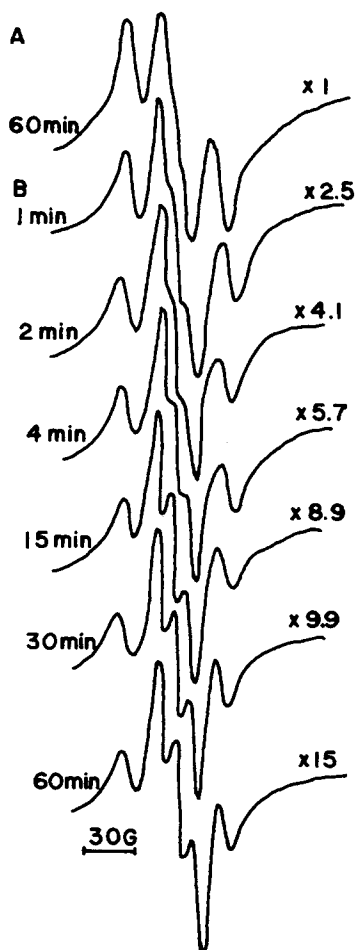


Fig. 5. ESR spectra of cellulose sensitized with 0.1-mmole/l. ferric ion, irradiated at 77°K with superhigh-pressure mercury lamp through pyrex window (A) for 60 min, and with high-pressure mercury lamp (B). Multiplication number represents the ESR relative signal intensity.

sorption curve (curve B of Fig. 1), which provided a definite hyperfine structure. A careful examination indicates that the spectrum was a poorly resolved multiplet, probably a five-line spectrum, generating from several kinds of radical species.<sup>13</sup> In an attempt to test the effect of further irradiation on changes in the line-shape of the ESR spectrum observed, irradiation was prolonged for as long as 360 min. Such further irradiation increased the overall intensities of the signal, but did not introduce any new features into the spectrum. Seemingly, the line-shape of the spectrum was virtually independent of the irradiation time.

When this irradiated sample was re-irradiated with light longer than 2537 Å from the high-pressure mercury lamp for only 1 min, the spectrum began to change and some humps began to emerge. When the irradiation time was prolonged to 4 min, a poorly resolved five-line spectrum was observed. After the sample was re-irradiated for 15 min, this change became more remarkable and a sharp five-line spectrum could be readily distinguished, as shown in Figure 5. When the sensitized sample was irradiated with light longer than

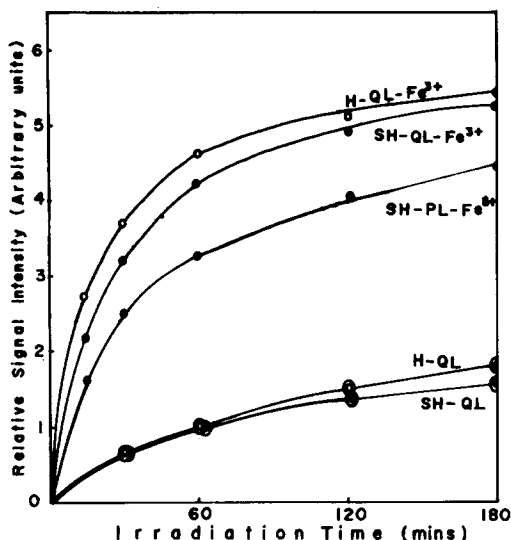


Fig. 6. Rate of formation of free radicals in cellulose irradiated with ultraviolet light: H-QL = high-pressure mercury lamp with quartz body; SH-QL = superhigh-pressure mercury lamp with quartz window; SH-PL = superhigh-pressure mercury lamp with pyrex window.  $\text{Fe}^{3+}$  = 0.1 mmole/l.

2800 Å from the superhigh-pressure mercury lamp through its quartz window, a five-line spectrum was observed, as shown in Figure 2. Moreover, when the sample was irradiated with light longer than 2537 Å from the high-pressure mercury lamp, it also exhibited an apparent five-line spectrum (Fig. 3), although the magnitudes of the ESR relative signal intensities were different, as is evident from the study of the rate of radical formation that is given in Figure 6. On the grounds of the above features, this could be ascribed in part to the differences of the wavelengths employed and the differing power supplies of the lamps.

#### Effect of Concentration of Ferric Ion in Cellulose

The ESR spectra of celluloses sensitized with different concentrations of ferric ion, irradiated with light longer than 3400 Å from the superhigh-pressure mercury lamp through its pyrex window for 90 min at 77°K, are illustrated in Figure 7.

When the ferric-ion concentration was as low as 0.1 mmole/l., cellulose resulted in a spectrum that had a three-line form with a relative signal intensity ratio 1:1:1. When the concentrations were increased, the ESR spectra observed also increased in relative signal intensities, so that the 1:1:1 three-line spectrum was changed to a five-line spectrum with an intensity ratio 1:2:0.8:2:1 at 20 mmoles/l. It is remarkable that the line-shape of the spectrum was essentially dependent on the magnitude of the ferric-ion concentrations. Moreover, it is also clear that an increase in ferric-ion concentration caused an increase in radical yield, as is evident from the study of the increase of the relative signal intensity of the spectrum.

In closing, it might be pointed out that the ferric ion plays an important role in radical formation in cellulose and, especially, that the sensitizing ef-

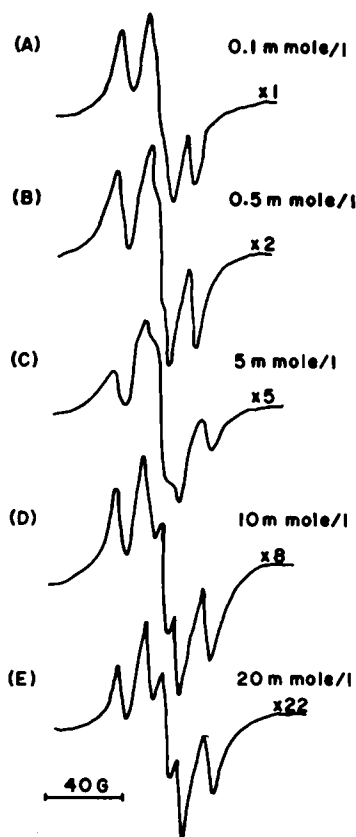


Fig. 7. ESR spectra of celluloses sensitized with various concentrations of ferric ion, irradiated with superhigh-pressure mercury lamp through pyrex window at 77°K for 90 min. A: 0.1 mmole/l.; B: 0.5 mmole/l.; C: 5 mmoles/l.; D: 10 mmoles/l.; E: 20 mmoles/l. Multiplication number represents the ESR relative signal intensity.

fect is more pronounced in the wavelengths longer than 3400 Å, i.e., the near-ultraviolet region. It was shown that by irradiation under suitable experimental conditions (i.e., different wavelengths and different concentrations of sensitizer in the system) several kinds of spectra, that is to say, several kinds of radical species, could be obtained.

Finally, it should be noted that each postulated photochemical reaction entails the formation of hydrogen atoms and/or formyl radicals as indicated in the previous studies.<sup>10</sup> Although no such atoms and radicals are detected by ESR spectroscopy in this work, it is reasonable to suppose that these lighter, highly mobile fragments obtain excess energy from the photosensitizer and recombine with themselves or, possibly, enter into secondary reactions with the parent molecule even at the low temperature of liquid nitrogen. In the case of the nonsensitized sample, the absorbed ultraviolet light imparts only slightly more energy than is needed to break the chemical bonds. Thus, little excess energy is imparted to the radicals produced with ultraviolet irradiation, and the hydrogen atoms and formyl radicals, which are still quite mobile, are not lost to the system.

All the spectra observed in this study are interpreted, and individual free-



radical species that generated the spectra observed are identified on the basis of the results obtained from a warm-up process. Although more detailed discussions of these experimental data will be presented in Parts VII and VIII of this series, it is convenient to summarize them here. Simply, the 1:1:1 three-line spectrum is a superposition made up of a single-line, a two-line, and a three-line spectrum, where the two-line component is predominant. The prominent five-line spectrum is made up of a single-line, a two-line, and a three-line spectrum, where the two-line spectrum is insignificant. It is believed that the free radicals that generated these spectra are formed by interaction of radiant energy with the cellulose-iron complex and/or by intramolecular energy transfer. The localization of energy initiated depolymerization, dehydrogenation, and dehydroxylation reactions, and these reactions produced several kinds of radical species. Spectra derived from these radical species are probably superimposed to form the intricate spectra.

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