

## Intramolecular Transfer of High Energy in Cellulose

JETT C. ARTHUR, JR. and TRINIDAD MARES, *Southern Regional Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, Louisiana*

### Synopsis

The intramolecular transfer of high energy in purified cotton cellulose has been demonstrated to occur over distances several times greater than the length of the *b* axis of a cellobiose unit. The electron spin resonance spectra of fibrous benzoylated cotton cellulose have shown that the concentrations of free radicals initiated in the cellulosic molecule by  $\gamma$ -radiation from  $\text{Co}_{60}$  are decreased by the presence of substituted benzoyl groups spaced at least as far apart as 70-80 Å. The retention of the breaking strength of fibrous cotton cellulose on exposure to  $\gamma$ -radiation is increased by substitution of benzoyl groups on the cellulose molecule. The substitution of benzoyl groups, spaced at least as far apart as 10-20 Å., results in about 80% retention of the initial strength of the fibrous cellulose at dosages as high as  $1.3 \times 10^{21}$  e.v./g. cellulose, as compared with about 20% retention of the initial strength of unsubstituted cellulose at the same dosage. Based on the breaking strengths of the irradiated fibrous celluloses, at a dosage of  $1.3 \times 10^{21}$  e.v./g. cellulose, the average calculated distances between molecular cleavages are increased from about 500 Å. for unsubstituted cellulose to about 3000 Å. for benzoylated cellulose (degree of substitution 2.0). These energy transfer effects in cellulose of high molecular weight indicate that polymeric carbohydrates can be radioprotected.

### INTRODUCTION

The energy transfer effects in the radiation chemistry of matter in the solid state are dependent on the mechanism of energy loss by the incident radiation to the chemical molecule, the initial random nonlocalized deposition of energy within the molecule, and the rapid localization of the energy in the molecule. The localization of the energy in the molecule results in chemical changes, depending on the properties of the matter irradiated, such as dehydrogenation, activation of long-lived excited sites, degradation of the molecule, or depolymerization. The time required for this presumed localization process is estimated not to exceed  $10^{-13}$  sec. Further it has been suggested that the effects of an initial nonlocalized deposition of high energy within matter can extend over distances ranging to 100 Å.<sup>1</sup>

The intermolecular and intramolecular transfers of high energy in the localization process in carbohydrates in the solid state have been shown to be dependent on the physical structure of the carbohydrate,<sup>2</sup> on certain complex formation of other molecules with the carbohydrate,<sup>3</sup> and on the substitution of chemical groups on the molecule.<sup>4,5</sup> The selective transfer

of energy either to the complexing molecule or to the substituted group results in a significant decrease in radiochemical yields of the chemical effects of high energy and consequently radio protection of the molecule. In the case of substitution of aromatic groups, particularly benzoyl groups, on glucosides, it has been suggested that intramolecular transfers of high energy can extend beyond the length of one glucose molecule.<sup>4,5</sup> This would be in line with distances, suggested above, over which the effects of nonlocalized deposition of energy may occur.

The energy transfer effects in the radiation chemistry of purified high molecular weight cotton cellulose have been investigated at this laboratory for a number of years.<sup>6-26</sup> The initial energy loss and deposition within the cellulose molecule by high energy radiation should not be hindered by the crystalline-amorphous nature of the fibrous cellulose. However, the intramolecular transfer and localization of energy within the molecule should be easily followed by determination of electron spin resonance spectra and by measurement of physical properties of the fibrous cellulose, in which neither of these evaluations involves changing the physical or chemical properties of the cellulose during the analytical process. Experimental data are presented in this report on the effects of intramolecular energy transfer in fibrous benzoylated cotton cellulose, in which transfer effects on the ESR spectra and breaking strengths of the irradiated, fibrous cellulose extend over several cellobiose units.

## EXPERIMENTAL

### Co<sup>60</sup> Radiation Source

The SRRL Co<sup>60</sup> radiation source, previously described by Arthur et al.,<sup>27</sup> was used. The dose rate, determined by ferrous-ferri dosimetry,<sup>28</sup> was about  $1.5 \times 10^{19}$  e.v./g.-hr. over the experimental volume irradiated.

### Preparation of Samples

Cotton cellulose of the Deltapine variety was purified by extraction with hot ethanol followed by boiling in dilute sodium hydroxide solution, precautions being taken to minimize air oxidation. The sodium hydroxide was removed by washing the cellulose with distilled water, then followed by souring with dilute acetic acid, neutralizing with dilute ammonium hydroxide, and again washing with distilled water.<sup>29</sup> The purified cellulose was allowed to condition at 21°C. and 65% R.H., resulting in a product with a moisture content of about 7%. The viscosity-average molecular weight of the purified cellulose was about 700,000. (Generally, for convenience in handling and in evaluating of the physical properties of the cellulose, the cotton was spun into 7s/3 yarn and wound into 18-yd. skeins prior to purification.)

Purified cotton cellulose was benzoylated by reacting benzoyl chloride in pyridine with dried cellulose to the desired degree of substitution, washed, and dried, according to the method of Malm and Hiatt.<sup>30</sup> In a typical

TABLE I  
Effects of  $\gamma$ -Radiation on the Strengths of Fibrous Purified Cotton  
and of Fibrous Benzoylated Cotton Cellulose<sup>a</sup>

Sample number	Preparation of yarn	Breaking strength, lb.	Elongation at break, %
A	Purified cellulose	10.8	16
B	A irradiated	2.7	9.3
C	A benzoylated slack, D.S. = 1.5	6.5	34
D	C irradiated	5.5	40
E	A benzoylated re- stretched, D.S. = 1.1	12.6	11
F	E irradiated	7.9	7.9
G	A benzoylated re- stretched, D.S. = 1.3	12.8	12
H	G irradiated	10.3	11

<sup>a</sup> Samples, containing regain moistures, were irradiated with Co<sup>60</sup>  $\gamma$ -radiation at ambient temperature in air to a dosage of  $1.3 \times 10^{21}$  e.v./g. cellulose.

experiment, purified cellulose in yarn form (12 g.) was dried in air for 30 min. at 110°C. and then immersed in about 12 times its weight of pyridine (152 ml.), preheated to the reaction temperature (varied from 65 to 100°C. as desired) and held in a beaker in a constant temperature bath. Benzoyl chloride, also pre-heated to the desired reaction temperature, was added in an amount (about 25 ml.) sufficient to react with all of the cellulosic hydroxyls. At a predetermined time, the reaction was stopped by transferring the benzoylated cellulose to pyridine (400 ml.) at about 25°C. The yarns were reacted in a slack condition with benzoyl chloride. Two procedures were followed after the reaction was stopped. In the first case, the yarns were left in a slack condition and washed by about four changes of cold pyridine (350 ml. each), followed by methanol (300–400 ml.), then thoroughly rinsed in water, and air-dried. In the second case immediately after the reaction was stopped, the yarns were stretched to about 80% of their original length and then treated as in the first case. Yarns, washed and dried slack, had lower breaking strength and higher elongation at break than yarns stretched before washing and drying, as shown in Table I.

### Methods

Samples of fibrous cellulose for the determination of the effects of  $\gamma$ -radiation on their electron spin resonance spectra, as a function of degree of substitution of benzoyl groups, were weighed to give exactly 0.1 g. of cellulose in each sample. These samples in yarn form were placed in glass containers and irradiated with  $\gamma$ -radiation from a Co<sup>60</sup> source at ambient temperature in air to the desired dosage. The irradiated samples were transferred in air to quartz tubes, and their spectra were determined within less than 15 min. after removal from the radiation source, in a Varian 4502-15 EPR spectrometer system at room temperature (22°C.).

Samples of fibrous cellulose for the determination of the effects of  $\gamma$ -radiation on their breaking strengths, as a function of degree of substitution of benzoyl groups and of dosage, were also placed in glass containers. The samples were irradiated in yarn form with  $\text{Co}^{60}$   $\gamma$ -radiation at ambient temperature in air to the desired dosages. Sufficient yarn was irradiated in each case in order that textile tests in accordance with ASTM methods, using the Instron, could be made.<sup>31</sup>

Analytical methods used have been previously described.<sup>19,30</sup>

## RESULTS

The effects of  $\gamma$ -radiation on the breaking strengths of fibrous purified cotton and of fibrous benzoylated cotton cellulose are shown in Table I and Figure 1. At the lower dosage ( $1.2 \times 10^{20}$  e.v./g. cellulose) degrees of substitution of benzoyl groups as low as 0.2 radioprotected the fibrous cellulose (Fig. 1A). At the higher dosage ( $1.3 \times 10^{21}$  e.v./g. cellulose) degrees of substitution of benzoyl groups as low as 0.2 offered some radioprotection of the fibrous cellulose. However, much greater radioprotection of the fibrous cellulose was obtained at degrees of substitution greater than 1.1 (Fig. 1B). The lower dosage is in the range that would be useful for radiation sterilization and for initiation of grafting reactions of cellulose reported elsewhere.<sup>8</sup> The higher dosage is a very severe test of the radioprotective effects of substituted benzoyl groups on fibrous cellulose.

As shown in Table I, the breaking strength of the benzoylated cellulose is dependent on the method of preparation of the yarn. However, comparison of samples C through G in Table I shows that the percentages of the initial strengths retained by these yarns after irradiation are about the same order of magnitude. Considering the process overall, it is seen that after irradiation sample H retains about 95% of the initial strength of the

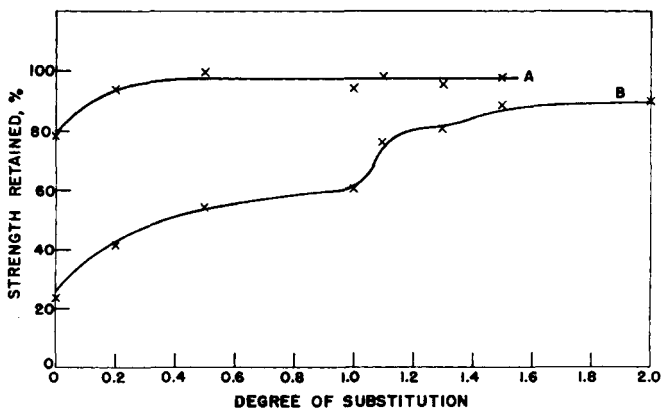


Fig. 1. Effects of  $\gamma$ -radiation on the breaking strength retained by fibrous benzoylated cotton cellulose as a function of degree of substitution and dosage: (A) dosage:  $1.2 \times 10^{20}$  e.v./g. cellulose; (B) dosage:  $1.3 \times 10^{21}$  e.v./g. cellulose.

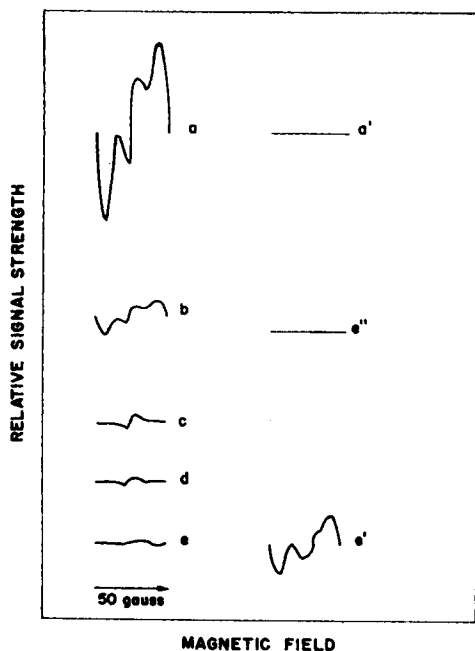


Fig. 2. Effects of  $\gamma$ -radiation on the electron spin resonance spectra of fibrous benzoyleated cotton cellulose as a function of degree of substitution: ( $a'$ ) purified cellulose; ( $a$ ) irradiated purified cellulose; ( $b$ ) irradiated benzoyleated cellulose, D.S. = 0.2; ( $c$ ) same as ( $b$ ), D.S. = 0.5; ( $d$ ) same as ( $b$ ), D.S. = 1.1; ( $e$ ) same as ( $b$ ), D.S. = 1.5; ( $e'$ ) same as ( $e$ ) with signal strength  $\times 10$ ; ( $e''$ ) benzoyleated cellulose, D.S. = 1.5. Dosage:  $2.7 \times 10^{20}$  e.v./g. cellulose.

purified cotton A, as compared with sample B which after irradiation retains only about 25% of this value.

The effects of substitution of benzoyl groups onto the fibrous cellulose molecule on their electron spin resonance spectra, following exposure of the cellulose to  $\gamma$ -radiation, are shown in Figures 2 and 3. Each sample, containing exactly equal amounts of cellulose, was exposed to the same dosage ( $2.7 \times 10^{20}$  e.v./g. cellulose). As shown in Figure 2 (curves  $a'$  and  $e''$ ), neither purification nor benzoyleation of the cellulose introduced any electron spin resonance in the molecule. In Figure 2a the ESR spectrum of irradiated purified cellulose is shown. With increasing degrees of substitution of benzoyl groups onto the cellulose, the relative signal strength of the spectra of the irradiated celluloses decreased, where curve  $a$  is for cellulose with D.S. = 0.0; curve  $b$ , D.S. = 0.2; curve  $c$ , D.S. = 0.5; curve  $d$ , D.S. = 1.1; and curve  $e$ , D.S. = 1.5. As shown in Figure 2e (and also in Table I and Fig. 1), benzoyleated cellulose is radioprotected, but not completely, even at high degrees of substitution. On ten fold magnification of the signal strength of the spectra shown in Figure 2e, the curve  $2e'$  is obtained. The structure of this spectrum is similar to that for irradiated purified cellulose shown in Figure 2a. This similarity suggests

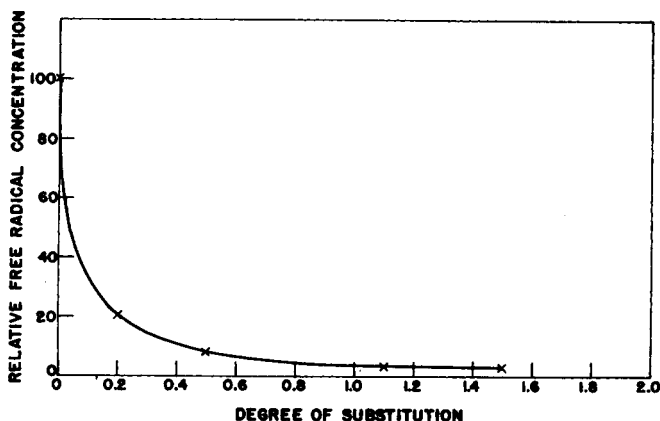


Fig. 3. Effects of  $\gamma$ -radiation on the free radical concentration of fibrous benzoylated cotton cellulose as a function of degree of substitution. Dosage:  $2.7 \times 10^{20}$  e.v./g. cellulose.

that although benzoyl groups radioprotect cellulose to a considerable extent, the localization of the nondissipated radiation-induced resonance in the cellulose molecule is not substantially altered.

The relative free radical concentration (derived from ESR spectra) of irradiated benzoylated celluloses as a function of degree of substitution of benzoyl groups onto the cellulose molecule is shown in Figure 3. It is seen that at low degrees of substitution of benzoyl groups the free radicals are dissipated to a great extent.

## DISCUSSION

It can be concluded that the substitution of benzoyl groups on the cellulose molecules radioprotected the molecules as evidenced (1) by the lower concentrations of free radicals formed within the cellulose and (2) by the higher retention of breaking strength of the fibrous cellulose with increasing degree of substitution of benzoyl groups. It is reasonable to conclude that intramolecular energy transfer occurred in the benzoylated cellulose in such a manner as to decrease chain cleavage, which results in loss in breaking strength of the cellulose, and to decrease the number of activated sites as indicated by the ESR spectra. Apparently, this intramolecular energy transfer can be affected by the presence of benzoyl groups at least several cellobiose units away from the place of initial deposition of high energy. One cellobiose unit in cotton fiber is about 10.3 Å. in length.<sup>32</sup>

Assuming that benzoyl groups are randomly substituted on the cellulose molecule and that each hydroxyl group is equally accessible for reaction, the maximum distance between benzoyl groups along the molecule can be calculated as a function of degree of substitution. With a probability of reaction  $\geq 0.95$  these distances were calculated as a binomial distribution<sup>33</sup> and are tabulated in Table II. In the experimental case, the assumptions

TABLE II  
Calculated Maximum Distance Between Benzoyl Groups as a  
Function of Degree of Substitution<sup>a</sup>

Degree of substitution <sup>b</sup>	Maximum number of cellobiose units per benzoyl group	Maximum distance between benzoyl groups, A <sup>c</sup>
0	$\infty$	$\infty$
0.2	7-8	72-82
0.5	3-4	31-41
1.1	1-2	10-21
1.5	1	10
2.0	1	10

<sup>a</sup> Calculated as a binomial distribution of benzoyl groups with a probability of reaction  $\geq 0.95$ .

<sup>b</sup> Assuming that benzoyl groups are randomly substituted on the cellulose molecule and that each hydroxyl group is equally accessible for reaction.

<sup>c</sup> In an experimental case for the same level of probability of reaction the maximum distance between benzoyl groups will be greater than that assumed in case b.

of random substitution and equal accessibility will not be exactly true. Therefore, actual experimental distances will tend to be greater than those calculated.

For the calculated maximum spacings of benzoyl groups on the cellulose molecule, the presence of benzoyl groups as far apart as 70-80 A. (D.S. 0.2) decreased the concentrations of free radicals as much as 70-80% in irradiated cellulose. The presence of benzoyl groups as far apart as 10-20 A. (D.S. = 1.1-1.5) increased the retention of the breaking strength of irradiated fibrous cellulose as much as 60%, even at dosages as high as  $1.3 \times 10^{21}$  e.v./g. cellulose. At dosages as low as  $1.2 \times 10^{20}$  e.v./g. cellu-

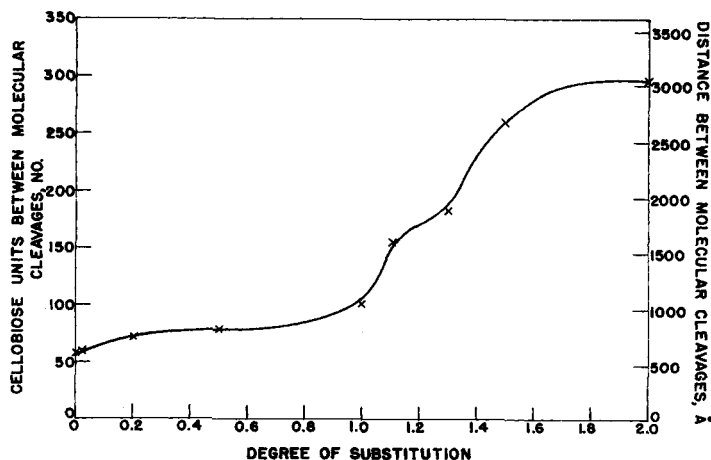


Fig. 4. Effects of  $\gamma$ -radiation on the calculated distance between molecular cleavages of fibrous benzoylated cotton cellulose as a function of degree of substitution. Dosage:  $1.3 \times 10^{21}$  e.v./g. cellulose.

lose, benzoyl groups as far apart as 70–80 Å. increased the retention of the breaking strength of the cellulose on irradiation.

Due to the insolubility of benzoylated cellulose in solvents normally used for cellulose, the changes in molecular weight due to the effects of radiation were estimated from the changes in breaking strengths. Sippel has shown, using photochemical energy, that the breaking strengths of regenerated cellulosic fibers are decreased linearly with increasing number of molecular cleavages.<sup>34</sup> We have also shown, using high-energy  $\gamma$ -radiation, that the breaking strengths of purified cotton cellulose are decreased linearly with increasing number of molecular cleavages.<sup>35</sup> On the basis of the assumption that the retention of the breaking strength of irradiated benzoylated cellulose is basically dependent on the molecular weight of the cellulose, and for the experimental data for the retention of the breaking strength of irradiated purified cellulose versus the number of molecular cleavages as a reference, the distance between molecular cleavages in irradiated benzoylated cellulose as a function of degree of substitution of the benzoyl groups was estimated, as shown in Figure 4. At a dosage of  $1.3 \times 10^{21}$  e.v./g. cellulose, the average estimated distances between molecular cleavages were increased from about 50 cellobiose units (500 Å.) for unsubstituted cellulose to about 300 cellobiose units (3000 Å.) for benzoylated cellulose (degree of substitution 2.0).

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Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers.

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### Résumé

On a démontré que le transfert intramoléculaire d'une énergie élevée dans la cellulose de coton purifiée se manifeste sur des distances plusieurs fois plus grandes que la longueur de l'axe-*b* d'une unité de cellulose. Le spectre de résonance de spin électronique de la cellulose de coton en fibre benzoylée a montré que les concentrations en radicaux libres initiés dans la molécule cellulosique par irradiation gamma à partir de cobalt 60, diminuent en présence de groupements benzoyles espacés d'au moins 70 à 80 Å. La rétention de la force à la rupture de la cellulose de coton fibreux par exposition à radiation gamma augmente par substitution de groupements benzoyles dans la molécule de cellulose. La substitution par des groupements benzoyles espacés d'au moins 10 à 20 Å, se traduit par une rétention de la force initiale de la cellulose fibreuse d'environ 80 pour cent, pour des doses aussi élevées que  $1.3 \times 10^{21}$  e.v./g de cellulose, alors que pour la même dose la cellulose non-substituée ne présente qu'une rétention de la force initiale que d'environ 20%. En se basant sur les forces à la rupture des celluloses fibreuses irradiées à une dose de  $1.3 \times 10^{21}$  e.v./g de cellulose, les distances moyennes calculées entre les olivages moléculaires augmentent depuis environ 500 Å. pour la cellulose nonsubstituée jusqu'à environ 3000 Å. pour la cellulose benzoylée (degré de substitution 2.0). Ces effets de transfert d'énergie dans la cellulose de haut poids moléculaire indiquent que les hydrates de carbone polymériques peuvent être radioprotégés.

### Zusammenfassung

Die intramolekulare Übertragung von hohen Energien in gereinigter Baumwollzellulose erfolgt über Abstände, die einige Male grösser sind als die Länge der *b*-Achse einer Zelloboseeinheit. Elektronenspinresonanzspektren von faserförmiger benzoylierter Baumwollzellulose haben gezeigt, dass die Konzentration der im Zellulosemolekül durch Kobalt-60-Gammastrahlung erzeugten freien Radikale durch die An-

wesenheit substituierter Benzoylgruppen herabgesetzt wird, die zumindest einen Abstand von 70 bis 80 A. besitzen. Die Retention der Bruchfestigkeit von faserförmiger Baumwollzellulose bei der Einwirkung von Gammastrahlung wird durch Substitution von Benzoylgruppen am Zellulosemolekül erhöht. Die Substitution von Benzoylgruppen in einem Mindestabstand von 10 bis 20 A. führt zu einer etwa 80 prozentigen Retention der Anfangsfestigkeit der Faserzellulose bei Dosen von bis zu  $1,3 \times 10^{21}$  e.v./g Zellulose im Vergleich zu einer etwa 20 prozentigen Retention der Anfangsfestigkeit unsubstituierter Zellulose bei der gleichen Dosis. Auf Grundlage der Bruchfestigkeit der bestrahlten Faserzellulose bei einer Dosis von  $1,3 \times 10^{21}$  e.v./g Zellulose erhöht sich der berechnete mittlere Abstand zwischen Molekülsplattungen von 500 A. bei unsubstituierter Zellulose auf etwa 3.000 A. bei benzoyleierter Zellulose (Substitutionsgrad 2,0). Diese Energieübertragungseffekte in hochmolekularer Zellulose zeigen, dass polymere Kohlehydrate gegen Spaltung geschützt werden können.

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