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Photo-Induced Radicals in Glucose and Cellobiose

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Synopsis

Photo-induced radicals in glucose and cellobiose, the model compounds of cellulose molecule, were studied by ESR spectrometry. Very poor formation of radicals in glucose as compared to those in cellobiose was observed. However, a spectrum showing a singlet line was easily produced by the use of light involving shorter wavelengths. It was estimated to be due to the radical formed at the reducing C_1 position of glucose molecule. Photo-irradiated cellobiose showed an ESR spectrum such as that of cellulose. By paper chromatography, the photo-irradiated cellobiose was confirmed to split into glucose through scission of glucosidic bonds in the molecule. The ESR spectrum of the acid-hydrolyzed cellulose similar to that of the unhydrolyzed sample was a seven-line spectrum, but the relative signal intensity was here markedly low. This phenomenon seems to be caused by the reduction of amorphous portion in the samples due to acid hydrolysis. It was concluded that the glucosidic bonds in cellobiose and cellulose molecules are very active toward light and play an important role in the radical formation in photo-irradiated samples.

INTRODUCTION

It has been considered that the scission of glucosidic bonds is the principal process[1,2] in the photoreaction of cellulose. In our ESR studies[3,4] of photo-irradiated cellulose, cellulose radicals showing singlet and triplet spectra were mainly observed. The radicals showing a singlet spectrum and appearing in all irradiated samples were inferred to be the alkoxy radicals produced at either the C_1 or C_4 position of the glucose unit by scission of glucosidic bonds.

The purpose of this study is to verify the reactivity of glucosidic bonds in the cellulose molecule toward light by comparing ESR spectra of photo-irradiated glucose and cellobiose, the model compounds of cellulose molecules, or acid-hydrolyzed cellulose to those of cellulose samples.

EXPERIMENTAL

Sample

Glucose and cellobiose used as the model compounds of cellulose molecule were reagent grade. Commercial dissolving pulp from softwoods (NDP) was used as cellulose sample. NDP samples were treated with 3*N* aqueous hydrochloric acid solutions at 100°C for 3 or 5 hr (ratio of material to liquid, 1:100) to

prepare a acid-hydrolyzed sample. Degrees of polymerization of the unhydrolyzed, 3-hr, and 5-hr hydrolyzed samples determined from the intrinsic viscosity in a cupriethylenediamine solution[5] at 25°C were 720, 110, and 91, respectively.

Chromatographic Analysis

Paper-chromatographic analysis of cellobiose irradiated in water with a high-pressure mercury lamp at room temperature was carried out by employing a developer of a mixture of *n*-buthanol, acetic acid, and water with ratio 4:1:5 and a detecting reagent of ammoniacal silver nitrate. Each spot was identified by comparing R_f values to those of glucose and cellobiose as the standard.

Measurements of ESR Spectra

A quartz tube (5-mm diameter) filled with the samples and substituted with nitrogen was put in an insertion-type Dewar flask and exposed at 77°K to radiation from a Toshiba high-pressure mercury lamp H400-P ($\lambda > 2200$ Å) or a Ushio superhigh-pressure mercury lamp HB-251A ($\lambda > 2800$ Å). All ESR measurements were made at 77°K with a Japan Electron Optics Laboratory JES-ME-X. Resonance spectra were observed with the x-band and 100 Kc field modulation.

RESULTS AND DISCUSSION

ESR spectra of cellubiose and cellulose irradiated with light of $\lambda > 2800$ Å for 2 hr are shown in Figure 1. The cellulose sample exhibited a seven-line spectrum. In the previous paper,[4] we have clarified on the ESR spectrum of photo-irrradiated cellulose that several components such as singlet with a line width of 16 gauss, doublet and triplet with splitting factors of 24 and 34 gauss, respectively, are superimposed on the seven-line spectrum. The singlet and doublet components were ascribed to the cellulose radicals produced by the scission of glucosidic bonds, while the triplet component resulted from the dehydrogenation of cellulose main chains. No radicals were detected on glucose employing the same

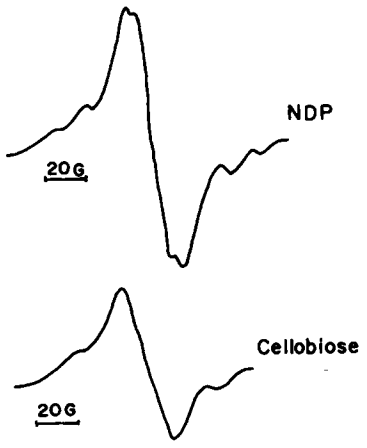

Fig. 1. ESR spectra of cellulose and cellobiose irradiated with light of $\lambda > 2800$ Å at 77°K for 2 hr.

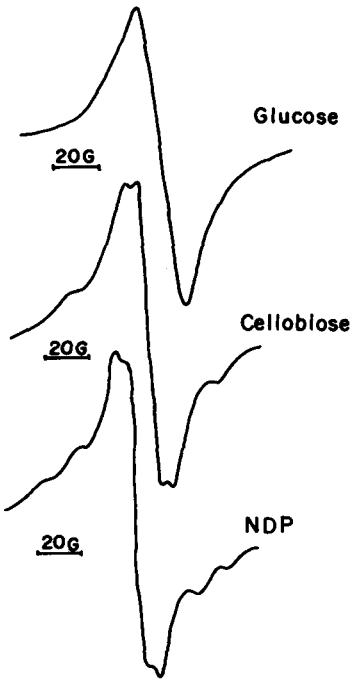

Fig. 2. ESR spectra of glucose, cellobiose, and cellulose irradiated with light of $\lambda > 2200$ Å at 77°K for 60 min.

irradiation conditions as those producing the cellulose radicals. However, cellobiose was observed to produce radicals showing a three-line spectrum under similar conditions. Thus, in the irradiating system with a light of $\lambda > 2800$ Å, glucose has little ability to form radicals as compared to cellobiose and cellulose.

In the system with light of $\lambda > 2200$ Å, glucose produced radicals showing a singlet spectrum with a line width of 23 gauss, as shown in Figure 2. On the other hand, the spectra of cellobiose and cellulose were almost alike in shape, indicating the formation of radicals of the same kind in the two molecules. Bains[6] reported that the ESR spectrum of γ-irradiated cellobiose is quite similar to that of rayon. As mentioned above, the spectra of the photo-irradiated glucose and cellobiose distinctly differed from each other, suggesting a difference in the radicals formed in both molecules by photo-irradiation.

Collins[7] examined the ESR spectrum of γ-irradiated glucose and deduced that the spectrum consists of two components, one a triplet which can be ascribed to radicals produced by either dehydroxylation at C_6 position or dehydrogenation at C_5 position of glucose; and the other, a singlet caused by radicals produced at the reducing C_1 position. It is inferred that the singlet spectrum obtained by us on the photo-irradiated glucose might correspond to the one observed by Collins. Tsuji[8] observed in his ESR studies of photo-irradiated ethylene–acrolein copolymer that acyl radicals are produced by the dissociation of a hydrogen atom from an aldehyde group, giving a sharp singlet spectrum.

Figure 3 shows relationships between relative signal intensity and irradiation time concerning glucose and cellobiose in the irradiating system with a light of $\lambda > 2200$ Å. A considerably higher intensity of photo-irradiated cellobiose was

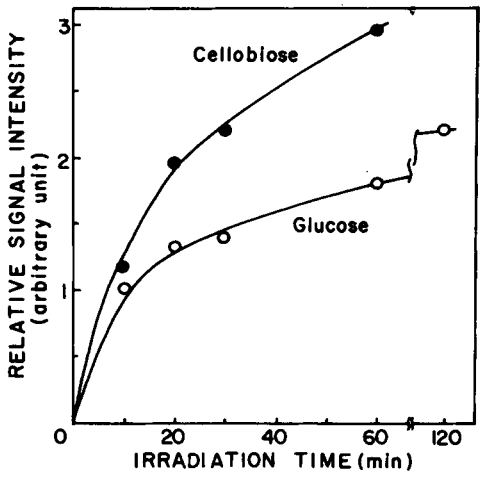

Fig. 3. Formation of radicals in glucose and cellobiose in irradiating system with light of $\lambda > 2200$ Å.

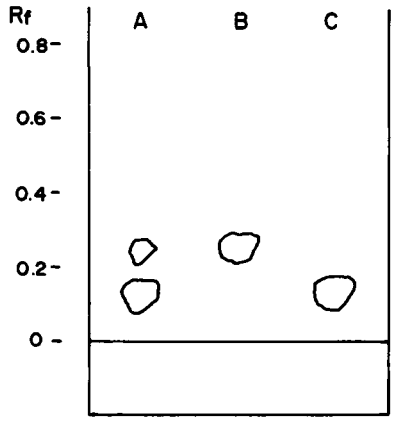

Fig. 4. Chromatographic analysis of cellobiose (A) irradiated with light of $\lambda > 2200$ Å at room temperature for 3 hr. Standards: (B) glucose; (C) cellobiose.

observed as compared to that of glucose, indicating a more ready radical formation in cellobiose. The reason of the higher activity of cellobiose toward light than glucose must be attributed to the glucosidic bond involved in the cellobiose molecule.

Paper-chromatographic analyses of cellobiose irradiated with light of $\lambda > 2200$ Å at room temperature were examined, and the results are shown in Figure 4. The chromatographs of 3 hr-irradiated cellobiose as well as glucose and cellobiose are shown in the figure. The glucose spot was detected in the chromatographs of all irradiated cellobiose, which became clearer with longer irradiation time. This is considered to be due to the formation of glucose from the photo-induced scission of glucosidic bonds of the cellobiose molecule. Dilli and Garnett[9] examined the chromatographic analysis of γ-irradiated disaccharides and observed the formation of glucose owing to the scission of glucosidic bonds. In the photo-irradiation of cellulose,[10] similar scission of glucosidic bonds seems to take place, leading to a sharp lowering in the degree of polymerization of samples.

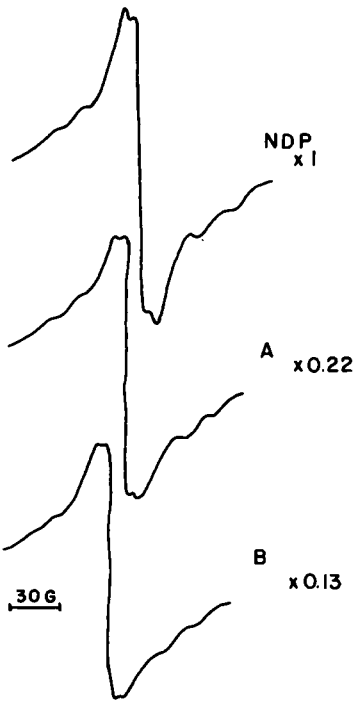

Fig. 5. ESR spectra of acid-hydrolyzed NDP irradiated with light of $\lambda > 2200$ Å at 77°K for 60 min. (A) and (B) represent the ESR spectra of NDP samples hydrolyzed for 3 hr and 5 hr, respectively. Number represents the relative intensity of the spectrum.

Accordingly, it is natural to consider that the glucosidic bond of the cellobiose molecule is very active toward light, resulting in the same radical formation as in the case of cellulose.

Figure 5 shows the ESR spectra of acid-hydrolyzed cellulose samples. The hydrolyzed samples exhibited seven-line spectra like those of unhydrolyzed samples, but their relative signal intensities were markedly lower. This lowering of the activity toward light seems to be mainly caused by a reduction of the amorphous portion of the sample. It has already been reported[11] that the attack of light at the crystalline portion of cellulosic materials is very difficult. The glucosidic bond in the amorphous portion, being easily injured by the action of light, can be broken away by acid hydrolysis, resulting in inactive radical formation.

From above examination, scission of glucosidic bonds is considered to be the principal process in the photoreaction of cellobiose and cellulose, and it is concluded that the glucosidic bonds play an important role in the radical formation in photo-irradiated samples.

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