Carbon-13 and Proton Nuclear Magnetic Resonance Studies of Cellulose Nitrates

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ABSTRACT: ^1H (220 MHz) and ^{13}C NMR (25.2 MHz) spectra of partially and completely nitrated products of cellulose were analyzed. While the ^1H spectra provided only limited structural information, the ^{13}C spectra were found to be very useful for qualitative and quantitative analyses of the distribution of substituted anhydroglucose (AHG) units in these products. Molecular structure data were obtained which confirm the previous conclusion that nitration of cellulose is an equilibrium reaction. The ratios of the equilibrium constants for the three types of hydroxyl groups of the AHG units toward nitration were determined to be 1.8, 1.0, and 5.8 at positions 2, 3, and 6, respectively.

Many of the industrially useful cellulose derivatives are those in which the hydroxyl groups of the anhydroglucose (AHG) units are not completely substituted. It is well known that the degree of substitution (DS) of a cellulose derivative may have profound effects on its properties. Moreover, since each AHG unit of a cellulose molecule is a trihydric alcohol, consisting of a primary and two secondary hydroxyl groups, the distribution of substituents in these trihydric alcohol units could be different for cellulose derivatives with very similar overall DS. Indeed, cellulose products with different substituent distribution have been found to exhibit very different properties.[1]

There are many analytical methods for determining the average DS of a variety of cellulose derivatives. However, the number of reliable methods for investigating the substituent distribution is very limited. For cellulose ethers a frequently used technique involves the complete hydrolysis of the ethers and quantitative analysis of the derived substituted sugars.[2] This technique is not generally applicable to the analysis of cellulose esters because the ester groups may also undergo hydrolysis or exchange.

High resolution ^1H and ^{13}C NMR spectroscopy has not been extensively applied to structural analysis of cellulose derivatives. The inherent difficulties associated with the ^1H NMR technique have been reviewed by Barker and Pittman.[3] Only by acetylation of cellulose acetate with perdeuterated acetic anhydride were Goodlett and coworkers able to determine the acetate distribution in the AHG units from the acetyl methyl proton spectra.[4] Ho et al. utilized ^1H spectra for analyses of DS and the moles of ethylene oxide incorporated into the AHG units (MS) of hydroxyethylcellulose.[5] Similar information was subsequently obtained from the corresponding ^{13}C spectra.[6]

In this work we have obtained high resolution ^1H and ^{13}C NMR spectra of a number of nitrocellulose or cellulose nitrates (NC) to investigate the microstructure of these macromolecules and the mechanism of cellulose nitration.

Experimental Section

Samples of industrial NC grades of E. I. du Pont de Nemours and Company, Inc., and Hercules, Inc., were used in this study without further purification. They ranged from 1.9 to 2.3 DS. The synthesis of these commercial products has been described in the literature.[7,8] Samples with a lower degree of substitution were prepared in our laboratory, using various mixtures of nitric acid, sulfuric acid, and water.[7] The intrinsic viscosity numbers in tetrahydrofuran at 30 °C exceeded 0.4 in all cases. Cellulose trinitrates were synthesized by nitration of cotton linters and industrial NC samples with nitric acid in the presence of phosphorus pentoxide at ice temperature.[9] Overall degree of substitution values were obtained using the nitrometer[9] or the modified DiVarda method.[7]

In this work we found that perdeuterated dimethyl sulfoxide (Me_2SO-d_6) provides the best solvent for high temperature NMR study. Me_2SO-d_6 solutions were prepared to contain at least 10% by weight of polymer. Generally homogeneous solutions were obtained except for the case of the sample with 0.4 DS, of which the solution contained an appreciable amount of gel particles.

The 220 MHz spectra of the sample solutions were recorded on a Varian HR220 NMR spectrometer at 90 °C. Proton chemical shifts were measured with respect to an internal reference, hexamethyldisiloxane (HMDS).

Proton noise decoupled (22.6 and 25.2 MHz) ^{13}C NMR spectra were obtained from a Bruker WH-90 Fourier transform NMR spectrometer and a Varian XL-100 NMR spectrometer, respectively. The latter was also equipped with a Fourier transform accessory with a Nicolet data system. The spectral measurement conditions which we used for this work followed closely those in our previous analysis of polymer microstructures.[10] The spectra were obtained at 85–90 °C. The carbon chemical shifts are reported with respect to the internal tetramethylsilane (Me_4Si) reference. The peak areas were determined by spectral integration or tracing over the peaks with a planimeter.

Results and Discussion

A schematic presentation of the eight possible AHG units of a cellulose derivative is presented in Figure 1 along with the standard method of labeling the carbon atoms.[11] Only for the case of DS = 3, i.e., complete substitution, does a cellulose derivative normally have all uniformly substituted AHG units designated (2, 3, 6). The examples are cellulose trinitrate and cellulose triacetate. For the cases of DS < 3, all eight differently substituted AHG units shown in this figure could be present in the cellulose products. In this work, our aim has been to characterize the overall distribution of substitution of the three positions on the AHG units. We have not addressed the question of inter- or intrachain homogeneity.

1. Proton Spectra. Figure 2 depicts the 220 MHz ^1H Me_2SO-d_6 solution spectra of two samples with DS = 3 and 2.3. For the fully nitrated product, there are five major features covering the range of about 4.0 to 5.7 ppm from HMDS. The assignments of these reasonance peaks to the various protons were made using spectral integration and comparison with previously reported spectra of the xanthated and acetylated products of some simple carbohydrates.[3,12]

On the other hand, the corresponding ^1H spectrum of the partially nitrated cellulose exhibits at least 12 resonance peaks, of which many are only partially resolved. This is not unexpected because there are a number of similar but nonequivalent ring methine protons, methylene protons, and hydroxyl protons in the eight different AHG units. A reliable spectral interpretation is very difficult to make without the aid of an extensive study of model

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Table I
Observed Carbon Resonance Peaks of Cellulose Nitrates

sample	DS[a]	chemical shift, ppm (Me_4Si), for carbon 1[b]				carbons 2, 3, 4, 5, 6[c]									
cellulose trinitrate	3.0			98.2					78.7	77.6		75.5			70.1	
cellulose 3,6-dinitrate	1.8	103.2				84.0						75.6			70.5	
DHC 12 (Du Pont)	2.3	103.1	101.8	98.3	96.7	83.4	82.3	79.2	78.7	77.7		75.6			70.3	
RS 1/4 Sec (Hercules)	2.3	103.2	101.8	98.4	96.9	83.6	82.4	79.2	78.8	77.9		75.7			70.4	
DLC 17 (Du Pont)	2.0	103.1	101.5	98.3	97.0	83.6	82.4	79.4	78.7	77.9	76.3	75.7	73.6	73.0	70.5	
SS 1/4 Sec (Hercules)	2.0	103.1	101.7	98.4	96.9	83.6	82.3	79.2	78.8	77.9	76.2	75.7	73.6	72.9	70.5	
A	1.2	103.7	101.7	98.4	96.9	84.1	82.2		78.9	77.8		75.7	74.1	72.9	70.8	60.3
B	0.4		101.7					79.7	79.0	77.7		74.7		72.8	70.7	60.1

[a] Average degree of substitution. [b] The resonance peaks at 103.1 and 101.7 ppm are doublets separated by 0.7 ppm. [c] Only the positions of the well-resolved peaks.

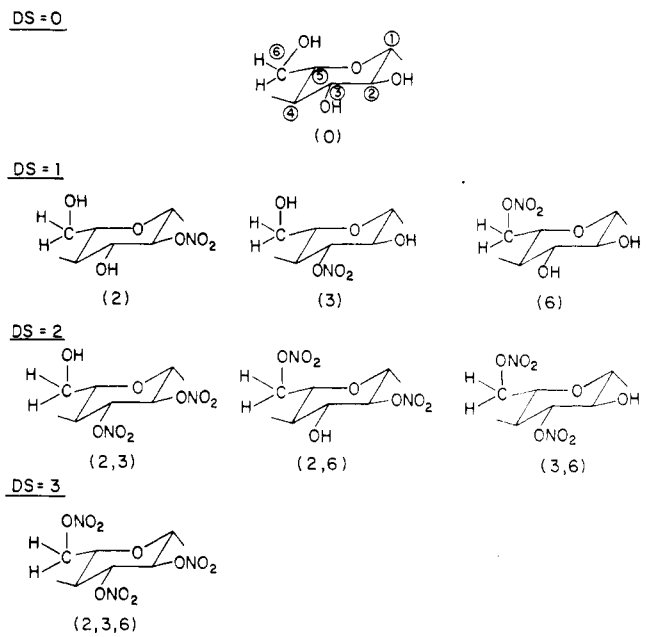

Figure 1. Anhydroglucose units in cellulose nitrates DS = the average degree of nitration. Circled numbers designated the standard method of labeling carbon atoms.

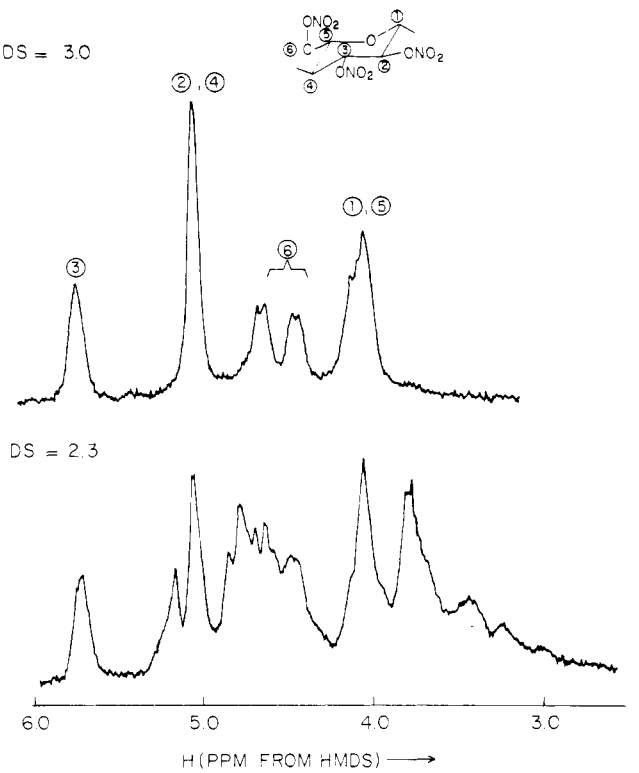

Figure 2. ^{1}H NMR spectra (220 MHz) of Me_2SO-d_6 solutions of cellulose nitrates at 90 °C. For DS = 3 the peak assignments are indicated.

compounds. However, since the methine protons of carbon 3 bearing the nitrate group can still be clearly resolved at 5.7 ppm, this peak is useful for quantitative determination of the extent of nitration of the hydroxyl group on that carbon.

2. Carbon-13 Spectra. In view of the limited utility of 220 MHz ^{1}H NMR spectroscopy for investigating the microstructure of NC, we examined the corresponding ^{13}C spectra. In Figure 3 are presented the 25.2 MHz proton noise decoupled ^{13}C spectra of several samples of cellulose nitrate. The observed carbon resonance peak positions are summarized in Table I. From the ^{13}C NMR study of Dorman and Roberts[13] and others[14] on substituted glucoses and cellobioses, we can assign the peaks in the lowest field region of about 100 ppm to the hemiacetal carbons (no. 1) and the highest field peak at about 60 ppm in the spectrum of DS = 0.4 to the methylene carbons (no. 6) of the primary hydroxyl groups. Upon nitration this methylene carbon peak is shifted downfield at about 70 ppm to overlap other resonance peaks. The complex spectrum covering the range 84–70 ppm arises from the four remaining ring carbons. Some of these assignments were confirmed by off-resonance spin decoupling.

Since more than one resonance peak is observed for the hemiacetal carbons of the partially nitrated celluloses, the shielding of that carbon may be sensitive to the extent of nitration of its neighboring secondary hydroxyl groups. A horizontal expansion of this spectral region is illustrated in Figure 4. The observed four major resonance features were attributed to the four possible nitration patterns of the two secondary hydroxyl groups at carbons 2 and 3.

In order to confirm these assignments we have examined the systematic variation of the hemiacetal carbon spectra with the degree of substitution. As a starting point, the single peak observed for the trinitrate was assigned to the case of carbon 1 having two neighboring nitrate groups. Since nitration of hydroxyl groups at carbons 2 and 3 is expected to yield γ (shielding) and δ (deshielding) effects, respectively, to carbon 1 and the magnitude of the γ effect

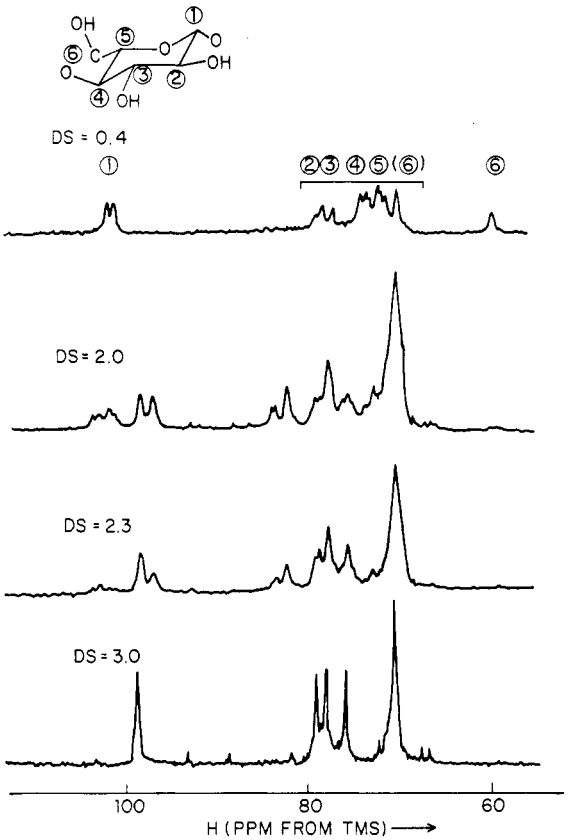

Figure 3. Proton noise-decoupled ^{13}C NMR spectra (25.2 MHz) of cellulose nitrates dissolved in Me_2SO-d_6 at 80 °C.

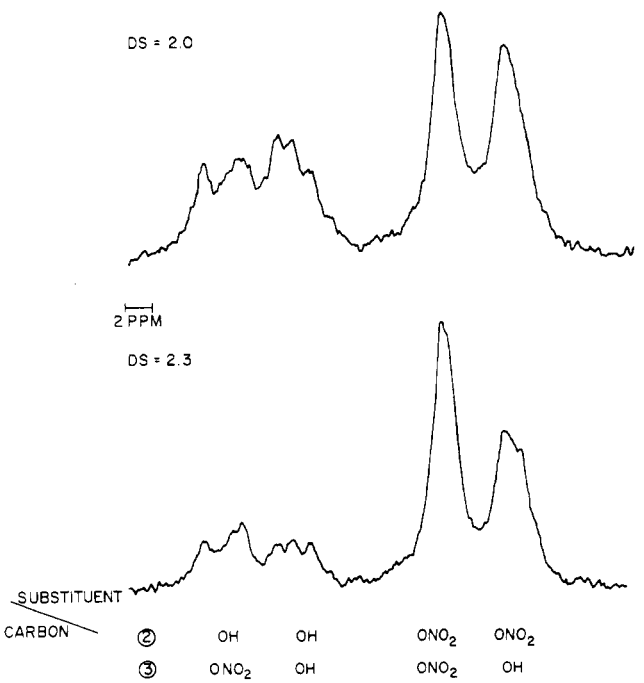

Figure 4. ^{13}C spectra (25.2 MHz) of cellulose nitrates in the hemiacetal carbon region. (The corresponding substitution patterns of the secondary hydroxyl groups are also shown.)

to be greater than that of the δ effect, the spectral assignment shown in Figure 4 is consistent. This is further supported by the fact that the peak intensities of the lower field doublet increase with decreasing degree of substitution.

We have also obtained the ^{13}C spectra of several model polymers. More than 20 years ago Falconer and Purves reported that selective denitration of cellulose trinitrate

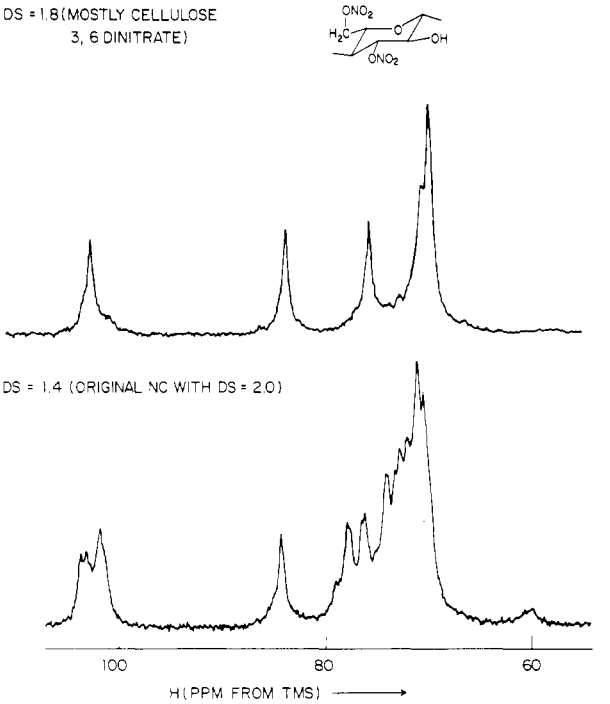

Figure 5. ^{13}C spectra (25.2 MHz) of denitrated products of cellulose nitrates at 85 °C.

could be achieved by reaction with hydroxylamine in pyridine. The product was almost exclusively cellulose 3,6-dinitrate.[15] The 25.2 MHz ^{13}C spectrum of such a denitrated product is depicted in the upper half of Figure 5. Only one hemiacetal carbon resonance peak is observed at 103.2 ppm which exactly corresponds to our previously assigned case of C_2 = OH and C_3 = ONO_2, i.e., a secondary hydroxyl group at carbon 2 and a nitrate group at carbon 3.

A similar denitration reaction was carried out on a commercial NC with DS = 2.0. Its ^{13}C spectrum is shown in the lower half of Figure 5. In comparison with its precursor spectrum of Figure 3, the higher field doublet of carbon 1 centered at 99 ppm is completely removed by denitration; the observed two peaks closely correspond to the lower field doublet of about 101 ppm. The additional peak at 101.7 ppm which is due to C_2 = OH, C_3 = OH arises from the presence in the precursor NC of the AHG units (2), (2,6), (0), and (6). Therefore, ^{13}C NMR data on the model polymers not only provided support to the spectral assignments but also showed that the selective denitration mechanism of Falconer and Purves is valid and independent of the chemical nature of the substituent on its neighboring carbon 3.

In the spectral analysis of carbons 1 and 6, we have neglected the possible shielding effects of substituents located farther than four bonds away as well as the substitution patterns of the neighboring AHG units. ^{13}C NMR (25.2 MHz) spectra did not appear to be very useful for studying the sequence placements of the AHG units in partially nitrated cellulose.

From the ^{13}C spectra of carbons 1 and 6 the changes in chemical shift by replacing the hydroxyl proton with a nitro group β, γ, and δ to the carbon of interest amount to 10, −5, and 1.5 ppm, respectively. Spectral assignments made by using these chemical shift changes as a qualitative guide are given in Table II for carbons 2, 3, 4, and 5 of cellulose trinitrate and cellulose 3,6-dinitrate. Comparison of the chemical shift data on the two model NC polymers led to another set of substituent parameters for nitration, i.e., $\beta(NO_2)$ = 8.2, $\gamma(NO_2)$ = −6.4, and $\delta(NO_2)$ = −0.1 ppm.

Table II
Calculation of Carbon Chemical Shifts of Cellulose Nitrates

substituents at positions			chemical shift, ppm (Me_4Si)[a]			
2	3	6	C_2	C_3	C_4	C_5
ONO_2	ONO_2	ONO_2	78.7	77.6	75.5	70.1
OH	ONO_2	ONO_2	70.5	84.0	75.6	70.5
ONO_2	ONO_2	OH	78.7	77.6	75.6	76.5
			(78.7)	(77.6)	(77.0)	(75.1)
ONO_2	OH	ONO_2	85.1	69.4	81.9	70.2
			(83.7)	(67.6)	(80.5)	(68.5)
OH	OH	ONO_2	76.9	75.8	82.8	70.2
			(73.7)	(72.6)	(79.0)	(68.6)
OH	ONO_2	OH	70.5	84.0	75.7	76.5
			(68.7)	(82.6)	(72.5)	(75.1)
ONO_2	OH	OH	85.1	69.4	82.0	76.6
			(83.7)	(67.6)	(79.0)	(73.6)
OH	OH	OH	76.9	75.8	82.1	76.6
			(73.7)	(72.6)	(77.5)	(73.6)

[a] Except for the first two lines, the chemical shifts were calculated using the following two sets of additive parameters: (A) $\beta(NO_2) = 8.2$, $\gamma(NO_2) = -6.4$, $\delta(NO_2) = -0.1$, and (B) $\beta(NO_2) = 10.0$, $\gamma(NO_2) = -5.0$, $\delta(NO_2) = 1.5$. Calculation was carried out using cellulose trinitrate as the reference. Results from set (B) are included in parentheses.

Table III
Carbon Peak Intensity Measurements of Cellulose Nitrates

		integrated peak intensities[a]	
sample	DS[b]	carbon 1	carbons 2, 3, 4, 5, 6
DLC 12P	1.9	31	157
SS 1/4	2.0	21	111
DHC 12	2.3	20	109
RS 1/4	2.3	22	108
HC 17	2.2	20	96
DHC 17	2.0	21	101
A	1.2	29	153

[a] In arbitrary units. [b] Average degree of substitution.

These parameters may be compared with those derived from the chemical shift data of monosubstituted glucoses. For the carboxy methyl substituent it was found that β = 8.1–9.5 ppm, γ = −0.8 to −1.4 ppm, and δ = −0.3 to −1.1 ppm.[6b]

Table II also summarizes the calculated chemical shifts for carbons 2, 3, 4, and 5 of the six other partially substituted and unsubstituted AHG units. In these calculations both sets of substituent parameters were employed. Even though nearly all of the calculated carbon resonance peaks have been observed in the spectra of the NC polymers (see Table I), we cannot decide which set of parameters is more reliable. However, it is clear that the ^{13}C spectra of carbons 2, 3, 4, and 5 of NC obtained at 25.2 MHz are not well enough resolved to be very useful for quantitative structure determination.

3. Quantitative Structural Analysis. Spectral integration of the fast pulsing proton-decoupled ^{13}C spectra of several NC samples revealed that the peak intensities of the hemiacetal carbon region are, within experimental errors, one-fifth of the total intensities of all of the higher field peaks. Some pertinent data are presented in Table III. It follows that the spin–lattice relaxation times and the nuclear Overhauser effect (NOE) factors of all six carbons of the AHG units must be very similar; therefore, the peak area measurements can be used for reliable quantitative structural analysis.

The extents of nitration of the three hydroxyl groups, of which the sum is the DS, can be calculated from the spectra of the hemiacetal and methylene carbons, e.g., the extent of nitration of the secondary hydroxyl group at carbon 2 or 3 is given by

$$n_2 = R_2/(1 + R_2)$$

$$n_3 = R_3/(1 + R_3)$$

where R's are the ratios of peak intensities

$$R_2 = (I_3 + I_4)/(I_1 + I_2)$$

$$R_3 = (I_1 + I_3)/(I_2 + I_4)$$

where I_1–I_4 are the peak intensities (in arbitrary units) of the four major hemiacetal carbon resonances from low to high field.

For the primary hydroxyl group at carbon 6, the extent of nitration is

$$n_6 = 1 - I_6$$

where I_6 is the normalized peak intensity of the methylene carbons at about 60 ppm. The overall degree of substitution is DS = $n_2 + n_3 + n_6$.

Table IV
NMR Determinations of Extents of Nitration in Cellulose Nitrates

	extent of nitration at[a] position			DS[b]	
sample	2	3	6	NMR	others[c]
B			0.4	0.4	0.4
A	0.3 (2)	0.1 (9)	0.8 (0)	1.3 (1)	1.22
DLC 17	0.5 (8)	0.5 (4)	0.8 (3)	1.9 (5)	1.95
SS 1/4	0.5 (5)	0.5 (1)	0.8 (7)	1.9 (3)	1.98
DHC 12	0.7 (7)	0.6 (2)	1.0 (0)	2.3 (9)	2.28
RS 1/4	0.7 (0)	0.5 (9)	1.0 (0)	2.2 (9)	2.30

[a] The extent of nitration of hydroxyls at carbons 2, 3, and 6 was determined from ^{13}C NMR data. [b] Average degree of substitution. [c] DS determined by analysis of nitrogen.

For the primary hydroxyl group at carbon 6, the extent of nitration is

$$n_6 = 1 - I_6$$

where I_6 is the normalized peak intensity of the methylene carbons at about 60 ppm. The overall degree of substitution is DS = $n_2 + n_3 + n_6$.

The results in the last two columns of Table IV show that the ^{13}C NMR determinations of DS are in very good agreement with those determined using the nitrometer and the modified DiVarda methods. These data also indicate that the primary hydroxyl groups are preferentially nitrated. In fact, the relative reactivities of the hydroxyl groups toward nitration decrease from the position 6 ≫ 2 > 3. This observation is very consistent with the previous studies on the substitution reactions of cellulose and esterification of aliphatic alcohols.[1,7]

It was reported that during a rate-controlled substitution reaction of cellulose interference may occur between the secondary hydroxyl groups.[1] If this occurred during nitration, there should be a very small number of AHG units with both secondary positions nitrated in a sample of DS ≤ 2.0. However, examination of the hemiacetal carbon spectrum of a sample of 2.0 DS in Figure 4 revealed that the peak intensity corresponding to the case of $C_2 = ONO_2$ and $C_3 = ONO_2$ is very strong. The above-mentioned mutual interference, if it occurred at all, is minimal during nitration. This is consistent with the fact that cellulose nitration is known to be an equilibrium rather than a rate-controlled reaction.[1,7,8]

For quantitative analysis of the various AHG units in a partially nitrated cellulose, we first examined the methylene carbon peak intensity at about 60 ppm. If it is negligible, the distribution of the AHG units can be completely determined from the hemiacetal carbon spectrum. This is largely the case for NC with DS ≥ 2.2.

Table V
Distribution of Anhydroglucose Units[a] in Cellulose Nitrates

DS[b]	fraction of anhydroglucose units							
	(0)	(2)	(3)	(6)	(2,3)	(2,6)	(3,6)	(2,3,6)
0.4	0.6 (0)			0.4 (0)				
1.2	0.1 (3)	0.06	0.03	0.4 (2)	0.02	0.1 (8)	0.1 (0)	0.06
1.9	0.0 (3)	0.05	0.03	0.1 (8)	0.05	0.2 (4)	0.1 (8)	0.2 (4)
2.2				0.1 (5)		0.3 (1)	0.1 (7)	0.3 (7)

[a] The designations of the anhydroglucose units were illustrated in Figure 1. [b] Average degree of substitution.

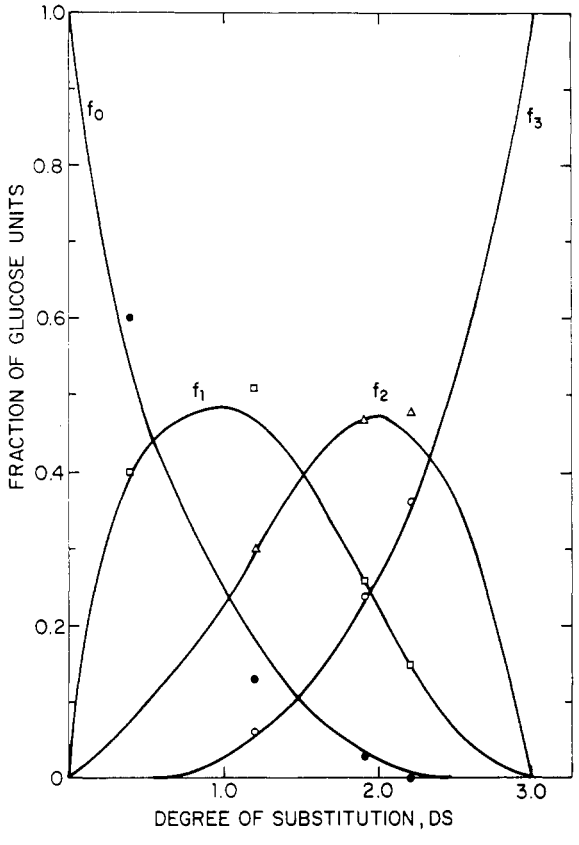

Figure 6. Calculated and observed distribution of substituent for equilibrium cellulose nitration (equilibrium constants of $K_3 = K_2 = K_6 = 1 = 1.8 = 5.8$).

However, where there is an appreciable peak due to the primary hydroxyl group, a further simplifying assumption can be made, i.e., the extent of nitration of the primary hydroxyls has little or no effect on the nitration of the secondary hydroxyls. Then the distribution of the AHG units in samples with DS ≤ 2.2 can be similarly calculated from the hemiacetal carbon spectrum. The results are summarized in Table V.

4. Mechanism of Nitration of Cellulose. An extensive amount of theoretical and experimental evidence, primarily based on the analyses of the composition of the nitrating acids and that of the spent acid, has been accumulated to demonstrate that cellulose nitration is an equilibrium reaction.[1,7,8] However, quantitative determination of the reaction of the individual hydroxyl group has not been possible in the past. These ^{13}C NMR data present an excellent opportunity for such an analysis.

A detailed description of the equilibrium reaction theory is presented in the Appendix. The equations which relate the equilibrium constants to the concentrations of the AHG units are

$$K_2/K_3 = (2)/(3) = (2,6)/(3,6)$$

$$K_6/K_3 = (6)/(3) = (2,6)/(2,3)$$

where K_2, K_3, and K_6 are the equilibrium constants of hydroxyl groups at positions 2, 3, and 6, respectively. The fractions of monosubstituted AHG units in the cellulose derivative are designated as (2), (3), and (6). Similarly, (2,6) and (2,3) represent the fractions of the disubstituted AHG units.

Using these equations and the data of Table V, we found that $K_2/K_3 = 1.8 \pm 0.2$ and $K_6/K_3 = 5.8 \pm 0.6$. With the newly determined equilibrium constants for cellulose nitration and the equations of the Appendix, the distribution of AHG units can be calculated for any sample nitrated under these equilibrium conditions. Figure 6 presents a graphical summary of such calculations along with the experimentally observed values. Therefore, our ^{13}C NMR analysis of NC provides detailed structural evidence which confirms that cellulose nitration is indeed governed by the equilibrium processes at the hydroxyl groups of the AHG units.

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Appendix. Distribution of Substituents in the Equilibrium Substitution Reaction of Cellulose

The theory for the equilibrium substitution reaction of cellulose was formulated by Spurlin[1] with the following basic assumptions: (1) all AHG units in the cellulose molecules are available for reaction, (2) the ratios of the reaction rate constants of the three hydroxyl groups remain constant throughout the reaction, (3) the reactivity of the hydroxyl group is independent of the state of substitution of its neighboring hydroxyl groups, and (4) end group effects are negligible.

If the equilibrium reaction of the AHG units is described by

$$C_6H_{10}O_5 + AB \rightleftarrows C_6H_9O_5A + HB$$

$$K = [C_6H_9O_5A][HB]/[C_6H_{10}O_5][AB]$$

or

$$\frac{[C_6H_9O_5A]}{[C_6H_{10}O_5]} = \frac{[AB]}{[HB]}K \qquad (1)$$

Let n_2, n_3, and n_6 be the fractions of the AHG units that contain substituents in the 2, 3, and 6 positions, respectively, then from eq 1 we obtain

$$n_2/(1 - n_2) = kK_2$$

or

$$n_2 = kK_2/(1 + kK_2) \qquad (2)$$

Similarly

$$n_3 = kK_3/(1 + kK_3) \quad (3)$$

$$n_6 = kK_6/(1 + kK_6) \quad (4)$$

where k is a constant denoting the substituting power of the reaction medium, and K_2, K_3, and K_6 designated respectively the equilibrium constants for the substitution reactions of the hydroxyls at positions 2, 3, and 6.

The fraction of the completely substituted AHG units, f_3, is

$$f_3 = (2,3,6) = n_2n_3n_6 = k^3K_2K_3K_6/[(1 + kK_2) \times (1 + kK_3)(1 + kK_6)] = k^3K_2K_3K_6/d \quad (5)$$

$$(2,3) = n_2n_3 - (2,3,6) = k^2K_2K_3/d \quad (6)$$

$$(2,6) = k^2K_2K_6/d \quad (7)$$

$$(3,6) = k^2K_3K_6/d \quad (8)$$

$$(2) = n_2 - (2,3) - (2,6) - (2,3,6) = kK_2/d \quad (9)$$

$$(3) = kK_3/d \quad (10)$$

$$(6) = kK_6/d \quad (11)$$

where (2), (3), and (6) are the fractions of AHG units with substituents only in the positions named. Similarly, (2,3) designates the fraction of AHG units containing substituents only in the 2 and 3 positions.

The equations for the fractions of unsubstituted, monosubstituted, and disubstituted AHG units are

$$f_0 = 1/d \quad (12)$$

$$f_1 = k(K_2 + K_3 + K_6)/d \quad (13)$$

$$f_2 = k^2(K_2K_3 + K_2K_6 + K_3K_6)/d \quad (14)$$

The average degree of substitution of the cellulose derivative is

$$DS = n_2 + n_3 + n_6 = 3 - 3f_0 - 2f_1 - f_2 \quad (15)$$

An additional set of correlations can also be derived as follows:

$$(2)/f_1 = K_2/(K_2 + K_3 + K_6) \quad (16)$$

$$(3)/f_1 = K_3/(K_2 + K_3 + K_6) \quad (17)$$

$$(6)/f_1 = K_6/(K_2 + K_3 + K_6) \quad (18)$$

$$(2,3)/f_2 = K_2K_3/(K_2K_3 + K_2K_6 + K_3K_6) \quad (19)$$

$$(2,6)/f_2 = K_2K_6/(K_2K_3 + K_2K_6 + K_3K_6) \quad (20)$$

$$(3,6)/f_3 = K_3K_6/(K_2K_3 + K_2K_6 + K_3K_6) \quad (21)$$

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A Nitrogen-15 Nuclear Magnetic Resonance Study on the Copper(II) Complex of Poly(L-lysine)

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ABSTRACT: Nitrogen-15 nuclear magnetic resonance spectra of 46% ^{15}N-enriched poly(L-lysine) in aqueous solutions at different pHs were obtained. On the addition of a small amount of the copper(II) ion, the ^{15}N signal of the side chain amino group almost disappeared in the alkaline pH region, while the signal of the amide nitrogen remained. This fact indicates that the side chain amino groups have much more tendency to bind to the copper(II) ion than to the amide groups even in alkaline solutions.

The copper(II) complex of poly(L-lysine·HBr) (PLL) has a stereospecific catalytic activity for the oxidation of L-3,4-dihydroxyphenylalanine (DOPA) and is regarded as a metallo enzyme model of DOPA oxidase.[2] Several workers have investigated the copper(II) complex of PLL by means of potentiometric, circular dichroism and other physicochemical techniques. They discussed the conformations and properties of the PLL–Cu(II) complex in aqueous solution, especially the mode of interaction with copper ion.[3–6] Nozawa and Hatano proposed a model in which the side-chain amino groups coordinate to the copper(II) ion in a planar tetragonal form below pH 8, but

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