Partial degrees of substitution in cellulose nitrates determined by means of ^{13}C magnetic resonance studies

D. T. Clark and P. J. Stephenson
Department of Chemistry, University of Durham, South Road, Durham City, UK

and F. Heatley
Department of Chemistry, University of Manchester, Manchester, UK
(*Received* 26 *November* 1980; *revised* 3 *February* 1981)

High resolution ^{13}C n.m.r. proton noise decoupled (75.5 MHz) spectra have been recorded for a series of nitrated celluloses and denitrated cellulose nitrates. From the detailed spectral assignments an analysis of the partial degrees of substitution and distribution of nitrate groups in the β-D-glucopyranose residues is presented. The data are compared with the predictions of a model based on the constancy of ratio of three equilibrium constants for nitration–denitration at the C2, C3 and C6 positions for differently substituted β-D-glucopyranose residues and it is shown that the situation is considerably more complex than provided for by the model. Analysis of the anomeric ^{13}C carbon region produces some sequence information which indicates non-random distribution of nitrate ester groups.

INTRODUCTION

Despite the extensive literature[1,2] on the technical nitration of cellulosic materials covering a period of more than a century, there are still fundamental questions which remain unresolved. It is now firmly established, however[3], that under the conditions of interest in most technical nitrations, the final degree of substitution *DOS** of the bulk material is under thermodynamic control and in recent publications[4] we have shown that this is also true in the outermost few tens of Angstroms, although the convolution of factors which determine the overall stoichiometry are such that the surface is often distinctively different from the bulk[4].

One of the most intriguing aspects of the nitration and denitration of cellulosic materials which is not as yet fully understood is the substantial change in interchain spacing as a function of degree of substitution[5]. The fact that such spacings differ for materials of the same *DOS* produced by either nitration or denitration must reflect the detailed differences in chemical microstructure and substitution patterns in individual and sequences of β-D-glucopyranose residues.

Although extensive investigations have now been made of overall *DOS* over a variety of nitrating and denitrating conditions[4] little information has been available on the partial *DOS* at the C6 primary and C2 and C3 secondary sites in individual glucose residues. The first indication that equilibrium *DOS* at different sites in the glucose residue were not the same came from the iodination experiments of Murray and Purves[6]. By specifically displacing primary nitrate esters by iodide (typically NaI in acetyl acetone) it was shown that the partial *DOS* for the primary site in any nitrocellulose was always greater than that for the secondary sites. Unfortunately with materials of $DOS > 2$, which include all those of technical importance, considerable degradation occurs during the reaction and electron micrographs reveal[7] that the fibrous structure which is maintained on the nitration (or denitration) of cellulosic materials is completely destroyed by the process. With such extensive degradation it becomes difficult to quantify data on materials of high *DOS*. Indeed attempts to use the reaction to quantify partial *DOS* for the C6 primary site as far as the surface of cellulosic samples nitrated or denitrated for short periods (~15 s) are concerned, proved conclusively that although the bulk fibrous structure is retained, extensive degradation occurs for the surface regions[7].

An important advance in this area has recently been reported by Wu[3]. By careful examination of the noise decoupled ^{13}C n.m.r. spectra of model systems, he has shown that it is possible to assign components in the region ~100 ppm to the low field of TMS to the anomeric (C1) carbon in the variously substituted glucose residues. This has demonstrated unambiguously that the equilibrium partial *DOS* is in the order C6 > C2 > C3. An analysis based solely on the anomeric carbons has certain inherent weaknesses which can largely be eliminated by using the remainder of the ^{13}C data originating from C2–C6 once appropriate assignments have been confirmed. Here, therefore, we present a detailed ^{13}C n.m.r. analysis of the substitution patterns in both nitrated and denitrated cellulosic materials. The prime objectives of this study (which refers essentially to the bulk and which complements our recent studies of the surface aspects of such processes[4]) may be summarized as follows. To investigate:

(a) nitration in different acid mixes for fixed periods of time;

(b) denitration in different acid mixes for fixed periods of time; and

(c) denitration in a given acid mix as a function of time.

For the sake of completeness we include in *Figure 1*, the structural units of relevance to the discussion.

* *DOS* is defined here in terms of average number of nitrate ester groups per β-D-glucopyranose residue.

0032-3861/81/081112-06$02.00

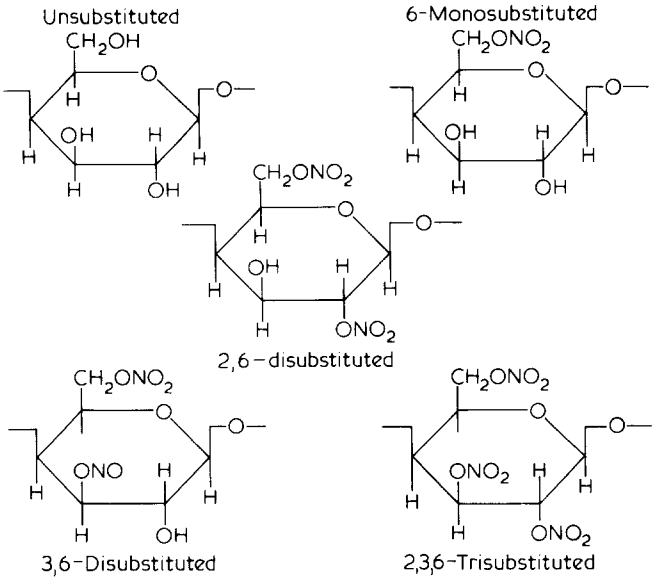


Figure 1 Diagram showing the 5 basic structures of cellulose nitrate discussed in this work

EXPERIMENTAL

Nitrated material for analysis in this work was prepared from dewaxed cotton linters (Hercules Powder Co.) of Shirley fluidity 8.8 and approximate degree of polymerization, 1100. Standard nitration methods were employed, based on the Mitchell[8] procedure; washing and drying processes for both nitrated and denitrated samples has been described in an earlier publication[4b]. Nitrations were carried out for 2 h—a period which we have shown[4b] gives rise to homogeneously nitrated material. 10% by wt solutions of the polymer were made up in dimethylsulphoxide-d_6. The ^{13}C n.m.r. proton noise decoupled (75.5 MHz) spectra were recorded on a Varian Associates SC300 spectrometer at 75°–80°C with a typical acquisition time of 12 h corresponding to the accumulation of $\sim 10^5$ transients. The carbon chemical shifts are reported with respect to the internal tetramethylsilane (TMS,Me_4Si) reference. Peak areas were determined by spectral integration. Low temperature 25°–29°C n.m.r. spectra were also recorded but were found to be broad and poorly resolved due to the high viscosity, whereas high temperature conditions $\approx$90°C as used by Wu give discoloured solutions and additional small peaks on long acquisition times (see the data in ref 3). We have also observed these phenomena but to a lesser extent and the nitrogen contents of certain samples have been determined by a modified Kjeldahl method and found to be comparable with the *DOS* calculated from analysis of the n.m.r. data and the percentage nitrogen expected from standard tables[1] for nitration in the particular acid mixes used.

RESULTS AND DISCUSSION

Analysis of partial DOS

The difficulties of an analysis of partial *DOS* based solely on the anomeric region are clear from the spectrum shown in *Figure 2*. (The spectrum is for a nitrated material *DOS*, initially 2.83 denitrated in 82% HNO_3 for a period of 20 s. Whilst the components at 99.7 and 98.4 ppm assigned[3] to the anomeric carbon in trisubstituted and 2,6-disubstituted residues are well-resolved, the lower field region arising from 3,6-disubstituted and 6-monosubstituted glucose residues is largely unresolved. Comparison of the whole series of spectra for nitrated and denitrated materials, however, does allow an unambiguous assignment of the higher field portion of the ^{13}C n.m.r. spectra arising from C2–C6. Thus, the component at 85.2 ppm arises from C3 in 3,6-disubstituted glucose residues whilst the component at 83.2 ppm corresponds to C2 in 2,6-disubstituted glucose residues. As will become apparent, the nuclear Overhauser enhancements (*NOE*) for C1–C5 are essentially the same so that the ratio of the peak areas allows the direct determination of the ratio of disubstituted products. Taken in conjunction with the total integral for the lowest field region for the anomeric carbons and the area ratios for the two higher field components, this allows a partitioning of substitution pattern into tri-, di- and monosubstituted glucose residues. The intense components at 80.2, 79.1 and 76.9 ppm are then assigned to C3, C4 and C2, respectively, in the trisubstituted glucose residues. The minor component at 74.5 ppm arises from C2 in the 3,6-disubstituted residues and its intensity is the same as that of the component at 85.2 ppm arising from C3 in the 3,6-disubstituted residue

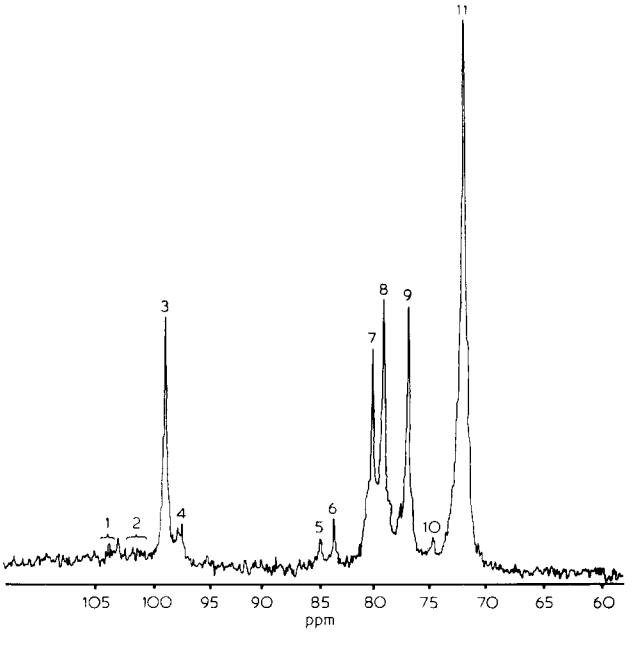


Figure 2 ^{13}C n.m.r. decoupled (75.5 MHz) spectrum of 2.8 *DOS* material denitrated for 20 s in 82% HNO_3/18% H_2O (shifts recorded in ppm with respect to TMS)

Peak No.		Assignment
1	C1 in	3,6-disubstituted
2	C1 in	6-monosubstituted
3	C1 in	trisubstituted
4	C1 in	2,6-disubstituted
5	C3 in	3,6-disubstituted
6	C2 in	2,6-disubstituted
7	C3 in	trisubstituted
8	C4 in	trisubstituted
9	C2 in	trisubstituted
10	C2 in	3,6-disubstituted
11	C6 and C5	(coincident in frequency and shift insensitive to remaining substitution pattern)

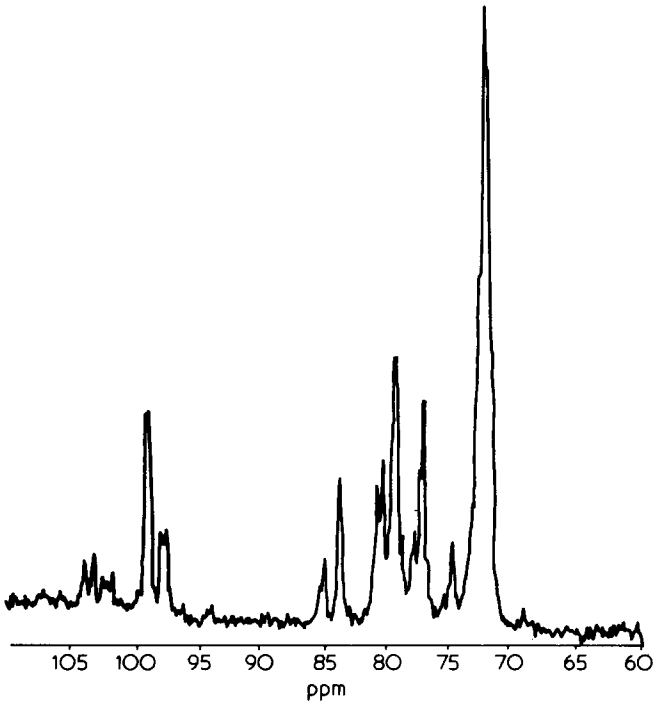


Figure 3 ^{13}C n.m.r. decoupled (75.5 MHz) spectrum of 2.8 *DOS* material denitrated for 5 min in 82% HNO_3/18% H_2O

as required by this assignment. It should also be noted that the intensity of the component at 83.2 ppm arising from C2 in the 2,6-disubstituted residues is the same as that of the highest field component of the anomeric carbon region again as required for a consistent assignment. The intense peak at 71.6 ppm corresponds to C6 nitrated material (shift insensitive to remaining substitution pattern) and to C5 which is fortuitously coincident in frequency. Since we would anticipate that C5 would have a comparable *NOE* to C2–C4 we may subtract the ratioed intensity for the C5 component from the total integrated intensity for the component at 81.6 ppm and this provides an estimate of the correcting factor to account for the expected difference in *NOE* for the methylene group of C6. The factor of 1.5 derived from this analysis has then been used to estimate the extent of non-nitrated glucose residues in appropriate cases from an analysis of the component at 60.5 ppm assigned to C6 ($-CH_2-OH$).

Before considering the data in detail we may note that our limited objective has been to investigate partial degrees of substitution in variously nitrated and denitrated cellulosic materials and partitioning of substituted β-D-glucopyranose residues amongst the mononitrate, dinitrate and trinitrate esters. We have not addressed ourselves to the important question of sequence distribution. It is clear, however, that such information is potentially available, particularly from the low field anomeric carbon region which is particularly susceptible to subtle changes in magnetic environment.

As one example of the likely difficulties in abstracting such information, *Figure 3* shows the ^{13}C n.m.r. spectra for a denitrated sample (82% HNO_3, 5 min reaction time). The high field anomeric region shows considerable fine structure; however, even with a 12 h accumulation time the *S/N* is not adequate to explore this in any detail. The n.m.r. analysis (see below) gives an overall *DOS* of 2.31 with ~50% of the β-D-glucopyranose residues being trisubstituted and ~20% being 6-monosubstituted, the partitioning between the disubstituted derivatives being 2:1 in favour of the 2,6 compared with the 3,6 derivative. Since Wu[3] has shown that substitution at C6 largely leaves the anomeric region unaffected, sequence distribution will be manifest from the effect of substitution at the C3 position in adjacent rings. On this basis we might anticipate that the lowest field component assigned to the anomeric carbon in the 3,6-dinitro substituted β-D-glucopyranose residues would be basically a doublet structure since the β-D-glucopyranose units linked to C1 will either have a nitrate ester group present (trinitro) or absent (2,6-dinitro, mononitro) at C3′. The shift in the anomeric region attributable to a nitrate ester functionality at C3 is ~1.3 ppm (the average splitting between both the first 2 and the second 2 components of the anomeric region). On the basis that a substituent at C3′ is one bond further removed, we might anticipate that the shift would be significantly smaller (observed 0.8 ppm) than for a C3 substituent in the ring in question. Since the shift at the anomeric carbon for a C6 nitrate ester function is known to be small, this provides a consistent overall description of the effect of a long range substituents. It is interesting to note that the derived substitution pattern for this sample would give approximately, for an octad sequence: 4-trinitrate, 3-dinitrate (1 of which would be 3,6-disubstituted) and 1 mononitrate ester β-D-glucopyranose residue. On a random basis, therefore, we might expect a 3:2 (2,3,6 and3,6 vs. 2,6-dinitrate plus mononitrate) intensity ratio for the low field region. Even with the relatively poor *S/N* ratio for the spectra in *Figure 2* it is clear that the intensity ratio is more nearly 3:4 and this seems to indicate non-random sequence distribution. The broadened nature of the components also indicates that although longer range effects are small they are none the less significant, and this becomes even more apparent in the analysis of the component centred at 104.7 ppm attributable to the anomeric carbon in β-D-glucopyranose residues with unsubstituted C2 and C3 positions. On an octad basis, this signal, originating from the anomeric carbon, should primarily show splitting originating from the presence or absence of a nitrate ester group in the C3′ position at the adjacent ring (attached to the anomeric carbon). Statistically, there is a probability ratio of 0.6 that a nitrate ester group is present in the C3′ position. However, the two outside components of the triplet (separated by 0.8 ppm) are of roughly equal intensity. This indicates that the cumulative effect of longer range shift effects (from C2) are probably important since a third component is also observed in an intermediate shift position. It is tempting to assign these three components in decreasing shift to low field as arising from adjacent β-D-glucopyranose residues which are either the trinitrate, 3,6- or 2,6-dinitrate derivatives, the indication again being that the sequence distribution is non-random. The more intense components at higher field (99.7 and 98.4 ppm), attributed to trinitrate and 2,6-dinitrate substituted β-D-glucopyranose residues, also exhibit fine structure. Thus the latter shows a 3 component structure which might be attributable to the lack or presence of nitrate ester functionalities at either or both of C3′ and C2′. The dominant component arising from the trinitrate at 99.7 ppm again suggests a rather specific sequence arrangement. In summary, therefore, it appears that sequence information might be accessible from detailed analysis of the anomeric carbon region which is especially sensitive to substitution pattern in the adjacent glucose residue.

Table 1 Nitration

Acid mix	N.m.r. *DOS* total	*DOS* partial			Percentage components				
		C_6	C_2	C_3	Tri	2,6	3,6	6 mono	Unsubstituted
18.7% HNO_3 59.3% H_2SO_4 21% H_2O	2.37	0.94	0.77	0.66	55 (46)	22 (28)	11 (14)	6 (11)	6
22% HNO_3 75% H_2SO_4 3% H_2O	2.62	1.0	0.87	0.75	62 (67)	25 (20)	13 (10)	– (3)	–
64% HNO_3 26% H_3PO_4 10% P_2O_5	2.83	1.0	0.94	0.89	83 (81)	11 (11)	6 (6)	– (2)	–

However, we foresee major problems in investigating this in any detail since the *S/N* ratio for the spectra in *Figure 2* is not sufficiently good and improvement with current instrumentation would not be feasible on a realistic time scale.

Partial DOS *for nitration in different acid mixes*

Having considered the basis of the assignments and subsequent analysis of data we may now proceed to a discussion of the data for partial *DOS* for nitration in the 3 different acid mixes described in the previous section. The data are shown in *Table 1*. Considering firstly the material of highest total *DOS* (2.83), no evidence has been detected for any monosubstituted residues and a partitioning between 83% trinitrate, 11% 2,6-dinitrate and 6% 3,6-dinitrate yields partial *DOS* of 1, 0.94 and 0.89 for C6, C2 and C3 carbons. The corresponding data for the nitrated material of lower *DOS* reveals that only for the material of 2.37 *DOS* is there any significant contribution from unsubstituted β-D-glucopyranose residues.

From the limited number of nitrocelluloses studied in detail by Wu[3] a general treatment of equilibrium partial *DOS* was suggested, the central feature of which is that the reactivity of a given hydroxyl group is independent of the substitution pattern. In the light of the crude examination of sequence distributions described above, the implication of such a model that reactivities and positions in adjacent β-D-glucopyranose residues do not depend on substitution pattern does not seem to be tenable and this raises doubts about the validity of a simplistic description of a series of complex equilibria in terms of only 3 parameters: namely, the ratios of equilibrium constants for substitution at the 3 sites (2, 3 and 6) in a given β-D-glucopyranose residue. Since the nitrated materials described here fall in a *DOS* range not explicitly examined in detail by Wu[3] but nonetheless covered by his distribution model it is of interest to compare the ^{13}C n.m.r. derived substitution patterns with those predicted by the simple equilibrium model. The data are shown in brackets in the relevant columns in *Table 1* and reveal tolerable agreement, the main discrepancy being the overestimate of the model of the extent of unsubstituted and monosubstituted β-D-glucopyranose residues. Since a large number of samples have been investigated in this work in the total *DOS* range 2.0–2.83 we will postpone a detailed comparison with the predictions based on Wu's model until a later section.

Denitration in different acid mixes for fixed periods of time

The denitration of 2.83 initial *DOS* starting material has been investigated in the 4 different acid mixes described in the experimental section. Analysis of the ^{13}C n.m.r. spectra provides the data displayed in *Table 2*. The first important point to note is that denitration to a total *DOS* of 2.0 provides no evidence for unsubstituted β-D-glucopyranose residues. The equal distribution of tri- and mononitrate substituted residues is fortuitously in agreement with Wu's simple model. However, this model predicts a substantially larger proportion of disubstituted products than are actually observed. Since the simple model essentially ignores medium effects, material of the same *DOS* produced either by nitration of denitration under different conditions should appear with the same distribution pattern. A comparison of the data in *Table 1* for *DOS* 2.37 with that in *Table 2* for *DOS* 2.43 again reveals tolerable agreement, the only major discrepancy being the partitioning between monosubstituted and unsubstituted residues. The denitration process is seen to be in the order C3>C2>C6. The equilibrium *DOS* decreases rapidly on going from fuming nitric acid to 79.1% nitric acid, which corresponds approximately in composition to the monohydrate.

Denitration in a given acid mix as a function of time

Starting from a material of *DOS* 2.83, samples have been examined by ^{13}C n.m.r. after periods of 1, 5, 20, 300 and 400 s denitration in 82% nitric acid. The data are displayed in *Table 3*.

We have previously shown by e.s.c.a. that denitration to a depth of ~100 Å[4] is at the equilibrium value for a given acid mix in a reaction time of 1 s and the fact that ^{13}C n.m.r. detects no difference with respect to the initial starting material merely reflects the small fraction of the total volume sampled by e.s.c.a. In 5 s reaction has penetrated considerably into the macrofibrils and significant differences are observed. Thus the *DOS* drops from 2.83 to 2.72 largely as a result of the denitration at the C2 and C3 positions.

The *DOS* of 2.15 at 40 min reaction time is essentially the equilibrium value and the data for samples studied after longer reaction periods (up to 12 h) provide identical data. The *DOS* is marginally lower than for the sample denitrated in 83% nitric acid, the data for which are displayed in *Table 2*. The distribution of substitution patterns are similar, the main difference being the higher percentage contribution of monosubstituted β-D-glucopyranose residues for the lower acid strength. This trend is maintained since for the 79.1% acid strength the *DOS* has dropped further to 2.0.

Table 2 Denitration in nitric acids for 2 h

Acid mix	Total *DOS* from n.m.r.	*DOS* partial			Percentage components				
		C_6	C_2	C_3	Tri	2,6-	3,6-	6-Mono	Unsubstituted
64% HNO_3 * 26% H_3PO_4 10% P_2O_5	2.83	1.0	0.94	0.89	83	11	6	–	–
95% HNO_3 5% H_2O	2.74	1.0	0.92	0.82	74	18	8	–	–
88% HNO_3 12% H_2O	2.43	1.0	0.77	0.66	55	22	11	12	–
83% HNO_3 17% H_2O	2.21	1.0	0.68	0.53	37	31	16	16	–
79,1% HNO_3 20.9% H_2O	2.00	1.0	0.56	0.44	31	25	13	31	

* Starting material

Table 3 Denitration in 82% HNO_3 as a function of time

Acid mix	Total *DOS* from n.m.r.	*DOS* partial			Percentage components				
		C_6	C_2	C_3	Tri	2,6-	3,6-	6-Mono	Unsubstituted
64% HNO_3 * 26% H_3PO_4 10% P_2O_5	2.83	1.0	0.94	0.89	83	11	6	–	–
82% HNO_3 1 s treatment	2.83	1.0	0.94	0.89	83	11	6	–	–
82% HNO_3 5 s	2.72	1.0	0.9	0.82	74	16	8	2	–
82% HNO_3 20 s	2.62	1.0	0.86	0.76	66	20	10	4	–
82% HNO_3 5 min	2.31	1.0	0.71	0.6	47	24	13	17	–
82% HNO_3 40 min	2.15	1.0	0.63	0.52	40	23	12	25	–

* Starting material

Comparison of data

The implication of the simplified analysis presented by Wu[3] is that material of a given *DOS* should show the same partitioning of substituted β-D-glucopyranose residues irrespective of the equilibrium conditions under which it is produced. That this is not entirely true is most readily apparent from a comparison of a series of nitrated and denitrated materials in the *DOS* range 2.0–2.83 where the major proportion of β-D-glucopyranose residues are either di- or trisubstituted. The data can most readily be appreciated from a histogram plot as shown in *Figure 4*. The striking feature evident from this data is that the ratio of the 2,6 to 3,6-disubstituted products does indeed appear to be largely independent of the medium as proposed by Wu[3]. However, we have previously drawn attention to the fact that for nitrated and denitrated materials of comparable *DOS* (2.37 vs. 2.43) the distribution of mono- and unsubstituted residues is different, and indeed for denitrated material down to a *DOS* of 2.0, there is no evidence for unsubstituted β-D-glucopyranose residues. Reference to Wu's distribution curves shows that if a simple model based on 3 equilibrium constants were applicable, a material of *DOS* 2.0 should have several percent of unsubstituted residues whilst for material of *DOS* 2.37 there should be no unstubstituted residues. The data in *Figure 3* therefore show in a graphical sense that the situation is considerably more complex than implied by Wu's elegant but simple analysis. The crude but nonetheless important observation that sequence distribution is not likely to be random also suggests that reactions at a given site in a glucose residue are influenced by the substitution pattern in adjacent rings and this again casts doubt on the validity of a simple model which *assumes* that within a given ring substitution at one site is independent of the substitution pattern at other sites in a given β-D-glucopyranose residue. Literature data also cast serious doubts on the validity of such an assumption since it is known from studies of denitration of simple model systems that rates are greatly influenced by structure[8]. Thus, denitration of ethylene glycol dinitrate (e.g. as a model of a 2,3-dinitrosubstituted β-D-glucopyranose residue) is an order of magnitude faster than for 1,4-butylene glycol dinitrate (e.g. as a model for 3,6-dinitrosubstituted β-D-glucopyranose residue). The relative rates

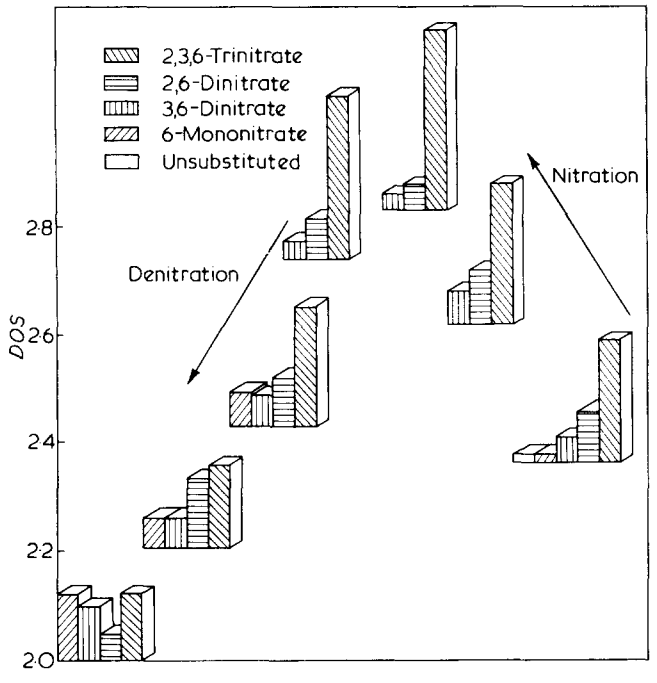
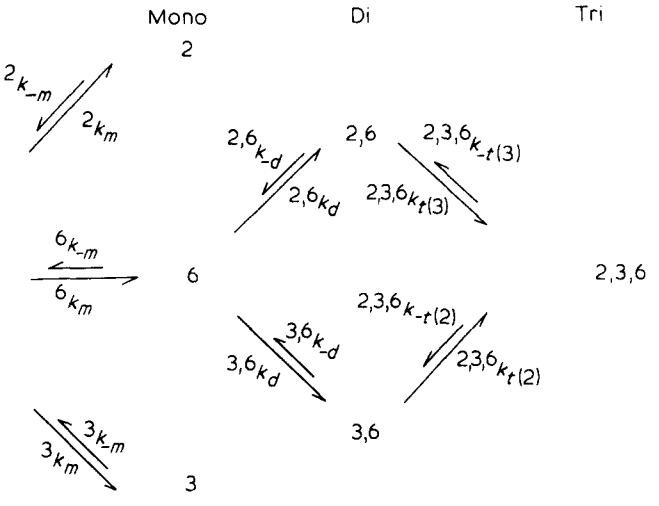


Figure 4 Block histogram of percentage components of tri-, di-, mono- and unsubstituted β-D-glucopyranose units in a range of nitrated and denitrated materials



Scheme A Partial reaction sequences involved in nitration–denitration equilibria for a β-D-glucopyranose residue. (Further reactions of the 2 and 3 monosubstituted residues have been omitted for the sake of clarity, see text)

of nitration and denitration at a given position in a substituted β-D-glucopyranose residue is thus likely to be grossly rather than subtly dependent on substitution pattern. Published data on relative rates of denitration of simple model systems show that a primary nitrate ester is particularly stable and, on the basis of this, the observed behaviour in denitration of the mononitro (6-substituted) residue being produced with no evidence for unsubstituted β-D-glucopyranose residues is readily understandable. Although it is not possible with the data available to quantify the discussion further, sufficient data is available to assess the likely ordering of relative rate and equilibrium constants and to this end we may consider the partial reaction sequences shown in *Scheme A*.

No evidence has been presented in the literature on rate data for the initial formation of monosubstituted derivatives other than the 6-substituted β-D-glucopyranose residue. However, the fact that a significant proportion of the glucose residues are unsubstituted in nitrated material of *DOS* 2.37 strongly suggests that the rate constants for nitration of the 2 and 3 sites in a given glucose residue increase with the partial *DOS* in the particular residue in question. This must be so since the literature data[9] on model systems indicates that the rate of a denitration step increases the more highly substituted the derivative. In terms of the partial *Scheme A* the rate constants for denitration of monosubstituted derivatives is certainly in the order $^{6}k_{-m} \ll {}^{2}k_{-m}, {}^{3}k_{-m}$. There is no available literature data on rates of nitration at primary and secondary sites in model systems; however the equilibrium constants for formation of the mononitrate esters are undoubtedly in the order $^{6}k_{m} > {}^{2}k_{m}, {}^{3}k_{m}$. Since the order of rate constants for denitration are likely to be $^{6}k_{-m} \ll {}^{2,6}k_{-d}$, $^{3,6}k_{-d} < {}^{2,3,6}k_{-t(2)}$, $^{2,3,6}k_{t(3)}$ the order of rate constants for nitration must be $^{6}k_{m} < {}^{2,6}k_{d}$, $^{3,6}k_{d} < {}^{2,3,6}k_{t(2)}$, $^{2,3,6}k_{t(3)}$. The constancy under both conditions of nitration and denitration of the 2,6 to 3,6 disubstituted residues implies that $^{2,6}k_{d}/{}^{3,6}k_{d} = {}^{2,3,6}k_{t(3)}/{}^{2,3,6}k_{t(2)}$, and this is consistent with a greater reactivity of the 2 position relative to the 3 position for a given partial *DOS* in the residue in question. In summary, therefore, the nitration–denitration reactions are considerably more complex than has been implied in the past and a simplified model based on only 3 equilibrium constants can only provide a crude qualitative picture of the partial *DOS* in nitrated or denitrated cellulose samples.

The development by Wu[3] of a convenient method for the elaboration of partial *DOS* in cellulosic material particularly with the refinements developed in this paper, however, does provide a basis for discussing the changes in lattice spacing which are observed in materials of the same *DOS* which have been prepared in different ways.

ACKNOWLEDGEMENTS

Thanks are due to SRC for provision of equipment and to the MOD for a research studentship for one of us (P.J.S.). Thanks are also due to Drs T. J. Lewis and F. S. Baker for helpful discussions.

REFERENCES

1 Miles, F. D., 'Cellulose Nitrate', Oliver and Boyd, London, 1955
2 Bikales, N. S. and Segal, L., 'Cellulose and Cellulose Derivatives, Part V', Wiley-Interscience, 1971
3 Wu, T. K. *Macromolecules* 1980, **13**, 74
4a Clark, D. T. in 'Characterization of Polymers by Means of Photon, Ion and Electron Probes', ACS Symposium Series (Ed. H. R. Thomas and D. W. Dwight) 1980, in press
4b Clark, D. T. and Stephenson, P. J., 'Propellants and Explosives', Proceedings of the Nitrocellulose Conference, Waltham Abbey, 1980 (Ed. T. J. Lewis), Plenum Press
5 Trommel, J., Communication No. 15, 1959 of the N.V. Koninklijke Nederlandsche Springstoffeen-Fabrieken. Henengrucht 204, Amsterdam-C, The Netherlands
6 Murray, G. E. and Purves, C. B. *J. Am. Chem. Soc.* 1940, **62**, 3197
7 Clark, D. T. and Stephenson, P. J., unpublished results
8 Mitchell, R. L. *Anal. Chem.* 1949, **21**, 1496
9 Svetlov, B. S. *Kinet. Katal.* 1972, **13**, 792