

## STRUCTURE OF COTTON-CELLULOSE DINITRATES ESTABLISHED BY PHYSICAL METHODS

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The structure of nitrate esters of cellulose has been studied by not only chemical but also physical methods such as x-ray diffraction and IR and  $^{13}\text{C}$  NMR spectroscopies. The structure of highly substituted nitrate esters prepared from various cellulose samples in  $\text{H}_2\text{SO}_4\text{—HNO}_3$  mixtures,  $\text{CH}_2\text{Cl}_2$ , and trifluoroacetic acid (TFAA) has been studied. It was shown that nitrate esters of various cellulose samples prepared in TFAA have slightly increased unit cell dimensions, i.e., the crystallites are larger compared with nitrates prepared in  $\text{H}_2\text{SO}_4\text{—HNO}_3$  mixtures and in  $\text{CH}_2\text{Cl}_2$ .

An investigation of cotton cellulose dinitrates prepared from cellulose treated beforehand with TFAA [1] and with different degrees of polymerization found that they differ in structural characteristics. The nitrate esters give two clearly defined peaks (reflections) in the diffractograms at  $2\Theta = 12\text{--}13^\circ$  and  $19\text{--}22^\circ$ . These are due to reflection from the planes (110), (200), (202), and (201) of cellulose nitrates. The diffraction maximum at  $20^\circ$  remains in the same place. The diffractograms lack reflections typical of the starting cotton cellulose, leading to the conclusion that the cellulose hydroxyls are evenly substituted upon nitration. The half-width of the (110) reflection of cellulose dinitrates prepared after preliminary reaction of the cellulose with TFAA decreases significantly ( $1.75\text{--}0.75^\circ$ ) compared with those prepared in other media. This indicates that the unit cell of the dinitrate is expanded.

We used IR spectroscopy to confirm the distribution of the nitro groups in cellulose dinitrates.

IR spectra of starting cotton cellulose (**1**) and the same cellulose (**2**) held for 30 min in conc. TFAA (1:100 ratio) at  $22^\circ\text{C}$  and then washed with hot and cold water until the washings were neutral have a characteristic band due to stretching of free hydroxyls at  $3600\text{--}3200\text{ cm}^{-1}$  and absorption bands at  $1700\text{--}4000\text{ cm}^{-1}$  that are characteristic of the glucopyranose ring of the starting cotton cellulose. The spectra show that cellulose after this treatment contains no trifluoroacetates. This is confirmed by a lack of absorption at  $1780\text{ cm}^{-1}$ , which is due to stretching of the trifluoroacetates.

The spectrum of the cellulose mixed ester (**3**), namely cellulose 6-monotrifluoroacetate dinitrate (**3**, Fig. 1) has absorptions at  $1620$ ,  $1280$ , and  $840\text{ cm}^{-1}$  [2] due to nitro stretches and an absorption at  $1780\text{ cm}^{-1}$  due to stretching of the trifluoroacetate. The spectrum of the 2,3-dinitrate after hydrolysis (**4**, Fig. 1) has no band at  $1780\text{ cm}^{-1}$ , indicating that the trifluoroacetate group was cleaved. A free hydroxyl on  $\text{C}_6$  of the glucopyranose appeared because the strength of the absorption of hydroxyl at  $3200\text{--}3600\text{ cm}^{-1}$  increased.

Spectra of cellulose dinitrates with substitution degree 2.0 contain a weak absorption at  $1780\text{ cm}^{-1}$ , confirming the hypothesis about substitution of the  $\text{C}_6\text{ OH}$  of the cellulose macromolecule unit by trifluoroacetate.

Spectra of the dinitrates also have a narrow strong band at  $1656\text{ cm}^{-1}$  that, according to the literature, corresponds to vibrations of a nitro group on  $\text{C}_2$  and  $\text{C}_3$  of the cellulose macromolecule unit [2]. The  $\text{C}_6$  hydroxyl remains unsubstituted because boiling in water cleaves the trifluoroacetates.

We previously determined that boiling cleaves the trifluoroacetates. This is evident in the spectrum (**4**, Fig. 1) from the disappearance of the band at  $1780\text{ cm}^{-1}$ .

The spectra make it possible to confirm that the  $\text{C}_6\text{ OH}$  in nitrates with a degree of substitution 2.0 is unsubstituted by nitro. This is consistent with the literature [1]. The presence in the spectra of cellulose partially substituted with nitrate of an asymmetric absorption at  $3100\text{--}3700\text{ cm}^{-1}$  with a maximum near  $3570\text{--}3590\text{ cm}^{-1}$ , corresponding to absorption of primary OH [1], confirms this.

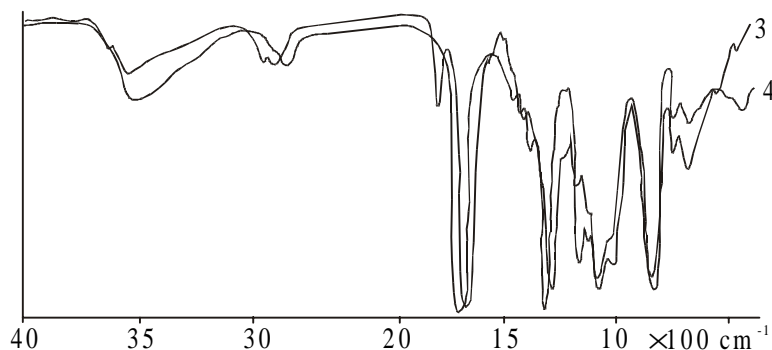


Fig. 1. IR spectrum of the mixed ester of cotton cellulose (3) and 2,3-dinitrate of cellulose (4).

$^{13}\text{C}$  NMR spectroscopy turned out to be fruitful for identifying cellulose nitrate esters of various substitution degree. The position of nitrates in the cellulose can be determined and the presence of chemically homogeneous dinitrates can be confirmed.

The spectra of the dinitrates, in contrast with those of the trinitrates, have more complicated lines. A series of additional signals at 96-102 and 79-84 ppm is observed. The signals near the resonances of  $\text{C}_5$  and  $\text{C}_6$  coalesce into one broad band with the main maximum at 70.2 ppm.

Signals at 83.5 and 82.3 ppm are assigned to resonances of  $\text{C}_2$  and  $\text{C}_3$  [3]. The presence of  $\text{NO}_2$  on  $\text{C}_2$  and  $\text{C}_3$  should cause signals at 78.6 and 77.6 ppm, indicative of substitution on  $\text{C}_2$  and  $\text{C}_3$ . The presence of a peak at 5.8 ppm in the PMR spectrum is unambiguous proof of the presence of a substituent on  $\text{C}_3$ , in agreement with the literature [3].

One of the indicators of homogeneous nitration is the behavior toward solvents. Nitrates with a varying degree of esterification have various solubilities. Slightly substituted cellulose esters (mononitrates) are insoluble in organic solvents. The most universal solvent for preparations with a degree of esterification 1.8-3.0 is acetone.

The good solubility of cellulose esters in acetone is consistent with the absence of cellulose fibers that are not nitrated and of monosubstituted glucopyranose units.

The unique solvent for nitrate esters is alcohol—ether mixtures (1:1 or 1:3) in which only nitrates of substitution degree 2.0 are soluble.

Thus, cotton cellulose dinitrates prepared after preliminary reaction with TFAA have larger crystallites than nitrates prepared in other nitrating mixtures and are chemically homogeneous disubstituted cellulose nitrate esters.

## REFERENCES

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