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### Fundamental Degradation Processes Relevant to Solar Irradiation of Cellulose: ESR Studies

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## Fundamental Degradation Processes Relevant to Solar Irradiation of Cellulose: ESR Studies

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### ABSTRACT

The objective of this work was to study the effect of solar radiation on cellulose by means of ESR techniques. It is shown by ESR spectra that outdoor exposure of cellulose to concentrated sunlight, regardless of the presence of oxygen and sensitizer, causes the polymer to degrade via free-radical processes. Particularly, it is shown that main-chain scission occurs under solar radiation. This phenomenon is accompanied by the formation of peroxide when oxygen is present. It is also revealed that photooxidation leads ultimately to discoloration of the polymer at exposed surfaces.

### INTRODUCTION

The deterioration of commercial cellulose products in outdoor applications has been ascribed to a complex set of reactions in which

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both the absorption of light and the presence of oxygen are involved. The first observation of this deleterious effect of sunlight on cotton and linen fabrics dates back to 1883, when Witz established that the photodegradation of the polymer is chemical in nature [ 1]. In the years following, a veritable torrent of papers related to photodegradation of cellulose has appeared. Several reviews on this field are available [ 2-9].

Historically, the most popular method for studying the photochemical reaction of cellulose is the method of analysis of degradation products, which involves a process of deduction based on observations of the overall behavior. In order to obtain an insight into the actual mechanism of the photochemical process involved, however, such a conventional method is inadequate, as it cannot provide unequivocal evidence for the formation of primary products, free radicals, or information on their structure.

A variety of techniques for detecting free radicals formed upon irradiation of polymers have been established. Among these, electron spin resonance (ESR) is one of the most direct and informative methods and has been used extensively during the past two decades for detecting and identifying free radicals in polymer systems [ 10-13]. In practice, many investigators have obtained fruitful results from ESR spectral studies of cellulosic radicals with various types of light sources [ 14-18]; however, if we are interested mainly in effects which occur in a terrestrial atmosphere, we must restrict our attention to a rather narrow band of the electromagnetic spectrum. In fact, we must concern ourselves primarily with the energy emitted by the sun and transmitted by the earth's atmosphere.

Thus, for our present purpose, we shall consider primarily the effects of sunlight, in the presence of oxygen and photosensitizer, on degradation of cellulose. The fundamental degradation processes will be examined by ESR techniques, which have not been previously applied to this problem.

## EXPERIMENTAL

Commercial dissolved pulp from softwood was used as the cellulose sample. The pulp was beaten in a blender, the portions passing a net of 40-mesh screen were discarded, and the remaining parts were collected and purified by extracting with hot ethanol-benzene (1:1 volume ratio) for 20 hr and rinsed with distilled water several times prior to air drying. The ferric chloride employed as a photosensitizer in this study was reagent grade and used without further purification. Ferric ion-sensitized samples were prepared by treating cellulose in aqueous ferric chloride solution at a liquor:solids

ratio of 100 ml:1 g at 45°C for 60 min, then filtering through a glass filter and air drying at room temperature [19, 26].

In an attempt to shorten the exposure time required for degradation, while avoiding extraneous effects or unnatural spectra distributions (as are observed with artificial light sources), schemes have been devised to concentrate natural sunlight on samples with 50 mirrors (each mirror is  $30 \times 30 \text{ cm}^2$ ), which were focused by a quartz lens into a parallel beam passing through sample tubes, as a kind of outdoor exposing device. These accelerated outdoor exposures were carried out between June and August at Isesaki-shi, Japan.

When irradiations were carried out at ambient temperature, in order to prevent overheating or burning of samples, forced air was circulated by fans, and the quartz lens systems were not used to focus the sunlight. When irradiations were carried out at 77° K, quartz sample tubes were inserted in Dewar flasks filled with liquid nitrogen.

For the ESR measurements, the cellulose sample was packed uniformly into a screw-cap quartz tube fitted with a rubber gasket and then evacuated at ambient temperature by a vacuum-line system ( $10^{-3}$  Torr) or filled with oxygen prior to solar radiation. The quartz tubes used were specially selected. It should be noted that no observable signals were produced in the quartz tubes by light during the irradiation sequences.

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 1 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

### Energy Distribution of Solar Radiation

According to the principles of photochemistry, the degradation by light is due to the absorption of specific wavelengths of light by specific chemical molecules in cellulose. Although pure cellulose is not a good absorber of ultraviolet light and some questions exist about the nature of the absorbing functional groups, some ultraviolet light is in fact absorbed by cellulose, as shown by the existence of cellulose fluorescence [21]. Further, the unavoidable trace impurities in cellulose might absorb light and initiate photochemical reactions within the polymer. For instance, irradiation of cellulose

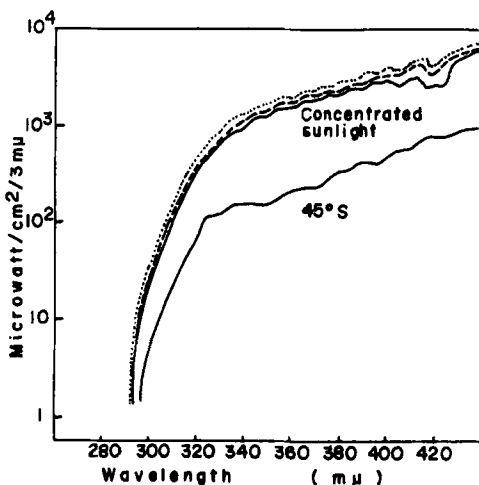


FIG. 1. Spectral energy distribution of concentrated solar radiation in (—) June, (- -) July, and (· · ·) August compared with direct sunlight at 45° S at summer noon (clear sky).

with the 514.5 nm line of an argon-ion laser results in fluorescence which has been attributed to trace amounts of transition metals in cellulose [22]. Once energy is absorbed in the system, photochemical reactions can occur.

Solar radiation, is usually defined as electromagnetic radiation between the wavelengths of 286 and 400 nm [23]. The absence of ultraviolet radiation (below 286 nm) is accounted for by its efficient absorption by atmospheric ozone and oxygen. The energy distribution of solar radiation as a function of wavelength, as observed at Isesakishi, is shown in Fig. 1. It was found that the exposure device used in this work provided about ten times as much radiation as ordinary 45° South exposure at the same location, and it also provided a trace of radiation at wavelengths below 300 nm.

The energies of light quanta and the bond dissociation energies of various bonds in cellulose are summarized in Table 1. For direct photolysis of cellulose, the exact energy required will depend on the nature of the bond and the atoms involved. The cleavage of either carbon-carbon or carbon-oxygen bonds of cellulose requires an energy of 80-90 kcal/mole. Removal of a hydrogen atom requires about 100 kcal/mole. Therefore, the energy requirements for the degradation

TABLE 1. Energy of Solar Radiation and Approximate Bond Dissociation Energies of Chemical Bonds in Cellulose Molecule

Wavelength (nm)		Energy (kcal/mole)	Bond dissociation
200		142.9	
253.7		112.7	
280		102.1	O-H
-----			
286	solar radiation ↓	100.0	
288.9		99.0	C-H
300		95.3	
307.5		93.0	C-O
325		88.0	
340		84.1	
344.6		83.0	C-C
360		79.4	
400		71.5	

of a cellulose molecule will be met by ultraviolet light of wavelength 3400 Å or shorter. It is apparent that the bond energies of the chemical bonds of cellulose are in the range of solar ultraviolet light. If energy is supplied in this form to these chemical bonds they can cleave and photodegradation will take place. Although we did not show that free radicals were formed in cellulose when irradiated with a super high-pressure mercury source ( $\lambda > 3400 \text{ \AA}$ ) [19, 20], ESR spectra of cellulose radicals were detected by Phillips et al. [16]. These investigators, using a high-pressure mercury lamp coupled with filters, found that light in the region from 3250 to 4000 Å is absorbed and results in formation of free radicals in cellulose. They concluded that the most active wavelength was 3600 Å, resulting in the most efficient formation of free radicals in the cellulose molecule. It is apparent that photochemical reactions will take place when cellulose is exposed to solar radiation.

## ESR Spectra of Photoirradiated Cellulose

### Untreated Cellulose

When purified cellulose was subjected to solar radiation for 360 min in vacuum and in oxygen at ambient temperature, no ESR signals were observed from the sample. When irradiation was carried out in vacuum at 77° K, a spectrum which had a five-line form with an intensity ratio of approximately 1:1.3:0.1:1.3:1.3 was observed (Fig. 2a). The intensity ratio of this spectrum is not the expected ratio for the interaction of the electron with four equivalent protons. It is believed that more than one kind of spectrum derived from several kinds of radicals are superimposed. In order to ascertain whether or not the spectrum shown in Fig. 2a represents a superposition of spectra, the exposed sample was subjected to a warming-up process [19, 24], that is, the sample was warmed from 77° K to 273° K for 3 min, and the spectrum recorded again at 77° K. Upon this treatment, the five-line spectrum changed remarkably to a single-line spectrum with a line-width of 16 gauss, as shown in Fig. 2b. Clearly, the two outermost lines with overall width of 24 gauss disappeared. Subtraction of the spectrum of Fig. 2b from that of Fig. 2a gives a doublet spectrum which is shown in Fig. 2c. Separation of these peaks is 24 gauss. From these spectra, it suggests that the singlet ( $\Delta H_{\text{msl}} = 16 \text{ G}$ ) and the doublet (24 G splitting) spectra, derived from two kinds of radical species, are superimposed.

When the sample was irradiated in oxygen under identical experimental conditions, a poorly resolved multiplet was observed, as shown in Fig. 3a. The relative signal intensity of this spectrum is reduced to 65% as compared with the spectrum observed from the sample exposed in vacuum (Fig. 1a). Concurrently, a new satellite line with weak signal intensity, which is marked with an arrow in Fig. 3a, was observed. Upon the warming-up process, the spectrum changed to a single-line spectrum (Fig. 3b) with a line-width of 15 gauss. Since the change of spectrum is analogous to that in the preceding sample, it is plausible to consider that a singlet and a doublet spectrum generated from two kinds of radicals are superimposed. The satellite line also disappeared upon warming up, which implies that this line is derived from a radical which is quite unstable upon warming. As the photochemical reaction was conducted in oxygen, and the relative signal intensity of the spectrum observed was reduced, there is little doubt that oxygen acts as a free radical scavenger in the system, and that free radicals formed in cellulose probably combine with oxygen to form peroxide radicals. Hence,

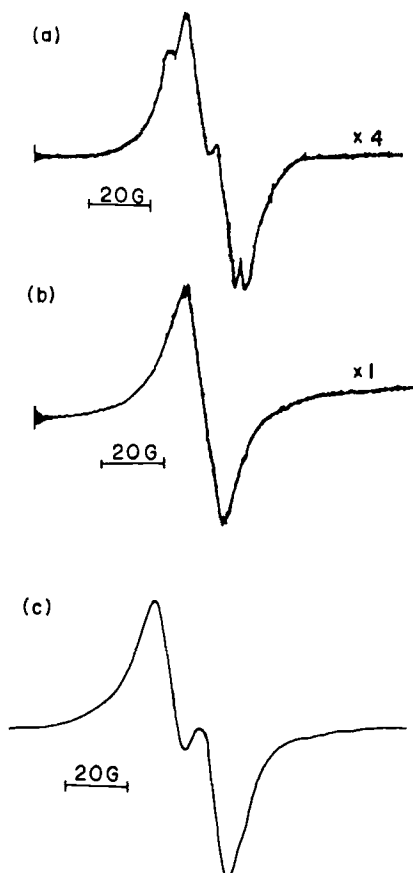


FIG. 2. ESR spectra of cellulose following exposure to concentrated solar radiation in vacuo at 77° K for 360 min: (a) immediately after the exposure; (b) same sample as (a) after warming for 3 min at 273 K, spectrum recorded at 77° K; (c) ESR spectrum obtained from graphical smoothing of spectra (a) and (b). Multiplication number represents the ESR relative signal intensity.

it is reasonable to suggest that the satellite line shown in Fig. 3 is derived from the peroxide radicals. This satellite line was not detected when the exposure was carried out in vacuo. In addition, the presence of peroxides in the exposed samples was detected by



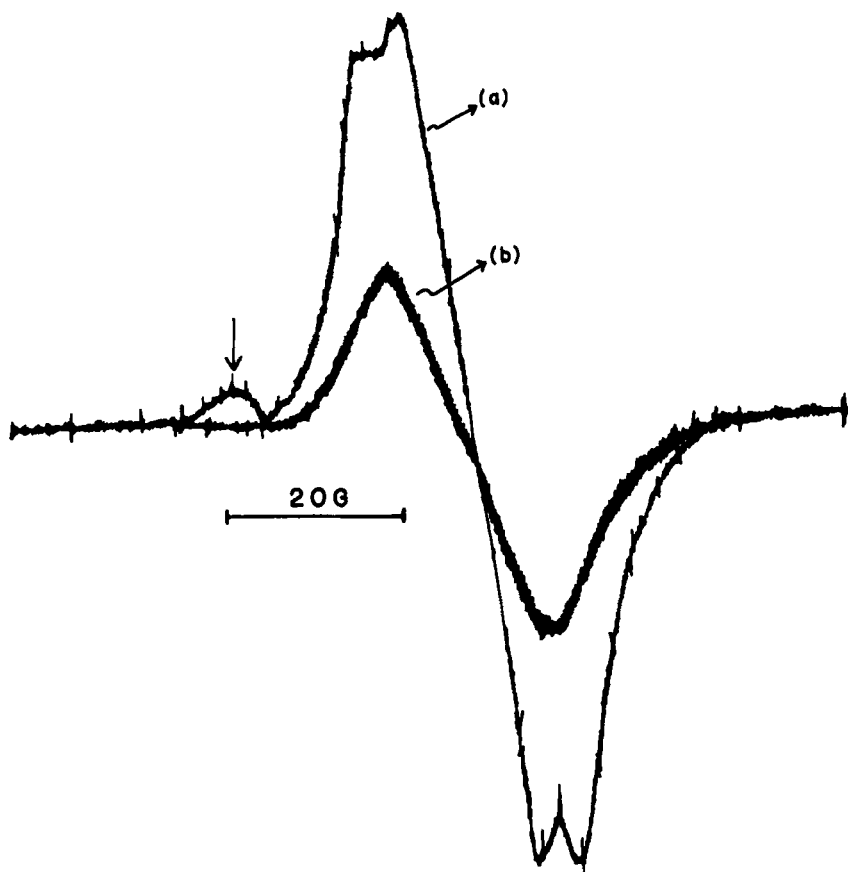


FIG. 3. ESR spectra of cellulose following exposure to concentrated solar radiation in oxygen at 77° K for 360 min: (a) immediately after the exposure; (b) same sample as (a) after warming for 3 min at 273° K, spectrum recorded at 77° K.

an iodometric method but could not be determined quantitatively due to the small sample weights used. Volatile product collection and identification from exposure of cellulose by mass spectrometry did not succeed because of the small quantities evolved.

It should be reported that when samples were exposed in oxygen at ambient temperature and at 77° K, yellowing of the surfaces of

samples was observed in most of the samples. Alternately, slight yellowing of samples was observed when exposure was carried out in vacuo. There is little doubt that yellowing reaction of cellulose is caused by oxidation in the presence of oxygen.

#### Ferric Ion-Sensitized Cellulose

Many chemicals including metal ions are known to be capable of promoting free-radical formation in cellulose irradiated with ultraviolet light [19, 25, 26]. In the present study, ferric ion-sensitized cellulose (5 mmole/liter) was subjected to solar radiation. When the samples were exposed in vacuo at ambient temperature for 360 min, no ESR signal was detected; conversely, in oxygen, a diffuse single-line spectrum ( $\Delta H_{msl} = 18$  G) of low intensity was detected (Fig. 4). This implies that free radicals are able to form under these conditions but that the concentration of free radicals is very low.

When the ferric ion-sensitized sample was exposed in vacuo at 77° K for 360 min, a prominent five-line spectrum with overall width of 66 gauss was observed (Fig. 5a). Since this spectrum exhibited intensity ratio 1:3.5:0.3:3.5:1 which is different from the theoretical intensity ratio, there is no doubt that several kinds of spectra were superimposed to form the five-line spectrum observed. When the exposed sample was subjected to warming for 3 min, the five-line

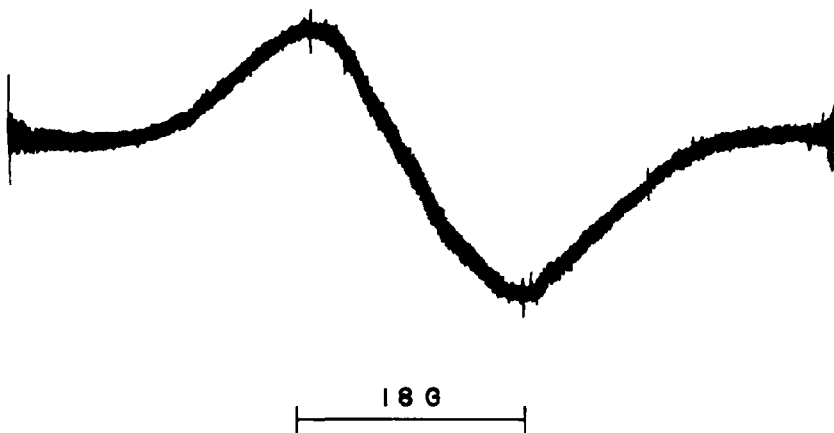


FIG. 4. ESR spectrum of ferric ion-sensitized cellulose following exposure to concentrated solar radiation in oxygen at ambient temperature for 360 min, and recorded at 77° K.

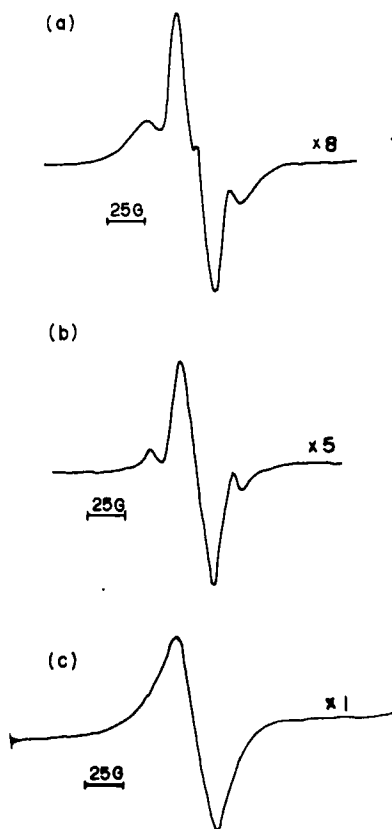


FIG. 5. ESR spectra of ferric ion-sensitized cellulose following exposure to concentrated solar radiation in vacuo at  $77^{\circ}\text{K}$  for 360 min: (a) immediately after the exposure; (b) same sample as (a) after warming at  $273^{\circ}\text{K}$  for 3 min; (c) same sample as (a) after warming at  $273^{\circ}\text{K}$  for 5 min. All spectra were recorded at  $77^{\circ}\text{K}$ . Multiplication number represents the ESR relative signal intensity.

spectrum changed to a three-line spectrum (33 G splitting) with intensity ratio 1:5:1 (Fig. 5b). Upon further warming (5 min), the three-line spectrum changed to a singlet spectrum with a line-width of 22 gauss. Therefore, the observed five-line spectrum could be interpreted on the basis of the relative signal intensity and spacings of hyperfine splitting, with the help of an atlas of ESR spectra [27]. The decomposition of the spectrum is shown in Fig. 6.

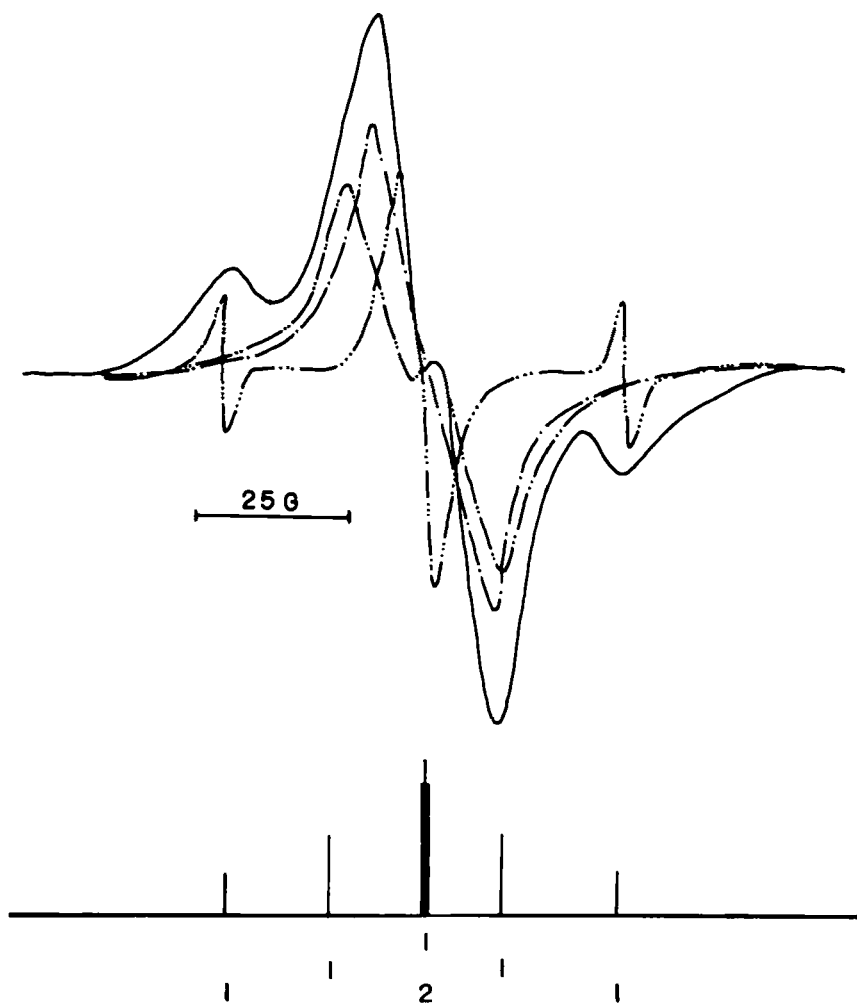


FIG. 6. Decomposition of ESR spectrum of ferric ion-sensitized cellulose, showing positions and theoretical relative intensities of (—) the lines obtained and for (---) singlet, (- · · -) doublet, and (- · · · -) triplet spectra.

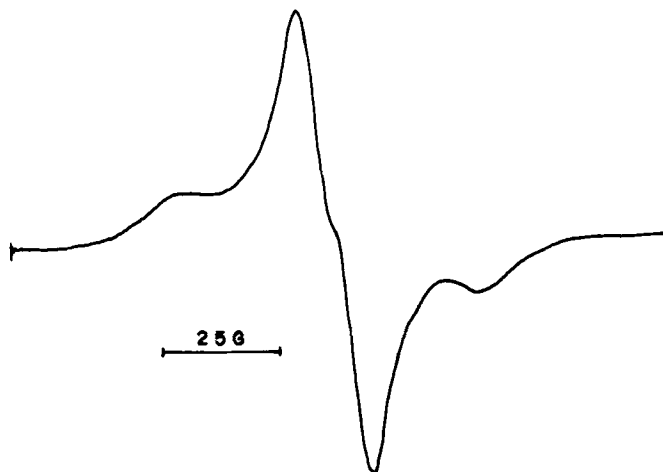


FIG. 7. ESR spectrum of ferric ion-sensitized cellulose following exposure to concentrated solar radiation in oxygen at 77° K for 360 min and recorded at 77° K.

When the sample was exposed in oxygen at 77° K for 360 min, a similar spectrum was observed, although the relative signal intensity is reduced (Fig. 7). Upon warming, similar decaying behavior was confirmed; therefore, the spectrum is resolved as a superposition of a singlet ( $\Delta H_{\text{msl}} = 20$  G), a doublet (24 G splitting), and a triplet (33 G splitting) spectrum. When exposure was carried out in oxygen, peroxy radicals were also formed simultaneously, but superimposed by the three-line spectrum and not detected. Although ESR signals were detected from cellulose exposed to concentrated solar radiation, it should be mentioned here that the relative signal intensities of the spectra were very weak as compared to those observed from samples irradiated with a super high-pressure mercury lamp (250 W,  $\lambda > 2800$  Å) or a high-pressure mercury lamp (400 W,  $\lambda > 2537$  Å). The comparison is summarized in Table 2. It is apparent that the rate of free-radical formation in cellulose under concentrated solar radiation is much less than that under artificial lamp irradiation. This could be due to the stronger intensity of the latter sources.

#### Mechanisms of Free Radical Formation

The above findings make it possible to distinguish direct photolysis and photosensitized degradation of cellulose, which proceed by different mechanisms of free-radical formation.

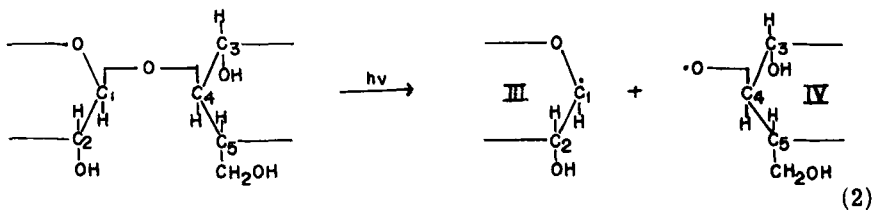
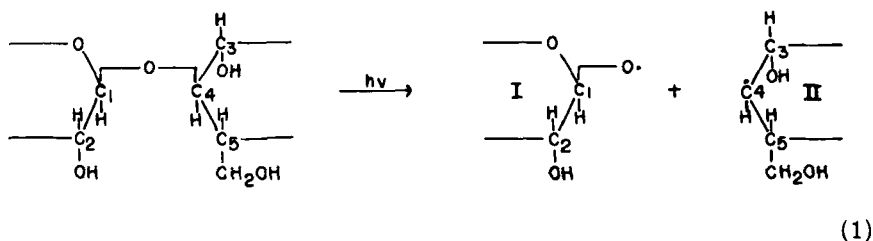
TABLE 2. Comparison of ESR Relative Signal Intensity from Cellulosic Radicals formed by Various Types of Radiation at 77° K

Light source	Irradiation time (min)	Sample <sup>a</sup>	Atmosphere	Spectrum	Relative signal intensity	Reference
Concentrated solar radiation	360	A	Oxygen	5(4 + 1)	0.1	This work
	360	A	Vacuum	5	0.15	This work
	360	B	Oxygen	5	0.7	This work
	360	B	Vacuum	5	1.0	This work
Super high-pressure mercury lamp (3400 Å)	90	A	Oxygen	1	0.2	[28]
	90	A	Vacuum	Nil	0	[28]
	90	B	Oxygen	5	34.1	[25, 26]
	90	B	Vacuum	5	38.5	[25, 26]
Super high-pressure mercury lamp (2800 Å)	60	A	Oxygen	5	15.4	[28]
	60	A	Vacuum	9(7 + 2)	20.5	[25, 26, 28]
	60	B	Oxygen	5	55.3	[25, 26, 28]
	60	B	Vacuum	5	59.3	[25, 26]
High-pressure mercury lamp (2537 Å)	60	A	Oxygen	5	22.4	[28]
	60	A	Vacuum	11(7+2+2)	25.7	[19, 28]
	60	B	Oxygen	5	83.9	[25, 26]
	60	B	Vacuum	5	92.5	[25, 26]

<sup>a</sup>Sample: A, untreated cellulose; B, ferric ion (Fe<sup>3+</sup>)-sensitized cellulose.

The mechanisms of initiation of free radicals in these two processes are, in general, by interaction of radiant energy with the cellulose molecule, and/or intramolecular energy transfer. The localization of the energy initiates depolymerization and dehydrogenation reactions.

In purified cellulose under solar radiation two kinds of radicals which generated a singlet and a doublet spectrum are confirmed as described in the previous section. It has been suggested that the ketonic carbonyl groups or acetal groups in cellulose are the light-absorbing groups [20, 29, 30], and that chain splitting occurs by photolysis of the bond between C<sub>1</sub> and C<sub>4</sub> of the anhydroglucose units in cellulose, with the production of free radicals. Generally, chain scission by the photoenergy of the light is the primary reaction resulting in radical formation. The reactions (1) and (2) are therefore assumed.



It is well known that alkoxy radicals of polymer exhibited a singlet spectra with line-width of 15 gauss [31-33] which applies to radicals I and IV. Concurrently, radical II is expected to interact strongly with a hydrogen at the C<sub>4</sub> position, and weak interaction with hydrogens at C<sub>3</sub> and C<sub>5</sub> positions to form a complicated spectrum, whereas, radical III is expected to interact strongly with a hydrogen at C<sub>1</sub> and weakly with a hydrogen at C<sub>2</sub>, reasonable, to form a doublet spectrum with a line-width of about 24 gauss. This radical species has been assigned by many carbohydrate chemists [34-37]. Accordingly,

the radicals III and IV probably form the doublet and the singlet spectra, respectively, as we observed from the purified cellulose after solar radiation. Since free radicals formed on the C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> positions of the anhydroglucose units by dehydrogenation should give rise to a triplet spectrum [37, 38], which was not observed in this study, this can be ruled out. Dehydrogenation from hydroxyl groups in anhydroglucose units also can be immediately ruled out since it requires more energy (102 kcal/mole) than the solar radiation provides (see Table 1). Dehydroxylation and dehydroxymethylation reactions can be precluded since no hydroxyl radicals (doublet, 43 G splitting [19, 26]), hydroxymethyl radicals (triplet, 18 G splitting [39, 40]), and formyl radicals (doublet, 129 G splitting [20]) were observed in this work. On the other hand, the cleavage of the C<sub>2</sub> and C<sub>3</sub> bond seemed to yield a doublet spectrum [41]; however, this spectrum was not detected in the system, because the two radicals, held together only by hydrogen, recombine rapidly [42, 43].

It is not known to what extent the free radicals were formed by irradiation with sunlight in the presence of oxygen. However, from the observation of the free radicals by means of ESR study, it is evident that light-induced radicals react with oxygen to form peroxide radicals. Although the peroxide content was not determined quantitatively in this work, it is believed that a small amount of peroxides was produced when the sample was irradiated in oxygen, as suggested by many authors [15, 28, 44, 45].

Free radicals were formed in cellulose upon concentrated solar radiation; nevertheless, no ESR signal could be detected at ambient temperature. This is because the radicals formed are too mobile at this temperature, and diffuse quickly through the sample and are quenched by interaction with other radicals or by recombination.

Photosensitized processes in cellulose are more complicated. Generally, cellulose and metal ions easily form chelates in nature [46-50]. The complex formed from cellulose and ferric ion has also been confirmed by Hon [26]. According to this study, it is plausible to consider that a chelate of cellulose with iron produced a new chromophoric group with absorption at 365 nm. Due to this new absorption center, radiant energy was absorbed by this complex followed by an energy transfer process to cellulose. Hence, the localization of the energy initiated photodegradation reactions. From the ferric ion-sensitized samples, three kinds of free radicals generated three kinds of spectra, namely, singlet, doublet, and triplet, were confirmed. The singlet and doublet spectra could be interpreted as derived from radicals III and IV as discussed above. The triplet spectrum could be due to a radical formed at the C<sub>2</sub>, C<sub>3</sub>,



C<sub>5</sub>, or C<sub>6</sub> positions of the anhydroglucose units by dehydrogenation. Dehydroxylation was not taken into consideration in this study for reasons discussed above.

Finally, it should be stated that ferric ions may produce ESR signals upon solar irradiation [51, 52]. By comparing lineshape, splitting constants, and g-value of the spectra of photosensitized cellulose and ferric ions [53] with reference to the literature data, we are convinced that the spectra observed in this work are generated from free radicals in cellulose rather than from the ferric ions.

Based on the above findings, it is apparent that solar radiation is capable of degrading cellulose under appropriate conditions. An understanding of this important fact can be applied to explain deterioration of commercial cellulose products by sunlight. With a better understanding of the mechanism of outdoor photodegradation, there undoubtedly will be an increased effort to produce cellulosic materials with increased photoresistance and also to develop more effective stabilizers for these commercial products.

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