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Chemiluminescence Produced in Saccharides by Cold Plasmas

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ABSTRACT

Cotton cellulose and other saccharides varying in molecular size and in type of glucosidic linkage were treated with cold plasmas generated by radiofrequency (rf) radiation (13.56 MHz). Plasma treatment produced reactive centers on all compounds, and activated samples were capable of producing chemiluminescence (CL). CL was greatest for long-chain structures. Subsequent immersion of plasma-activated compounds in either $CHCl_3$, CH_3OH, or the 2:1 v/v mixed-solvent system ($CHCl_3$/CH_3OH) increased CL significantly, with the latter solvent and the large molecules exhibiting the greatest effect. Reagents that caused an increase in CL reduced intensity of the ESR (electron spin resonance) signal, indicating a possible dependence of CL on the decay of free radicals formed during plasma treatment. CL quenched by nitrogen gas was partially regenerated when nitrogen was exchanged with oxygen. CL decay curves showed an initial fast rate followed by a slower one and especially in case of large molecules indicated that at least two different excited states were responsible for observed CL. Consideration of molecular structures of saccharides in relation to CL and to previously reported changes in ESR, IR, and ESCA spectra leads to the conclusion that the glucosidic bond is the primary site of free-radical formation.

INTRODUCTION

Argon cold plasmas generated with radiofrequency (rf) radiation (13.56 MHz) have been used to alter physical and chemical properties of cotton fabric [1-3]. No gross topographical changes were evident nor were surface changes detectable with scanning electron micrographs. However, a permanent weight loss indicated some degradation of the cotton, and surface-dependent properties such as ease of wetability and dyeability increased after plasma treatment. These surface effects were long-lived and reproducible. Electron spin resonance (ESR), infrared (IR), and x-ray photoelectron emission (ESCA) spectra showed that the reactive sites created by cold-plasma treatment of cellulose were free radicals and carbonyl groups. The strong ESR singlet of plasma-treated cotton, similar to that produced by irradiation with ^{60}Co [4], is stable in dry nitrogen, decays slowly when exposed to ambient air, is destroyed by immersion in water, and is more sensitive to oxygen than to moisture in the air. Plasma-treated cotton displayed chemiluminescence (CL) that was greatest when the plasma-treated cotton was exposed to oxygen.

This is a report of a study of the CL of a series of model compounds selected to determine the effect of molecular size and the type of glucosidic bond on the CL produced by cold plasmas.

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EXPERIMENTAL

Materials

Cotton specimens were fabric from sheetings weighing 4 oz/yd^2, and which had been desized, scoured, and bleached.

Model compounds, with the exception of dialdehyde starch, were purchased from Sigma Chemical Company. Dialdehyde starch, obtained from Miles Laboratories, Inc., was 91.2% oxidized.

Argon and nitrogen were commercial-grade cylinder gases purchased from Union Carbide Corporation.

Methanol and chloroform were reagent grade.

Cold Plasma Treatment

The rf generator, the plasma reactor, and general operating conditions have been described [1]. Procedures described previously for cotton were also used with model compounds, except that each model compound was precisely weighed as four 50-mg portions in a single glass boat to assure uniformity of the plasma treatment. The

boat was centrally located in the reactor downstream from the external electrodes, and the system was evacuated to 25 mtorr before the gas was introduced at a flow rate of 6.5 cm^3/min. After a 5-min interval of gas flow, the rf generator was turned on, and rf power was adjusted to 40 W continuous power. Samples were exposed to the plasma for 30 min, rf power was turned off, and the system was returned to atmospheric pressure. Upon being removed from the reactor, the samples were kept in an argon atmosphere while being transported for testing.

Chemiluminescence

Chemiluminescence (CL) was monitored with a Packard 3255 liquid scintillation spectrometer equipped with low dark-noise photomultiplier tubes (RCA 4501/4V) and a Packard model 585 linear recorder. CL of each compound was measured neat before and after plasma treatment, and in the presence of either $CHCl_3$, CH_3OH, or the 2:1 v/v mixture ($CHCl_3/CH_3OH$). Empty vials and vials containing each solvent, monitored to determine any background CL, emitted equivalent amounts of light, showing that the solvents alone had no initial CL. Thus, for each compound tested, six specimens were simultaneously introduced into the scintillation counter. They were arranged in the sequence: (1) empty vial (V); (2) V + untreated compound; (3) V + plasma-treated compound; (4) V + plasma-treated compound + CH_3OH; (5) V + plasma-treated compound + $CHCl_3$; (6) V + plasma-treated compound + ($CHCl_3/CH_3OH$). Samples were transferred to vials in a dry box in an inert nitrogen atmosphere to avoid exposure to oxygen and moisture. They were then put into the scintillation spectrometer and allowed to stand for 1 min in the dark before counting was begun. After each specimen was monitored for 1 min, the next one in the sequence was automatically dropped into the "counting" chamber. There is a 13-sec delay between automatic removal of the "counted" specimen and the repositioning and monitoring of the next one in the series. The CL decay of each specimen was monitored for a minimum of 1 hr.

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RESULTS AND DISCUSSION

ESR signals of cotton after treatment with either nitrogen, air, or argon plasmas are similar; the CL intensities are also similar. However these parameters of the plasma-treated substrate are affected differently when exposed to different atmospheres. CL increases when exposed to moist air, decreases in the presence of dry nitrogen, and increases when dry oxygen is introduced. The

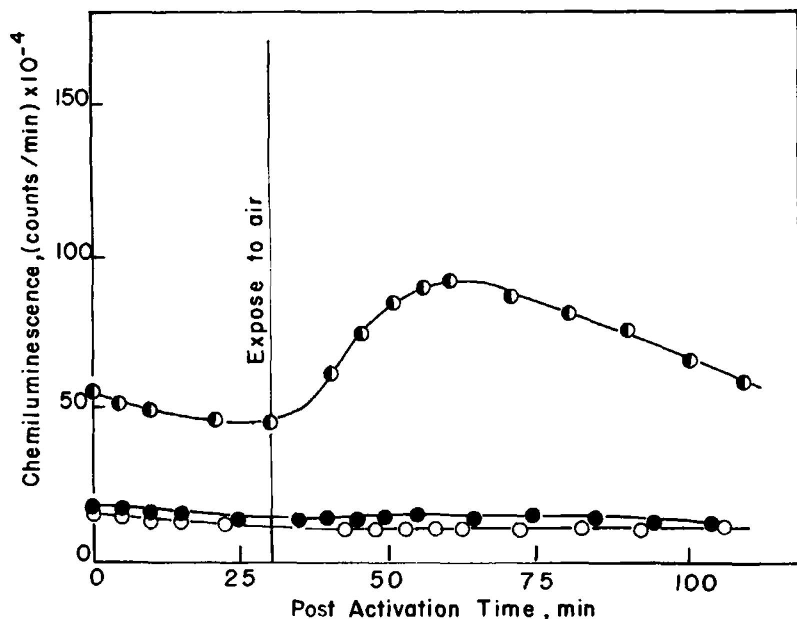

FIG. 1. Changes in CL of argon-activated, purified cellulose while stored in an inert atmosphere and upon subsequent exposure to ambient air: (○) unactivated; (◐) plasma-treated in open boat; (●) plasma-treated, sealed in argon in quartz tube.

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ESR signal of plasma-treated cotton decreases in moist air, increases in dry nitrogen, and decreases in dry oxygen. Because the agents that cause increases in CL reduce ESR signal strength, a reciprocal relationship may exist between CL and the ESR signal, and CL may depend upon the decay of free radicals formed during the plasma treatment.

Figure 1 shows the considerable change in CL resulting from the treatment of purified cellulose (Sigma Cell 100) with argon plasma and typifies changes in the CL of activated cellulose during storage in the inert atmosphere and when subsequently exposed to air. CL decays slowly with time while in nitrogen but increases sharply when exposed to air, reaches a maximum value, and decays at a rate more rapid than prior to the introduction of the air. Purified cellulose shielded from the UV radiations of argon by being sealed in argon-filled quartz tubes shows only negligible CL after plasma treatment, indicating that CL results only when the sample is in direct contact

TABLE 1. Chemiluminescence of Plasma-Activated Cottons in Different Reagent System[a]

Sample	Reagent system[b]	Relative CL (plasma activated)		
		Argon	Nitrogen	Air
1	Fabric (F)	1	1	1
2	F + C/M[b]	3	2	1.5
3	F + C/M + $\overline{CN}$[c]	60	30	15
4	F + C/M + $\overline{CN}$ + N_2	1	...	...
5	F + C/M + $\overline{CN}$ + N_2 + O_2	30	...	...

[a]Plasma treated for 30 min, 40 W rf, 150 mtorr.
[b]C/M = $CHCl_3/CH_3OH$ (2/1); $\overline{CN}$ = KCN.

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with the plasma. These data correlate with the ESR data previously reported for cotton [3].

Although the initial CL induced in cotton by nitrogen, air, or argon plasmas is similar, the activated cottons emit different amounts of light when placed in the same solvent system. Relative changes in CL (Table 1) are computed on the basis of the CL of each plasma-treated Cotton immediately after activation. In the presence of each chemical system, CL increases most after argon activation. The addition of argon-activated cotton to the $CHCl_3/CH_3$ mixture increases CL threefold, and light emission increases sixtyfold when argon-activated cotton is put into $CHCl_3/CH_3OH$ containing KCN. CL is quenched by flushing the system with dry nitrogen but is regenerated to one-half of its original value when nitrogen is replaced by oxygen.

CL is the emission of radiation from a chemically excited species that is formed as a result of a chemical reaction. In cold plasma reactors, free radicals and carbonyl groups are formed in the polysaccharide matrix [1-3]. Our plasma-treated polysaccharides exhibit CL to a certain degree, and this CL increases upon the addition of O_2 gas, upon the addition of $CHCl_3/CH_3OH$ solvents, and upon the addition of $\overline{CN}$ to the solvent system. When O_2 gas is added, the increase in CL is accompanied by a decrease in the ESR signal of the polysaccharide. The ESR signal is stabilized in an inert atmosphere such as N_2 or Ar, which inhibits CL of the polysaccharide.

CL can be produced by radical ion recombination reactions that produce heteroexcimers. The free energy of the reaction is

adiabatically and isothermally transferred into excitation energy of the ion pair, which can in turn dissociate to yield the lowest excited singlet state of the system. Ion pair rearrangement in reactions occurs only at close distances of approach, and in the solid polysaccharide system it is unlikely that such radical ions would be close enough to produce CL. However, upon the addition of a negative ion, such as the $\bar{CN}$ or $\bar{OH}$, the proximity of a radical cation and the added anion could produce CL.

CL of the neat compound stored in an inert atmosphere is probably the result of radiation from chemically excited carbonyl species within the cellulose matrix formed by plasma treatments.

Because of the possible formation of oxygen from the plasma irradiation of polysaccharides, even in the absence of an oxygen atmosphere, it is possible to form some peroxyls on the polysaccharide. In addition, carbon free radicals formed on the polysaccharides by such processes as dehydrogenation or dehydroxylation can react with molecular oxygen after the initial plasma treatment to form peroxy compounds, or electrons can be transferred to oxygen with the resultant formation of superoxide anions ($\bar{O}_2.$). Reactions between oxygen and carbon free radicals can also result in the formation of oxetanes that can in turn form excited carbonyl groups responsible for CL.

Possible reactions resulting in increased CL when plasma-activated polysaccharides are exposed to oxygen are the following:

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$$.O_2H + .O_2H \longrightarrow H_2O_2 + O_2 \quad (1)$$

$$.O_2H + \bar{O}_2. \longrightarrow H\bar{O}_2 + O_2 \quad (2)$$

$$.O_2H + .OH \longrightarrow H_2O + O_2 \quad (3)$$

Each of the reactions (1)-(3) produces enough energy for the excitation of molecular ground state oxygen, $3\Sigma_g$, to $^1\Delta g$ and $^1\Sigma g^+$ states, which require 22.4 and 37.5 kcal/mole, respectively [5]. Release of energies from the excited states or from products formed by a pooling of the excited states to O_2 dimers can account for the observed CL.

If the free electrons created in the polysaccharide matrix by plasma treatments are transferred to O_2 to form $\bar{O}_2.$, the latter will be stable only in the absence of protons. Thus, the addition of protons, either from water or an alcohol, can result in disproportionation of $\bar{O}_2\cdot$ anions as follows:

$$2\bar{O}_2 + 2H^+ \longrightarrow H_2O_2 + {}^1O_2 \quad (4)$$

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TABLE 2. Reproducibility of CL Measurement with Scintillation Counter

Saccharide	Vial			Vial + untreated compound		
	$\bar{x}$ (counts/min)	σ_x (counts/min)	CV (%)[a]	$\bar{x}$ (counts/min)	σ_x (counts/min)	CV (%)[a]
α-Glucose	23,127	1,402	6.06	22,099	924	4.18
β-Glucose	21,092	671	3.18	21,903	506	2.31
Maltose	26,480	1,492	5.63	27,784	1,719	6.19
Cellobiose	22,339	965	4.32	25,675	1,661	6.47
Fructose	26,197	1,318	5.03	25,057	957	3.82
Sorbitol	22,705	752	3.31	23,296	806	3.46
Dialdehyde starch	22,508	1,101	4.90	23,445	1,275	5.44
α-Cellulose[b]	23,500	741	3.16	25,874	777	3.00
Amylose	26,808	1,656	6.18	26,441	2,064	7.81
Amylopectin	25,282	1,433	5.67	25,632	1,200	4.68
Sigma Cell 100	27,820	1,439	5.17	32,423	2,507	7.73

[a] $CV = (\sigma_x/\bar{x}) \times 100$.

[b] α-Cellulose = fraction insoluble in 17% NaOH.

TABLE 3. Effect of Activation on CL Produced in Model Compounds

Glucosidic linkage type	Compound	CL ratio (CL_{ac}/CL_{uac})
α	Amylopectin	5.13
α	Amylose	5.00
β	Sigma Cell 100	4.45
β	α-Cellulose[a]	2.39
–	Dialdehyde starch[b]	2.42
β	D(+) Maltose (hydrate)	1.54
–	D-sorbitol	1.40
–	α-D(+) glucose	1.21
β	β-D(+) cellobiose	1.09
–	β-D(-) fructose	1.10
–	β-D(+) glucose	1.01

[a]α-Cellulose = fraction insoluble in 17% NaOH.
[b]Dialdehyde starch is 91.2% oxidized.

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Production of singlet oxygen is accompanied by CL also. The $\bar{O}_2\cdot$ anions are stable only in a hydrophobic medium and could be somewhat stabilized by carbonium ions created in the plasma-treated polysaccharide.

To determine the exact nature and location of reactive species responsible for CL, we initiated a study of the $CHCl_3/CH_3OH$ solvent system with model saccharides that varied in molecular size and in type of glucosidic linkages. Model compounds included: purified cellulose (Sigma Cell 100), α-cellulose, amylose, amylopectin, dialdehyde starch (91.2% oxidized), D (+) maltose hydrate, β-D(+) cellobiose, α-D(+)- and β-D(+)-glucose, β-D(-) fructose, and D-sorbitol. Although not a saccharide, sorbitol is the reduction product of D-glucose.

Because the CL of glass vials and of vials plus each solvent were equivalent, the empty glass vial (blank) and un untreated sample were used as controls to determine any background CL that might contribute to the overall light emission from the activated model saccharides. As measured by the scintillation counter, empty glass vials and the untreated saccharides display CL and the counts per minute of the vial and of the vial plus untreated compound are generally of the same order of magnitude (Table 2). Because those counts per minute remain

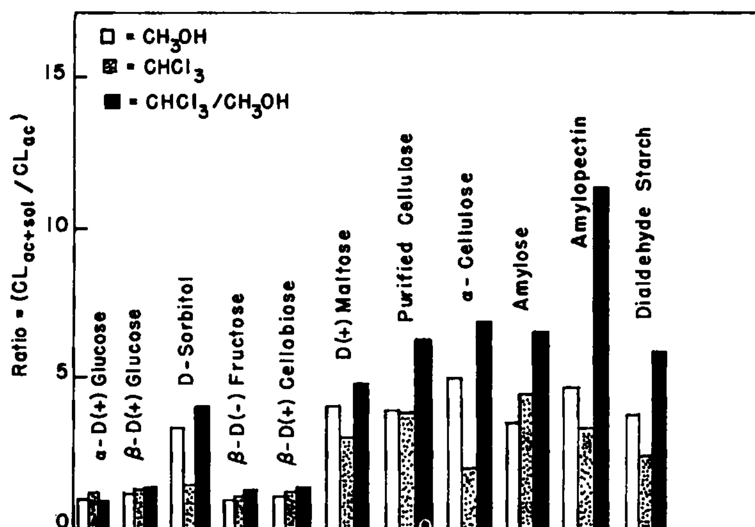

FIG. 2. Effect of immersion in various solvents upon CL of argon-activated compounds immediately after removal from the plasma reactor.

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essentially constant for the entire monitoring period, variability of these "control" values indicates expected reproducibility of CL data from the scintillation spectrometer. Statistical means ($\bar{x}$), standard deviations (σ_x), and coefficients of variation (CV) from counts per minute obtained on empty vials and on vials plus untreated model saccharides are recorded in Table 2. The CV range indicates that CL differences, to be significant, should be at least 10% of the grand mean calculated from readings on empty vials and on vials plus untreated model saccharides. This grand mean is 24,951 counts/min, and so only if CL values vary by at least 2,500 counts/min are they to be considered significantly different.

The effect of argon activation on CL varies with the compound. Typical ratios of CL immediately after argon activation to CL of the unactivated compound are given in Table 3. Plasma treatment least affects CL of glucose, fructose, or cellobiose. CL of long-branched-chain amylopectin and of amylose increase fivefold after activation. Activated celluloses show CL increases of 2.5 to 4.5 times. These data indicate that chain length, type of glucosidic linkage, and configuration at the anomeric carbon atom affect production of CL.

Immersions of activated samples in either CH_3OH, $CHCl_3$, or $CHCl_3/CH_3OH$ (2:1 v/v) further increase CL of all activated compounds

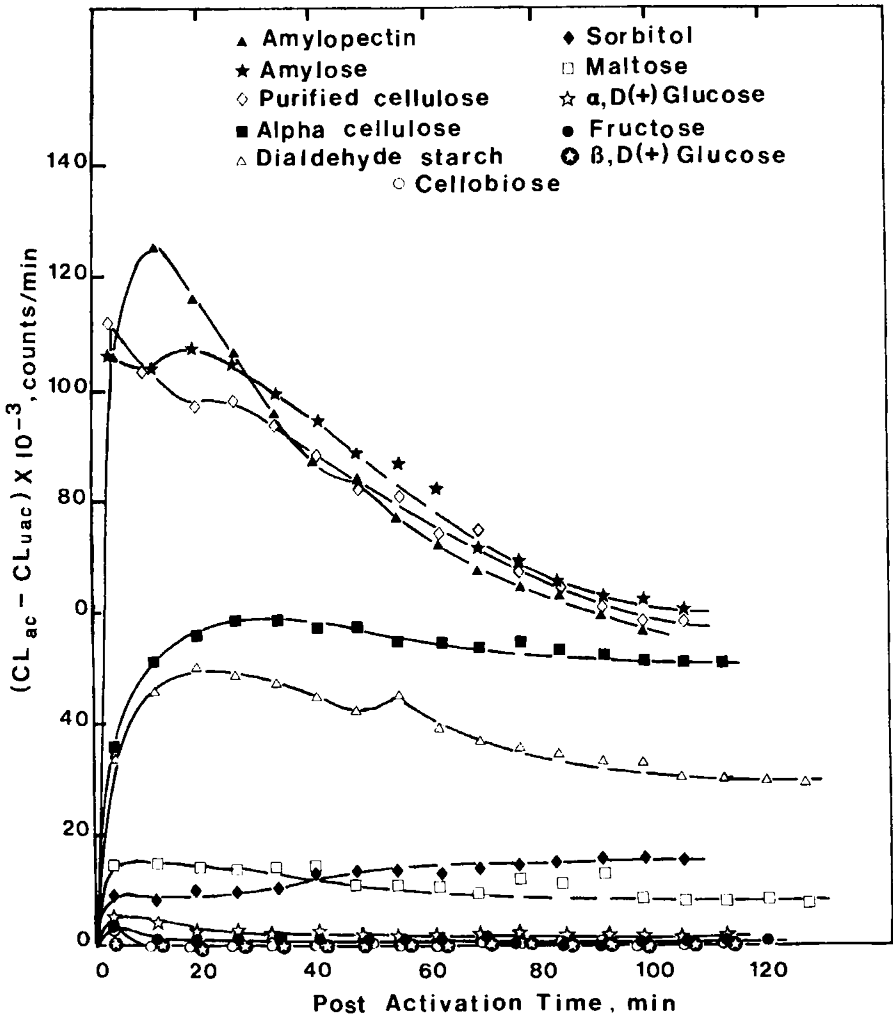

FIG. 3. Changes in CL of argon activated compounds during storage in an inert nitrogen atmosphere.

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except glucose, fructose, or cellobiose (Fig. 2). The magnitude of the increase, however, varies with the solvent as well as with the compound. Increases in CL are greatest upon immersion in the mixed solvent system and for long chain structures. Ratios of CL after activation and immersion in the solvent ($CL_{ac + sol}$) to CL of the activated compound in absence of solvent (CL_{ac}) indicate an elevenfold increase in Cl when activated amylopectin is immersed in $CHCl_3/CH_3OH$, and fourfold to sevenfold increase when other polysaccharides are treated similarly. These data suggest that energy or charides to the added reagent and that new excited species are possibly formed within the solvent.

Changes in CL with postactivation times vary with the model compound (Fig. 3). The graph, showing differences in the CL of activated and unactivated compounds in an inert nitrogen atmosphere versus postactivation time, clearly demonstrates that argon-activated glucose, fructose, or cellobiose does not produce CL (i. e., $\Delta CL \sim O$). With the exception of sorbitol, the CL of all other compounds increases initially and subsequently decays as postactivation time increases. CL of sorbitol increases slowly with time. As noted earlier, sorbitol is a sugar alcohol, and this unique behavior warrants further investigation. The rate of CL decay is greatest for the saccharides that exhibit the greatest CL after activation. Obvious changes in the slopes noted especially in CL versus time curves for amylose and Sigma cell 100 suggest that at least two different excited states are responsible for observed CL.

Figures 4-7 depict changes with postactivation time of CL resulting from subsequent immersion of activated saccharides in various solvents. Graphs show ($CL_{ac + sol} - CL_{uac}$) versus time and include data on all compounds that exhibit increased CL after immersion in the solvent, as well as the corresponding activated compound in the absence of solvent. Except for activated amylopectin in methanol (Fig. 7), the graphs indicate an initial fast rate of CL decay followed by a slower one. When activated amylopectin is immersed in CH_3OH, CL decays during the first 15 min, but thereafter it increases significantly, reaches a maximum, and seems to remain constant over the remainder of the testing period (about 2 hr). In general, long-chain saccharides that show the greatest increases in CL when immersed in solvents exhibit initially a faster rate of CL decay than do the smaller molecules. Figure 4 demonstrates that the decay curves of small molecules after approximately 2 hr are almost coincident with those of the corresponding activated compound in the absence of a solvent. Figures 5-7, on the other hand, show that with large molecules, CL decay curves at long times remain well above

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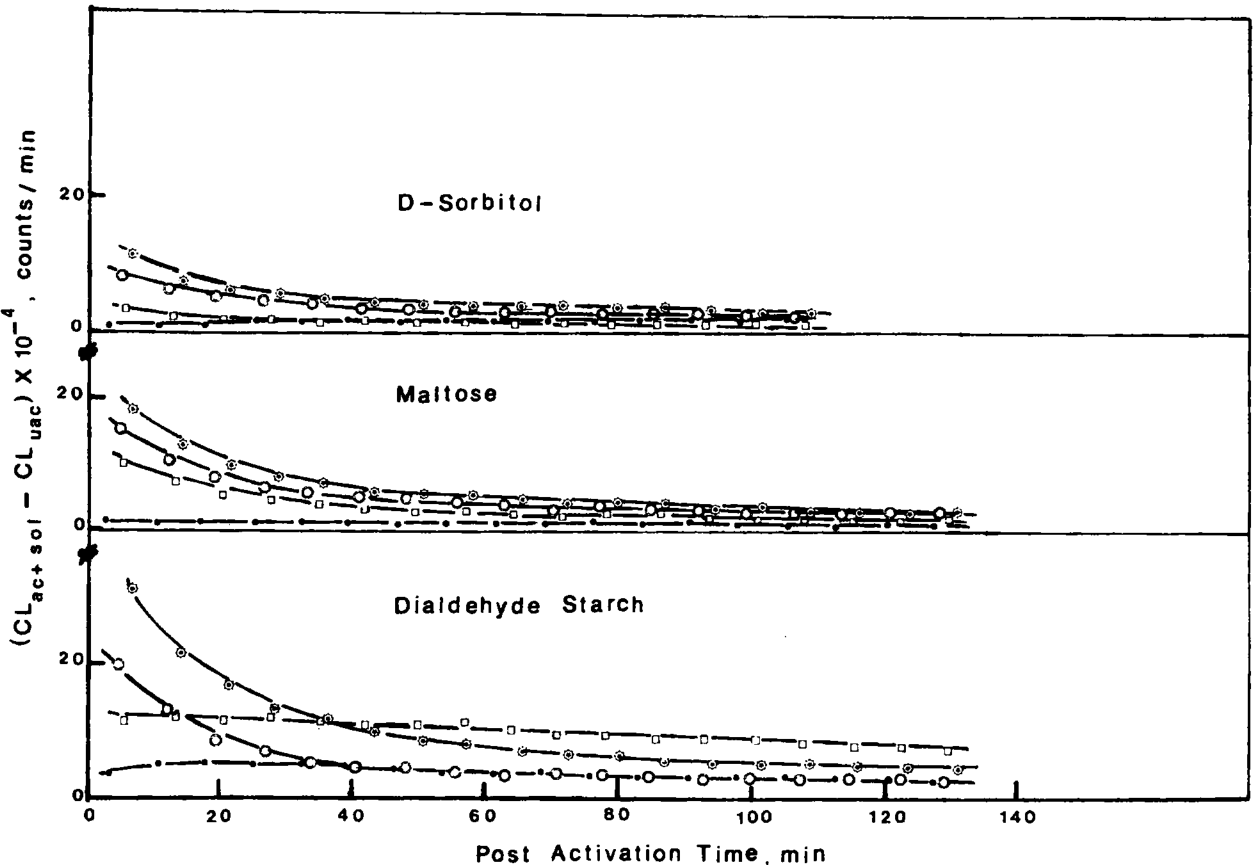

FIG. 4. Changes in CL because of argon activation (- • -) of D-sorbitol, maltose, and dialdehyde starch with postactivation time before and after immersion of activated compound in (○) CH_3OH, (□) $CHCl_3$ and (⊙) $CHCl_3/CH_3OH$ at 2/1 volume ratio.

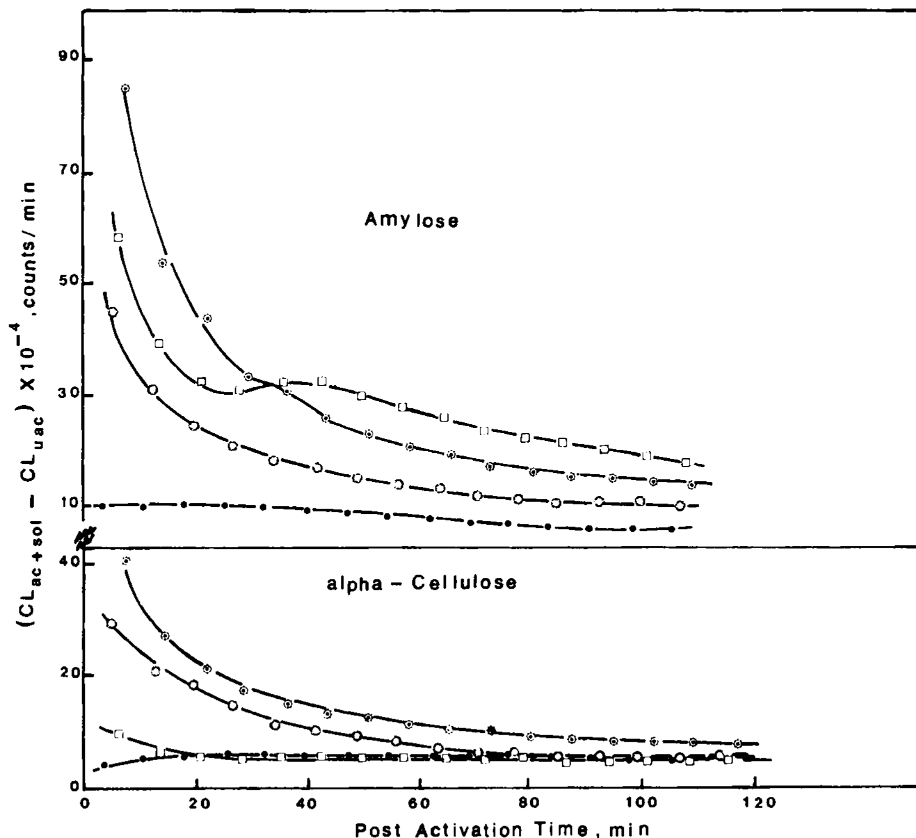

FIG. 5. Changes in CL because of argon activation (-•-) of amylose and α-cellulose with postactivation time before and after immersion in (○) CH_3OH, (□) $CHCl_3$, and (◎) $CHCl_3/CH_3OH$ at 2/1 volume ratio.

those of the corresponding activated compound prior to its immersion in a solvent. The latter effect could indicate the presence of a greater number of excited species in the large molecules or the presence and decay of a different excited state after solvent immersion.

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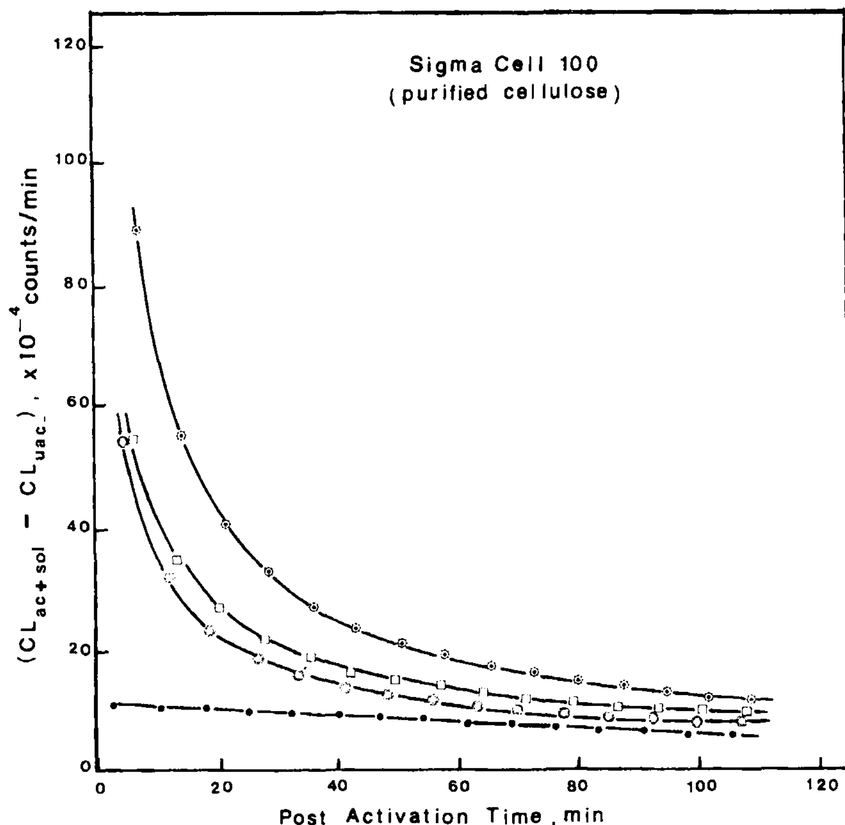

FIG. 6. Changes in CL because of argon activation (-•-) of purified cellulose (Sigma Cell 100) with postactivation time before and after immersion in (○) CH_3OH, (□) $CHCl_3$, and (⊙) $CHCl_3/CH_3OH$ at 2/1 volume ratio.

CONCLUSION

Energies of the electrons within a plasma range from one-tenth to a million electron volts. The highly energetic electrons have sufficient energy to break any bond in the saccharides, including rupture of the glucose ring itself. Consideration of the structures of model compounds in relation to the amount and nature of the production of light emitted after plasma treatment leads to the hypothesis that the

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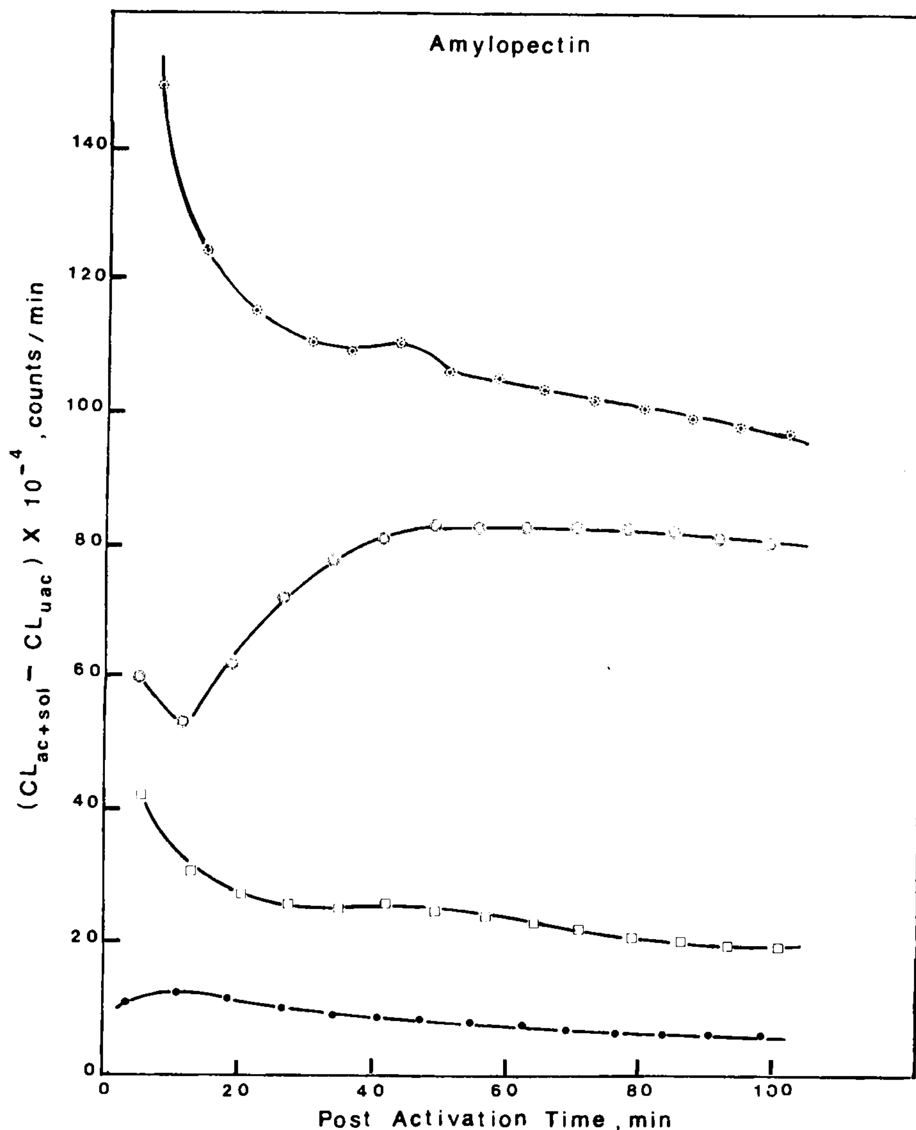

FIG. 7. Changes in CL because of argon activation (-•-) of amylopectin with postactivation time before and after immersion in (○) CH_3OH, (□) $CHCl_3$, and (⊙) $CHCl_3/CH_3OH$ at 2/1 volume ratio.

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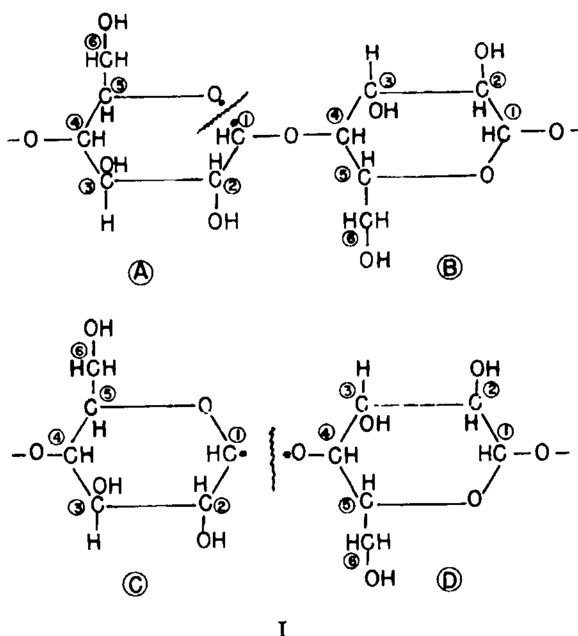
mechanism for producing CL is the same in all tested compounds and that the glucosidic bond is the primary location of excited species responsible for observed CL. Increased solubility of regenerated cellulose (rayon) [6] supports the proposed glucosidic bond rupture, and generation of carbonyl groups [1, 6, 7] after argon plasma treatment has been reported.

Possible free-radical formation at the C_1 and C_4 carbon atoms in the cellulose molecule as a result of plasma activation is shown in the structures I. Cleavage of the glucose ring at the C_1 carbon, which is attached to two oxygen atoms, or scission of the glucosidic bond (C and D) can subsequently produce two types of free radicals, one carbon (C.) and one Oxygen O.). Changes in the slopes of CL decay curves noted



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above, especially for long-chain saccharides, suggest that at least two different excited states are responsible for the observed luminescence. The O. on C_4 can easily rearrange into C=O, accounting for IR spectra [1], and possibly form an excited carbonyl capable of producing luminescence. The C. on C_1 can pick up oxygen from air, water, or a ruptured molecular structure to form an α-hydroxyperoxide that is also able to produce CL. The quenching of CL by nitrogen and the

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reviving of CL by flushing with oxygen supports the idea of the radical formation. Formation of an α-hydroxyperoxide can also account for the increases oxygen-to-carbon ratio observed by ESCA [1].

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Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U. S. Department of Agriculture over others not mentioned.

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