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The formation and stability of partially and completely substituted cellulose nitrite esters in dipolar aprotic solvents containing N_2O_4

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ABSTRACT

As some contradictions still exist concerning the mechanism of cellulose dissolution in N_2O_4–*N,N*,-dimethylformamide and N_2O_4–dimethyl sulfoxide systems, the problem of the existence and stability of cellulose trinitrite in these systems has been investigated using ^{13}C NMR spectroscopy. Cellulose trinitrite is definitely formed as a rather stable compound provided a very low level of water (0.01–0.02%) is maintained in the system. Upon addition of protic liquids (H_2O or MeOH), decomposition of the nitrite groups takes place in the order of stability C-2 $<$ C-3 $\ll$ C-6. On dissolving cellulose in a N_2O_4–Me_2SO system containing some water, a preferred nitrosation in the order C-6 $>$ C-2 $>$ C-3 was observed. The homogeneous nitrosation of cellulose dissolved in LiCl–*N,N*-dimethylacetamide indicated a reactivity of OH groups in the order C-6 $>$ C-3 $\geqslant$ C-2.

INTRODUCTION

N_2O_4 combined with a suitable dipolar aprotic solvent such as *N,N*-dimethylformamide (Me_2NCHO) or dimethyl sulfoxide (Me_2SO) has long been known to dissolve rather quickly and completely even high molecular weight cellulose, other polysaccharides, and also mixtures of cellulose and various synthetic polymers[1–6]. Different opinions still exist regarding the mechanism of this process of dissolution, especially with respect to cellulose nitrite formation and the stability of this compound in systems containing N_2O_4.

Those favoring the concept of cellulose nitrite formation during dissolution for the most part assume a heterolytic dissociation of N_2O_4 into NO^+ and NO_3^-, favored by an intermolecular interaction with a donor solvent such as Me_2NCHO or Me_2SO. Nakao[5] considered the primary formation of an ionic electron donor–

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acceptor (EDA) complex between N_2O_4 as a Lewis acid and the nucleophilic solvent, which subsequently reacts with cellulose to the nitrite ester. Clermont and Bender[7] concluded that a nitrite ester indeed formed based on IR studies of the N_2O_4–Me_2NCHO–cellulose system in which there was shown to be a dependence on temperature. Schweiger[8] observed, by precipitation of the polymer and its chemical and IR spectroscopic analysis, cellulose trinitrite formation in either Me_2NCHO or in an inert solvent such as benzene in the presence of tertiary amines like pyridine. As shown earlier[9], precipitates of cellulose nitrite with a ds of 2.6–2.9 can be obtained from systems containing N_2O_4 or NOCl by addition of triethylamine under strictly anhydrous conditions. Some stabilization of the nitrite group could be achieved by introducing a second substituent via a reaction between cellulose and a salt-like nitrosylic compound such as $NOSO_4H$ (refs. 9, 10). Portnoy and Anderson[11] identified a polymer film isolated from a N_2O_4–Me_2NCHO–cellulose system in the presence of pyridine as a cellulose nitrite, but they explicitely noted that the spectroscopic technique employed could not be applied in situ to the original liquid system. Hergert[12] mentioned the formation of cellulose nitrite on dissolving cellulose in N_2O_4–Me_2NCHO or N_2O_4–Me_2SO and concluded that the presence of 0.2–1.0% water is required in the N_2O_4–Me_2SO system to dissolve cellulose at room temperature[2]. Torgashov et al.[13] published a procedure for the precipitation of a highly substituted (ds 2.85–2.97) cellulose nitrite from systems of N_2O_4, cellulose, and an aprotic solvent by anhydrous diethyl ether without addition of amine. Gert et al.[14] reported WAXS studies on cellulose nitrite, prepared from native cellulose, indicating a regeneration of cellulose I by water vapour. But Torgashov et al.[13] also emphasize that no analytical procedure is presently available to identify a highly substituted cellulose nitrite in the original solution. Referring to earlier work of Ishii[15], Isogai et al.[16] indirectly confirmed, by ^1H NMR, the presence of a high-ds cellulose nitrite in the N_2O_4–Me_2NCHO–cellulose system.

Before considering the concepts of cellulose dissolution in N_2O_4-containing systems without covalent derivatization, an early publication of Fowler et al.[17] from 1947 should be mentioned. This assumed that a primary addition compound is formed between N_2O_4 and the aprotic solvent, which then dissolves the cellulose via H-bond interaction either with the N_2O_4 part or with the solvent part of this addition compound. In a recent review Golova et al.[18] summarized the present knowledge on cellulose dissolution in organic solvent systems, favoring a dissolution of cellulose in N_2O_4-containing systems without covalent derivatization of the polymer. Backed by quantum chemical calculations, Grinspan[19] postulated the formation of an EDA compound between the solvent and monomeric NO_2 instead of the dimer N_2O_4. This complex subsequently solvates the cellulose[18]. Grinspan et al.[20] reported on well-defined gaps in the phase diagrams of NO_2 and an aprotic solvent, and argued that cellulose is dissolved in those mixtures within a limited NO_2 : solvent ratio only. Laisa and Sarkov[21] also postulated an adduct formation between NO_2 and the aprotic solvent with subsequent dissolution of the cellulose.

In our earlier work[9] we observed a maximal ds of 1.5 for nitrite ester groups in the reaction of cellulose with salt-like nitrosylic compounds. ^{13}C NMR data obtained by us in connection with cellulose sulfation in the N_2O_4–Me_2NCHO system[22,23] led to the assumption of complete C-6 substitution by nitrite ester groups, along with partial substitution and/or an addition compound at C-2 and C-3.

Summarizing the present knowledge, the majority of authors favor cellulose nitrite formation on dissolution of this polymer in N_2O_4-containing systems. A direct proof of the existence of this cellulose ester in the reaction system is still missing. Furthermore, no data are available on the stability of nitrite ester groups in the different positions of the anhydroglucose unit (AGU).

Herein is summarized the results of experiments performed to resolve contradictions about the mechanism of dissolution of cellulose in mixtures of N_2O_4 with Me_2NCHO or Me_2SO, respectively, under well-defined conditions in which components of the reaction systems are characterized by ^{13}C and ^{1}H NMR spectroscopy. Principal points of this work address the question of the existence and stability of cellulose nitrite in these solutions and the dependence of this stability on temperature and protic additives.

EXPERIMENTAL

Materials.—Cellulose samples were commercial cellulose powder with a $dp_{Cuoxam} = 160$ (Heweten 10HZ^{R}, Zellstoff und Papierfabrik Weissenborn, Weissenborn/Sachsen), denoted as sample A, and an acid-hydrolysed rayon staple fibre with a $dp_{Cuoxam} = 40$, denoted as sample B.

Polar aprotic solvents Me_2NCHO and Me_2SO were first distilled and then dried with molecular sieve (Zeosorb 5 IM) to a water content of 0.01–0.02%. Analytical grade pyridine was distilled after drying over CaH_2. Methanol (analytical grade, $\leqslant 1.0\%$ water) was used without further purification.

Industrial grade N_2O_4 was used with a purity of 97–98%, the remaining 2–3% being HNO_3.

Preparation of cellulose nitrite solutions.—Cellulose trinitrite in Me_2NCHO. Cellulose sample A (10 g, dried for 15 h at 105°C) was swelled in dry Me_2NCHO (300 mL) at 20°C overnight. Subsequently the Me_2NCHO (200 mL) was removed in vacuo at 70°C. After cooling to −5°C, a solution of N_2O_4 (18.7 g, 3.3 mol per mol AGU) in Me_2NCHO was added, and the mixture was rigorously stirred under anhydrous conditions for 1 h at −5°C. ^{13}C NMR spectra were recorded after a 2-h storage at −10°C, and subsequently after 2 and 30 days storage at 20°C.

For comparison of NMR spectra, 25 mL of the above-mentioned mixture was mixed at 20°C with dry pyridine (3.4 mL, 5 mol per mol AGU). Addition of triethylamine to the system, instead of pyridine, resulted in exothermic side-reactions and precipitation of the polymer, as mentioned earlier[3].

Cellulose trinitrite in Me_2NCHO-d$_7$.—For recording 2D NMR spectra, a cellulose trinitrite solution was prepared with a polymer content of 12% (sample B) in dry Me_2NCHO-d_7.

Cellulose powder (0.5 g, dried at 105°C) was swelled at 70°C in 2.5 mL of Me_2NCHO-d_7 by simultaneously evaporating 0.5 mL of the solvent in vacuo. After cooling the mixture to 0°C, the cellulose was dissolved by adding excess N_2O_4 (6 mol per mol AGU).

Partially substituted cellulose nitrite in Me_2NCHO from cellulose trinitrite solution.—To 25 mL of cellulose trinitrite solution in Me_2NCHO prepared from sample A at −5°C, MeOH (0.47 mL, 1.5 mol per mol AGU) was slowly added with stirring at −5°C, which resulted in a yellowish cellulose nitrite solution with a ds = 1.9. On addition of more MeOH, the system coagulated rather quickly. In order to add water to a cellulose trinitrite solution in Me_2NCHO without phase separation, 50 mL of the above-mentioned trinitrite solution in Me_2NCHO was first mixed with dry pyridine (4.15 mL, 3 mol per mol AGU), and after storage for 1 day, a solution of water (0.42 mL) in pyridine (2.77 mL, 1.5 mol water and 2 mol pyridine per mol AGU) was slowly added under stirring at 20°C, resulting in a clear, yellow solution with a ds = 0.9 of nitrite groups. After addition of 2.5 mol of H_2O per AGU by an analogous procedure, the system coagulated after about 30 min.

Cellulose trinitrite in Me_2SO.—Cellulose (10 g, sample A, dried at 105°C) was stirred for 2 h at 20°C in dry Me_2SO (100 mL) in vacuo and then swollen overnight. Upon addition of N_2O_4 (23.5 g, 4 mol per mol AGU) at 20°C under stirring, the polymer at first dissolved but subsequently solidified as highly swollen, transparent gel particles. During 2 h stirring at 60–70°C, the gel again liquified to a dark brown-green solution, which solidified to a coherent gel on cooling. For determining the NMR spectra, the warm solution was transferred to the sample tube and measured at 50°C.

Partially substituted cellulose nitrite in Me_2SO from trinitrite solution.—To the above-mentioned trinitrite solution in Me_2SO, a mixture of water (2.2 mL, 2 mol per mol AGU) and dry Me_2SO (25 mL) was added dropwise within 20 min at 50°C, resulting in a light-green solution of cellulose nitrite with a ds = 1.8, which did not coagulate at room temperature.

Partially substituted cellulose nitrite in Me_2SO by dissolution of cellulose.—Air-dried cellulose containing 5% water (2.75 g, sample A) was swollen in Me_2SO (50 mL) containing water (0.25 mL) at 20°C. After 1 h the cellulose was dissolved by adding N_2O_4 (4.6 g) under stirring. The resulting light-green cellulose nitrite solution (ds = 1.9) had a content of 3.25 mol of N_2O_4 and 1.3 mol of H_2O per mol AGU.

NMR spectroscopical characterization.—The ^1H and ^{13}C NMR spectra were recorded using a Bruker MSL400 (400 MHz) and AM300 (300 MHz) instruments for the ^1H NMR spectra, and 100.63 and 75.47 MHz for the ^{13}C NMR spectra, respectively. Sample tube sizes were 5 mm for ^1H, and 10 mm for ^{13}C. The accumulation numbers were between 100 and 500 scans. Me_4Si was employed as

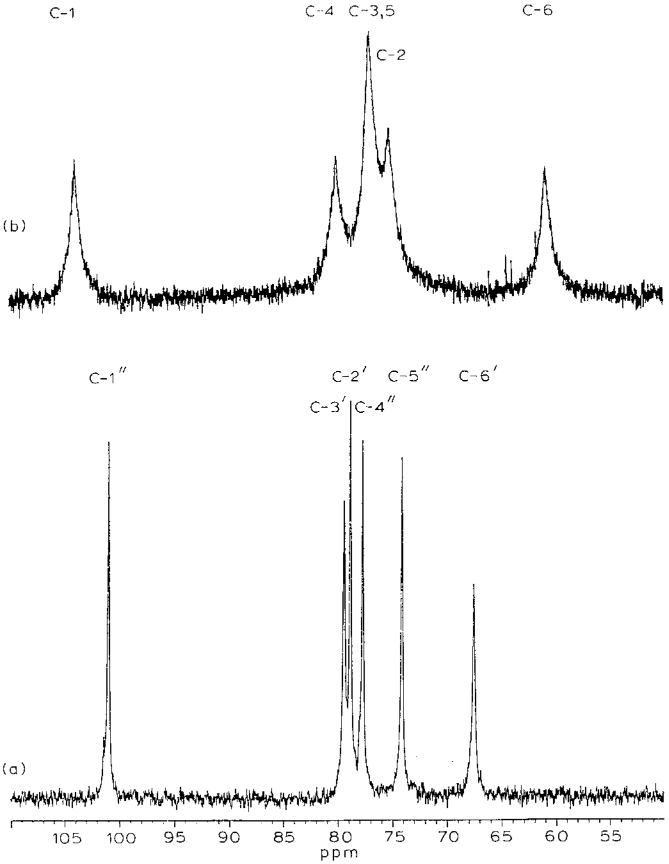

Fig. 1. Comparison of ^{13}C NMR spectra of cellulose solutions in (a) N_2O_4–Me_2NCHO and (b) LiCl–Me_2NCOMe (C-3 and C-5 signals are not resolved due to the scale of the reduction of the spectrum).

an internal standard. Assignment of the ^1H and ^{13}C NMR signals was achieved by ^1H–^1H COSY and ^{13}C–^1H COSY techniques. The COSY spectra were collected by using a 512 × 2048 data matrix, and 64 transients were acquired for each of 512 t_1 values. Spectral widths of 1740.9 Hz were used in both dimensions. The determination of the degree of substitution (ds) was performed by calculation of the signal integrals which were recorded under conditions of ^1H decoupling. The integrals of the substituted signals were compared with the sum of the integrals of the substituted and nonsubstituted signals.

RESULTS AND DISCUSSION

Cellulose trinitrite formation on dissolution in N_2O_4–Me_2NCHO.—After dissolution of cellulose sample A in the N_2O_4–Me_2NCHO mixture at room temperature under anhydrous conditions, the ^{13}C NMR spectrum of this system (Fig. 1a) was compared to that of a cellulose solution in LiCl–Me_2NCOMe (Fig. 1b), where according to refs. 24–26 no derivatization takes place. As can be seen in Fig. 1, the ^{13}C NMR spectrum of the cellulose–N_2O_4–Me_2NCHO system consists of six signals, like that of the cellulose solution in LiCl–Me_2NCOMe, but with a significant downfield shift at C-2, C-3, and C-6 of +2.8, 2.6, and 3.7 ppm, respectively. This is in general agreement with the observation that a substitution of OH groups within the AGU leads to a downfield shift of the signals of the directly bound C-atoms (marked C-2′, C-3′, and C-6′). The signals of the neighbouring C-atoms are shifted upfield by −2.8 ppm at C-1, −1.2 ppm at C-4, and −2.3 ppm at C-5 (marked C-1″, C-4″, and C-5″). These facts rather unambigously indicate a complete covalent derivatization of the OH groups in the C-2, C-3, and C-6 positions. No significant changes in the N_2O_4–Me_2NCHO system were detected when employing cellulose sample B of rather low dp instead of sample A.

In order to assess the stability of cellulose trinitrite in the N_2O_4–Me_2NCHO–cellulose system, solutions were examined for temperature dependence vs. the time of reaction under conditions of exclusion of air and moisture.

A preparation of the cellulose solution at a temperature of −5°C by intense cooling also proved to have no significant influence on the ^{13}C NMR spectrum as compared to the system obtained at room temperature up to 30 days.

A final, definitive assignment of the ^{13}C signals was achieved by 2D NMR spectroscopy via shift-correlated ^1H–^1H and ^{13}C–^1H COSY experiments of a 12% solution of cellulose trinitrite (sample B) in the N_2O_4–Me_2NCHO-d_7 system.

The result of the ^1H–^1H COSY experiment was the precise assignment of the ^1H signals of cellulose trinitrite, while the exact assignment of the ^{13}C signals was made from the ^{13}C–^1H COSY data (compare Figs. 2a and 2b).

Fig. 2a shows the contour plot of the ^1H–^1H COSY spectrum with projection on the horizontal axis. The peaks observed at 5.68, 5.14, 5.01, 4.93, 4.68, and 3.94 ppm correspond to the H-signals 3, 2, 6a, 1, 6b, and 5 or 4, respectively. Fig. 2b shows the contour plot of the ^{13}C–^1H COSY spectrum with projection spectra on the horizontal (^{13}C) and longitudinal (^1H) axis. Six peaks were observed at 100.6, 79.3, 78.9, 77.6, 73.7, and 67.7 ppm on the ^{13}C axis. The peaks assigned in Fig. 2a were also observed in the ^1H projection spectrum. The contour plot revealed that the ^{13}C peak at 100.6 ppm was correlated with the ^1H peak at 4.93 ppm, which assigned this ^{13}C peak to the C-1 carbon. In the same manner the ^{13}C peaks at 79.3, 78.9, 77.6, 73.7, and 67.7 ppm were respectively assigned to C-3, C-2, C-4, C-5, and C-6.

Effect of additives on the ^{13}C NMR spectrum of cellulose in N_2O_4–Me_2NCHO.— As no direct addition of water to this system could be carried out without precipitation of polymer, pyridine–water mixtures were employed, leading to the persistence of a one-phase system up to a water content of 2 mol per mol of AGU. At first it was determined that anhydrous pyridine, known to stabilize cellulose trinitrite ester, added to the system up to an amount of 5 mol per mol AGU did not induce any change in the ^{13}C NMR spectrum of cellulose trinitrite in N_2O_4–

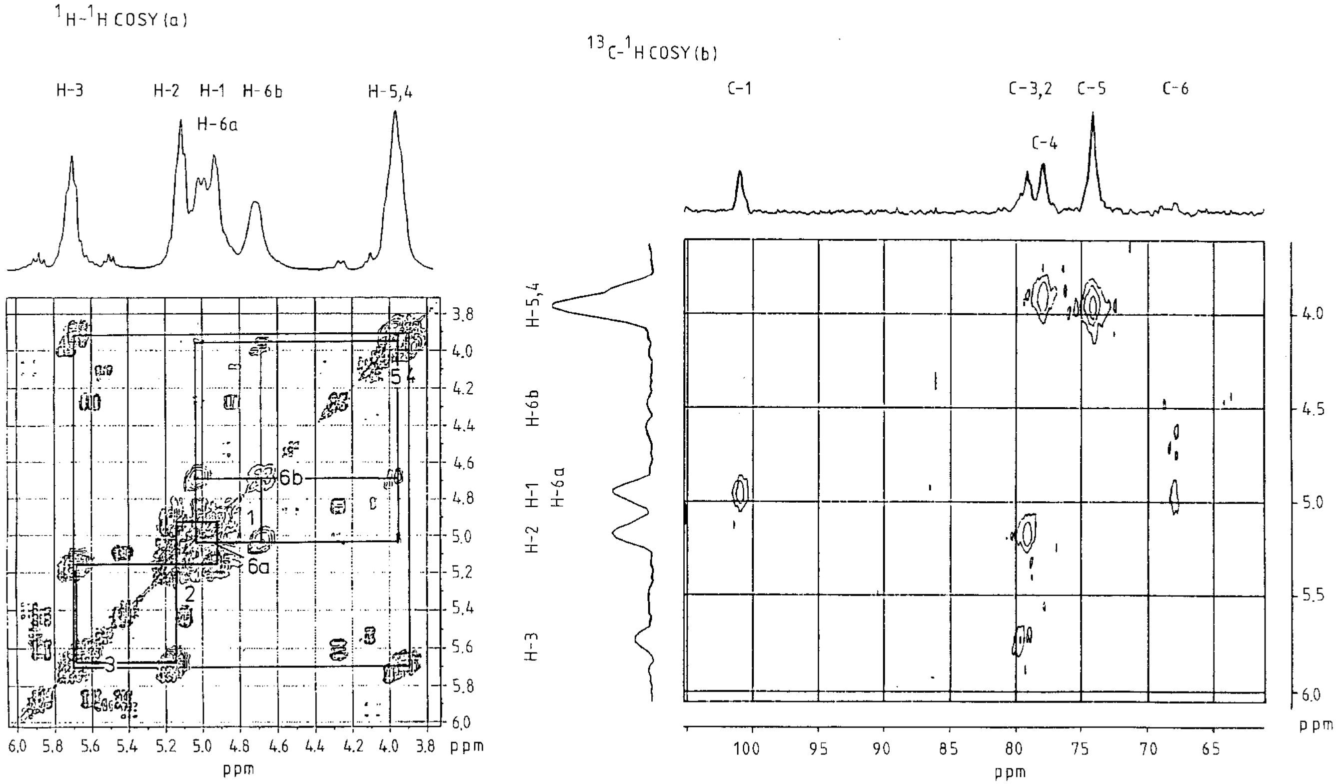

Fig. 2. ^{1}H–^{1}H (a) and ^{13}C–^{1}H (b) COSY spectra of the cellulose–N_2O_4–Me_2NCHO-d_7 system.

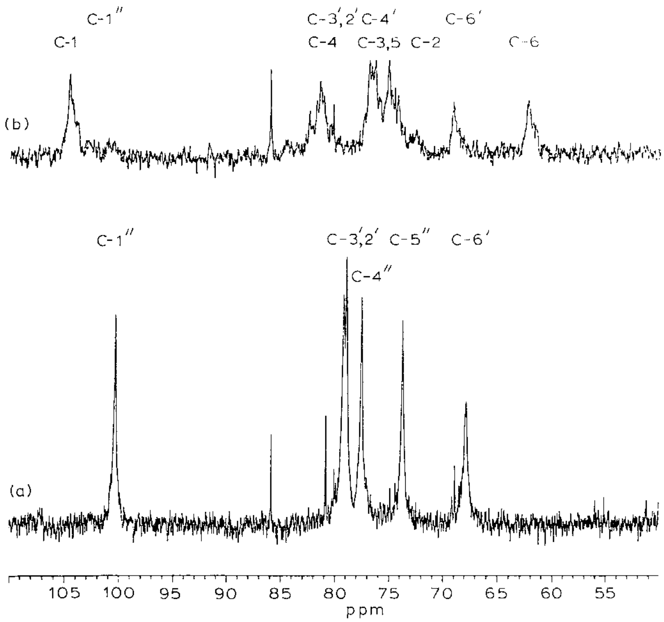

Fig. 3. ^{13}C NMR spectra of the system cellulose–N_2O_4–Me_2NCHO after addition of (a) dry pyridine and (b) pyridine containing water.

Me_2NCHO (compare Figs. 3a and 1). A cellulose nitrite solution containing 3.3 mol N_2O_4, 5 mol pyridine, and 1.5 mol H_2O per mol AGU, showed a definite change in the ^{13}C NMR spectrum (Fig. 3b): the spectrum of Fig. 3b indicates that all C-atoms of the AGU give rise to two signals, each corresponding to a substituted and an unsubstituted part. Obviously, a partial denitrosation takes place at all three positions in the order C-2 $\geqslant$ C-3 $>$ C-6 (ds of nitrite groups at C-2, 0.2; at C-3, 0.2; and at C-6, 0.5).

After slow addition, with cooling, of 1.5 mol of methanol (instead of the water–pyridine mixture) per mol of AGU, the nitrite groups were found to be partially eliminated at the C-2 and C-3 positions (ds C-2, 0.4; C-3, 0.5). In contrast, these groups were completely stable at the C-6 position, indicating a higher degree of stability for C-6 nitrite groups over those at either C-2 or C-3 (compare Table I).

Experiments on cellulose trinitrite formation in the N_2O_4–Me_2SO system.—As mentioned in the Experimental, this system solidified to a thermoreversible polymer gel at room temperature under the strictly anhydrous conditions employed. The ^{13}C NMR spectrum (Fig. 4a) shows essentially the same resonances as was observed for the N_2O_4–Me_2NCHO system, with small differences of ~0.3 ppm obviously being caused by solvent effects (Table I).

To determine unequivocally whether the complete substitution is really caused by nitrite ester groups and not by nitrate groups, a ^{13}C NMR spectrum of cellulose trinitrate in Me_2SO (ref. 27) was compared with the various nitrite systems (Table I). As can be seen in Table I, significant differences in chemical shifts are observed

TABLE I

^{13}C NMR chemical shifts and ds of cellulose dissolved in N_2O_4-containing systems

Solvent system	^{13}C NMR chemical shifts						ds			
	C-1	C-2	C-3	C-4	C-5	C-6	Total	C-2	C-3	C-6
N_2O_4–Me_2NCHO (sample A)	100.6	78.9	79.3	77.6	73.7	67.7	3	1	1	1
N_2O_4–Me_2NCHO (sample B)	101.0	78.9	79.4	77.7	74.1	67.5	3	1	1	1
N_2O_4–Me_2NCHO + Pyridine	100.3	78.9	79.2	77.5	73.7	67.8	3	1	1	1
N_2O_4–Me_2NCHO	104.5	75.0	76.5	81.4	76.5	62.2				
+ Pyridine–H_2O	100.5	82.4	84.4	76.8	74.2	69.0	0.90	0.20	0.20	0.5
N_2O_4–Me_2NCHO	104.8	73.7	73.9	79.0	73.9					
+ MeOH	100.4	81.9	83.7	77.6	72.7	68.2	1.90	0.40	0.50	1
N_2O_4–Me_2SO	100.6	79.1	79.3	77.7	74.0	67.9	3	1	1	1
N_2O_4–Me_2SO	104.5	72.6	74.1	77.9	74.1					
+ H_2O	100.5	80.2	83.6			66.5	1.8	0.30	0.50	1
N_2O_4–	104.5	72.6	73.9	77.6	72.6					
Me_2SO–H_2O	100.3	79.0	83.3			68.2	1.9	0.60	0.3	1
Cellulose trinitrate (Me_2SO)	99.0	79.2	77.9	76.3	70.6	70.6	3	1	1	1
LiCl–Me_2NCOMe	103.9	74.9	76.6	79.8	76.6	60.6				
LiCl–Me_2NCOMe	104.6	73.3	74.1	80.3	74.1	61.2				
+ N_2O_4	100.1	81.9	83.8	77.7	73.2	66.9	1.35	0.25	0.35	0.75

for most of the C-atoms between the cellulose trinitrate spectrum in Me_2SO and the N_2O_4–Me_2SO–cellulose system. It thus seems justified to rule out the formation of cellulose nitrate instead of the nitrite in the systems considered here.

Effect of water on the ^{13}C NMR spectrum of cellulose in the N_2O_4–Me_2SO system. —The addition of 2 mol water per mol AGU mixed with Me_2SO to the molten 8% polymer and 4 mol N_2O_4 per mol AGU containing cellulose trinitrite gel at 50°C led to a viscous light-green nongelling solution of a cellulose nitrite with ds = 1.8, which is stable at 20°C for weeks.

The ^{13}C NMR spectra (compare Fig. 4b and Table 1) of these water-containing systems indicate complete C-6 substitution, but a significant decrease of the partial ds at the secondary C-atoms, especially at C-2 (ds C-2, 0.5; C-3, 0.7). Included in Table I and Fig. 4c is the evaluation of a spectrum obtained from a system prepared by dissolution of air-dried cellulose (5% water content) in a mixture of N_2O_4 and water containing Me_2SO (3.3 mol N_2O_4, 1.3 mol water per mol AGU in the final solution). The resulting ds of 1.85 was similar to the cellulose nitrite sample obtained by denitrosation.

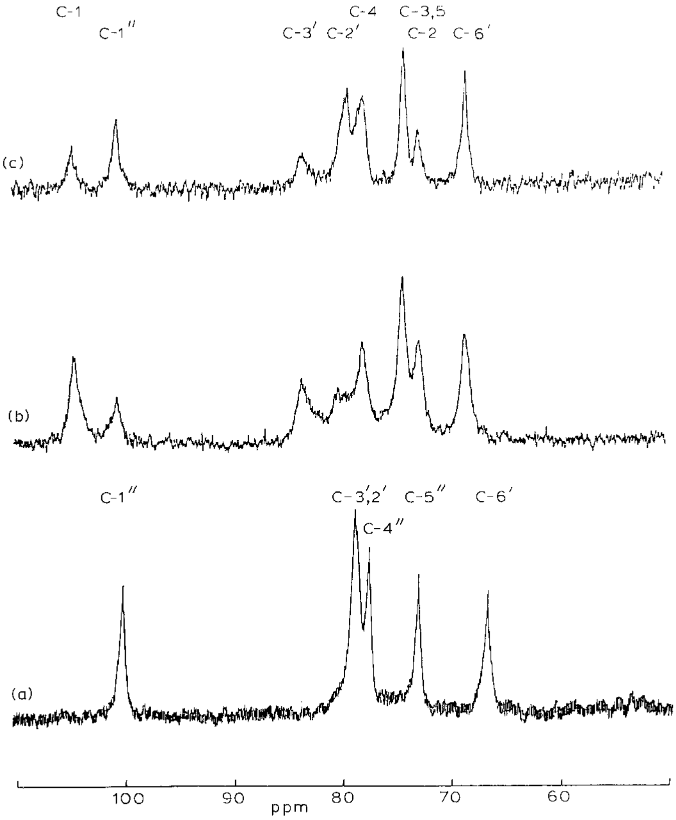

Fig. 4. ^{13}C NMR spectra of the cellulose–N_2O_4–Me_2SO system at 50°C (a) under dry conditions, (b) after denitrosation by water and (c) by nitrosation in the presence of water.

The comparison of partial nitrosation to denitrosation of cellulose indicated a preferred substitution of the C-6 OH groups and a high stability of nitrite ester groups in this position, while a significant difference does exist within the two secondary positions: on nitrosation in a water-containing system, the C-2 position is preferred, but it is less stable than the C-3 nitrite group to protic additives.

Homogeneous nitrosation of cellulose in the LiCl–Me$_2$NCOMe system.—The ^{13}C NMR spectrum presented in Fig. 5 (see also Table I) indicates the distribution of nitrite groups in the LiCl–Me_2NCOMe system.

The differences in cellulose nitrosation in the N_2O_4–Me_2NCHO or N_2O_4–Me_2SO system on one hand, and the system LiCl–Me_2NCOMe–N_2O_4 on the other hand, can be understood on the basis of competition between nitrite formation and the intermolecular interaction of cellulose with the solvent system. Me_2NCHO and Me_2SO show only a rather weak interaction with cellulose, and the N_2O_4–solvent complex can attack the cellulosic OH groups at the preferred C-6 position, hindered only by diffusion during the dissolution process[28].

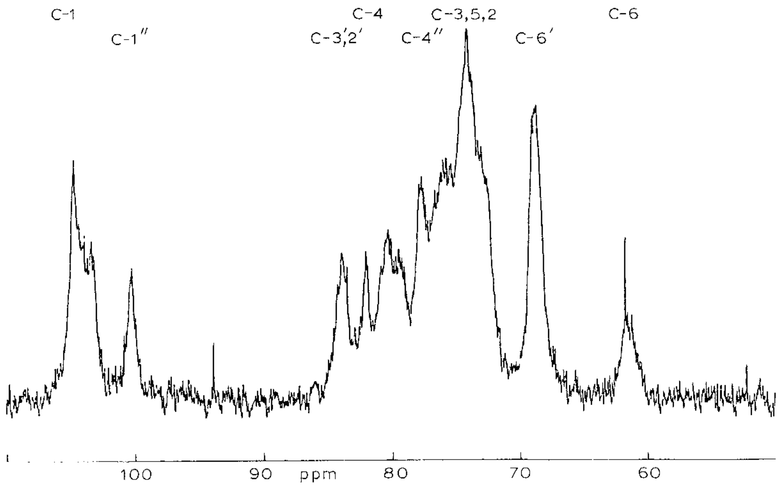

Fig. 5. ^{13}C NMR spectrum of the cellulose–LiCl–Me_2NCOMe system after nitrosation with N_2O_4.

In the LiCl–Me_2NCOMe–N_2O_4 system, the interaction between N_2O_4 and the OH groups is impeded by a strong complexation of cellulose by the nonderivatizing LiCl–Me_2NCOMe solvent system. This competition leads to a rather low ds in nitrite groups in all three positions, even at a molar excess of N_2O_4 (ds C-2, 0.25; C-3, 0.35; C-6, 0.75).

CONCLUSIONS

It can be definitely concluded from our results that, in the process of dissolution of cellulose in the N_2O_4–Me_2NCHO and N_2O_4–Me_2SO systems, cellulose trinitrite is formed under strictly anhydrous conditions and is stable for a long period in the range of temperatures investigated.

Addition of water or methanol to these anhydrous systems leads to a partial denitrosation, which shows a pronounced regioselectivity, i.e., a remarkable high stability of nitrite groups in the C-6 position as compared to those at either C-2 and C-3. The same pronounced difference of stability is also observed on nitrosation in a water-containing system, indicating a preferential substitution at C-6. The preferential substitution at C-2 on nitrosation compared to C-3 and the rather fast decrease in nitrite group content on denitrosation at the same position is unexpected, and may be caused by steric hindrance at the C-3 position.

In summary, we observed in our systems an order of reactivity of cellulose OH groups in the dissolution process to be C-6 $\gg$ C-2 > C-3 and an order of stability of nitrite ester groups in the homogeneous phase to be C-6 $\gg$ C-3 > C-2.

The remarkably large difference in regioselectivity of nitrosation of cellulose by N_2O_4–wet Me_2SO and LiCl–Me_2NCOMe is caused, in our opinion, by the homogeneous conditions at the start of the reaction and by the complexation of OH groups in the latter system.

The two controversarial opinions that exist in the literature on the mechanism of dissolution of cellulose in the N_2O_4–Me_2NCHO or Me_2SO system may be reconciled by the assumption that a derivatization to a cellulose trinitrite occurs under strictly anhydrous conditions in these solvents with an excess of N_2O_4, but that only a partial nitrosation takes place in these systems in the presence of some water. In the case of nonderivatizing cellulose solvent systems, the structure and stability of H-bridge complexes between OH groups of cellulose in the different positions and the low molecular solvent components play an important role in regulation of regioselectivity in subsequent derivatization reactions.

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