ESR Study of Intramolecular Energy Transfer in the Radiolysis of Cellulose Furoates

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Synopsis

The substitution of 2-furoyl, 5-methyl-2-furoyl, 2-furanacryloyl, or 5-bromo-2-furoyl groups on fibrous cotton cellulose increased the radiation resistance of cellulose, as indicated by the retention of strength of the modified fibrous cellulose at high dosages of γ-radiation compared with that of irradiated, unmodified fibrous cellulose. The presence of electropositive or electronegative substituents on the furan groups did not significantly change their radioprotective effects for cellulose. Electron spin resonance (ESR) spectra of irradiated celluloses indicated that the long-lived free radical sites were similar, if not the same, in both irradiated, unmodified, and modified celluloses. The radioprotective effects of furan groups for cellulose were attributed to absorption of energy from the secondary radiations, primarily the secondary electrons, by the groups due to their π-electron-type structures. The absorption of energy by the groups apparently decreased the localization of energy on carbon C_1 or C_4 on the cellulose molecule which would result in depolymerization and loss in breaking strength of the fibrous cellulose. The radioprotective effects of furan groups for cellulose were similar to those of benzenoid groups.

INTRODUCTION

When cotton cellulose in the solid state is exposed to γ-radiation from ^{60}Co, a small fraction of the incident energy from the γ-radiation is randomly absorbed in the cellulose molecule which initiates ionization of some of the low atomic number elements which compose the cellulose. γ-Radiation of lower energy than the incident radiation and electrons are formed in the cellulosic structure. These secondary radiations can initiate ionization reactions similar to those of the incident radiation and chemical reactions, until the radiations have passed through the cellulosic structure or until their energy has been absorbed by the cellulose molecule. The absorption of energy from the secondary electrons formed would be several times more likely than absorption of energy from the γ-radiation.[1] The localization of energy in the cellulose molecule initiates chemical reactions in the molecule, generally of the oxidative degradation type.[2,3] The de-

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polymerization reaction of the cellulose molecule, which is initiated also leads to changes in the physical properties of fibrous cellulose, particularly decreases in the breaking strength of the fibers.[4]

It has been reported that the substitution of aromatic groups on the cellulose molecule affected localization of the energy from the incident and secondary radiations in such a manner as to minimize the depolymerization reaction and the loss in breaking strength of the fibrous cellulose and to decrease the oxidative degradation reactions. This radioprotective effect was attributed to the absorption of the energy of the secondary electrons by the aromatic groups, due to their π-electron-type structure, and then to the dissipation of the energy as heat or light. This effect was shown to extend over a range equivalent to several cellobiose units.[5–9]

Experimental data are presented in this report which indicate that the substitution of other groups with π-electron-type structures on cellulose also radioprotect the cellulose molecule. The radioprotective effects of furan groups for cellulose are compared with the reported similar effects of benzenoid groups.

EXPERIMENTAL

[60]Co Radiation Source

The SRRL ^{60}Co radiation source, previously described, was used.[10] The dose rate, determined by ferrous–ferric dosimetry,[11] was about 5.4×10^{19} eV/g-hr over the experimental volume irradiated.

Preparation of Samples

Cotton cellulose of the Deltapine variety, spun into 7s/3 yarn, was purified as previously described.[12] The purified cellulose was conditioned at about 21°C and 65% relative humidity. The product had a moisture content of about 7% and a viscosity-average molecular weight of about 700,000.[13] In a few experiments, cotton cellulose spun into 12s/3 yarn was used.

Cellulose furoates were prepared by the reaction of cotton cellulose with 2-furoyl chloride, 5-bromo-2-furoyl chloride, 5-methyl-2-furoyl chloride, or 2-furanacryloyl chloride in pyridine as the acid scavenger with N,N-dimethylformamide (DMF) as the solvent. The bromo-substituted cellulose furoate underwent nucleophilic displacement reaction with pyridine, N,N-dimethylcyclohexylamine, or triethylamine to give the corresponding quaternary salt.[14]

In general, dry DMF (200 ml) was placed in a round-bottomed flask (500 ml) and then the desired amount of acid chloride was added. Dry pyridine, twice the amount of acid chloride, was added dropwise over a period of about 15 min. The mixture was thoroughly shaken until a homogeneous solution was obtained. Cotton cellulose in the form of yarn (4–8 g) which had been dried in air at 60°C for 2 hr was placed in

the reaction flask.   The contents of the reaction flask, with continuous stirring, were heated in an oil bath at 78°–80°C.   Atmospheric moisture was excluded from the reaction flask by use of a drying tube.   After the desired time of reaction, the yarns were removed from the solution and washed twice with DMF (100 ml each time) and then immersed in methanol at 50°–60°C.   In one procedure, the yarns were left in the slack condition during the washing with methanol.   In another procedure, the yarns were stretched to about 75% of their original length and then washed with methanol.   Then the yarns were placed in 10% KHCO₃ solution for 30 min and finally thoroughly washed with distilled water.   The yarns were equilibrated for 24 hr at about 25°C and 50% relative humidity.   The extent of the reaction was determined by the increase in weight of these conditioned samples over conditioned samples of the control yarn.[14,15]

Methods

Samples of cellulose and cellulose furoates were irradiated in glass containers in air at ambient temperature (about 25°C) to a dosage of about 1.1×10^{21} eV/g.   Within 10–20 min after removal from the radiation source, samples of each of the irradiated and control celluloses (60–80 mg) were transferred in air to quartz tubes.   Then the ESR spectra of the celluloses were recorded at 25°C with a Varian 4502-15 EPR spectrometer system.   The breaking strengths of samples of the fibrous celluloses were determined in accordance with ASTM methods with the Instron tester.[16]

RESULTS AND DISCUSSION

The effects of γ-irradiation on the breaking strengths of fibrous purified and furoylated cotton celluloses are shown in Table I.   The breaking strengths of the control unirradiated yarns were dependent on the extent of chemical modification and on the conditions under which the treated yarns were dried, that is, under slack conditions or restretched and under tension.   Generally, the control yarns which had lower breaking strengths were those dried under slack conditions; the control yarns which had higher breaking strengths were those dried under tension.

The substitution of furan groups on cellulose increased the radiation resistance of the cellulose molecule, as shown by retention of the breaking strengths of the modified fibrous celluloses after exposure to γ-radiation. A high radiation dosage (many times greater than that which would be used to initiate free radical reactions or to sterilize cotton products) was used to demonstrate the radioprotective effect of the furan groups.   The radioprotective effects of furan groups for the modified celluloses were shown at the lowest degree of substitution (0.17) used.   At higher degrees of substitution, increased radioprotection of the modified celluloses was shown.

TABLE I
Effect of Furoylation on Radiation Resistance of
Cotton Cellulose

Derivative	Degree of substitution (DS)	Breaking strength of yarn, lb		Retention of strength, %
		Control	Irradiated[a]	
Purified yarn (7s/3)	0.00	10.52	2.47	23
2-Furoyl	1.24	11.59	7.35	63
	2.73	2.40	2.25	94
5-Methyl-2-furoyl	1.22[b]	7.37	3.89	53
	1.22[c]	13.60	9.63	71
	1.45[c]	6.81	4.08	60
	1.45[c]	11.49	8.37	73
2-Furanacryloyl	0.65	10.52	6.53	62
	1.92	3.90	2.58	66
5-Bromo-2-furoyl	51%[d]	7.05	5.13	73
	151%[d]	4.80	3.87	81
	10%[e]	3.50	1.51	43
Purified yarn (12s/3)	0.00	5.24	1.25	24
2-Furoyl	0.17	3.08	1.36	44
	0.70	4.95	2.88	58
	1.13	4.77	2.80	59
	2.73	1.50	1.37	91

[a] Radiation dosage 1.1×10^{21} eV/g.
[b] Dried under slack conditions.
[c] Dried under tension.
[d] Add-on from pyridine.
[e] Add-on from N,N-dimethylcyclohexylamine.

The ESR spectra of the irradiated celluloses are shown in Figure 1. The ESR spectrum for each of the irradiated modified celluloses is very similar to that for the irradiated purified cellulose, indicating that the substitution of different furan groups on cellulose did not affect the site of localization of energy which resulted in the formation of long-lived free radicals. In each case, the spectra are triplets, which indicates that the free radical site is probably on carbon C_5 and was formed by a dehydrogenation reaction at carbon C_5. The localization of energy on carbon C_1 or C_4 would probably result in formation of a short-lived free radical, in the depolymerization of the cellulose molecule, and in a loss in breaking strength of the fibers. The substitution of these furan groups on cellulose apparently decreased localization of energy on these carbons, thereby increasing the radiation resistance of cellulose. Although difficult to quantify, it was also noted that the substitution of these furan groups on cellulose decreased the intensity of the spectra recorded for long-lived free radical sites in irradiated cellulose. That is, the concentration of long-lived free radicals was less in modified celluloses than in purified celluloses irradiated to the same dosage. This effect also appeared to increase with increase in degree of substitution of furan groups on cellulose.
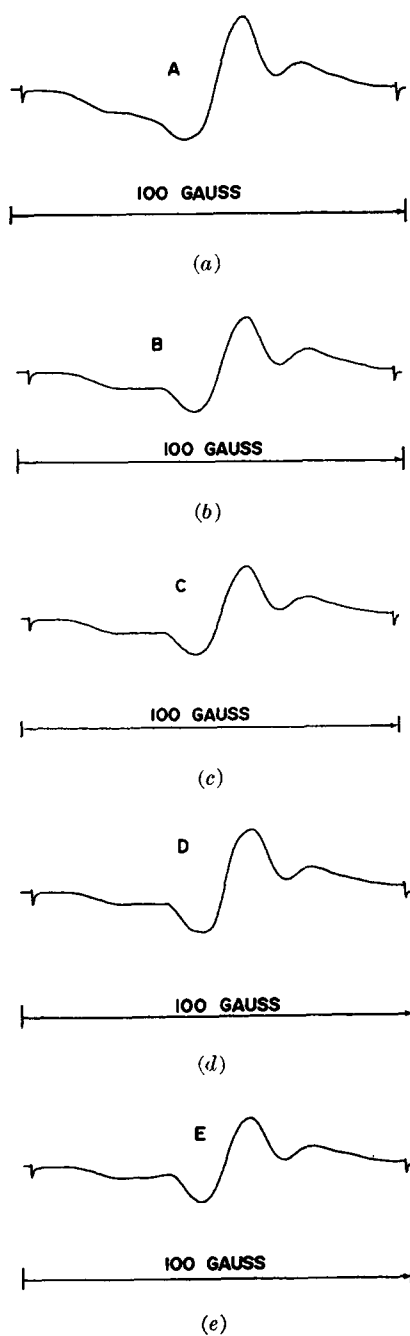
Fig. 1. ESR spectra of irradiated celluloses containing furan groups: (A) purified cotton cellulose; (B) 2-furoyl cellulose, DS = 0.21, (C) 5-methyl-2-furoyl cellulose, DS = 0.27; (D) 2-furanacryloyl cellulose, DS = 0.65; (E) 5-bromo-2-furoyl cellulose, 51% add-on.

It had been previously shown that substitution of benzoyl, benzhydryl, trityl, cinnamoyl, α-naphthoyl, and phenyl carbamoyl groups on the cellulose molecule, through linkages that were not cleaved during irradiation, radioprotected cellulose.[5−9] The substitution of furan groups on the cellulose molecule, as reported here, also radioprotected cellulose. As in the case of benzenoid groups, the radioprotective effects of furan groups for cellulose appeared to be related to their π-electron-type structure. In cellulose furoates, the groups are attached through an ester linkage to the cellulose molecule. At about the same degree of substitution on the cellulose molecule, furan groups appeared to be less effective as radioprotectants than benzenoid groups.[5−9]

Based on the ESR spectra of the irradiated cellulose furoates, as compared with that of irradiated unmodified cellulose, the furan groups appeared to be resistant to cleavage or degradation by γ-radiation. The long-lived free radical sites formed in both irradiated unmodified cellulose and irradiated cellulose furoates appeared to be similar, if not the same. The presence of electropositive and electronegative substituents on the furan group apparently did not significantly change their radioprotective effects for cellulose, as shown by the retention in breaking strength of the irradiated cellulose furoates compared with irradiated cellulose.

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