BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume XIII, No. 6 1965

ORGANIC CHEMISTRY

Structure of Cellulose—Nitric Acid Knecht Compounds. I. Spectroscopic Examination

by

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Presented by T. URBAŃSKI on March 17, 1965

It is known that O-nitration of cellulose occurs when 70 or more per cent nitric acid acts on cellulose [1]. With less-concentrated nitric acid (e.g. 68%), an addition compound known as the Knecht compound is formed [2].

Various molecular formulae ranging from $C_6H_{10}O_5 \cdot HNO_3$ to $2C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O$ have been suggested for this product [1].

Some authors believe that formation of the Knecht compound is an introductory step to the process of nitration [3].

The present paper deals with UV and IR spectroscopic examination of the Knecht compound. It was also necessary to complete the existing spectroscopic data for spectra of cellulose, nitrocellulose and nitric acid.

So far only a brief note [4] has appeared on the ultraviolet reflection spectrum of the Knecht compound.

It was found to contain a 270—305 mμ band not present in the spectrum of nitrocellulose. The authors considered that this fact supports the view that the Knecht compound is an individual substance differing from nitrocellulose.

Jones and Miles [5] examined ultraviolet absorption spectra of nitrocelluloses (10.9—14.1% of N). The absorption curves show a maximum close to 220 mμ and a shoulder below 300 mμ with a low extinction coefficient.

The infrared absorption spectrum of cellulose has been examined [6], [7]; investigations by Zhbankov [8] are particularly important for our work.

Zhbankov established which absorption bands should be assigned to primary hydroxylic groups (at carbon 6). He also established the frequencies and intensities of the bands of cellulose oxidized with dinitrogen tetroxide at carbon 6 and with periodic acid at carbons 2 and 3.

Infrared spectra of nitric acid and nitrogen dioxide (and dinitrogen tetroxide) have been also examined [9]—[11]. This may be of importance, because the tetroxide is formed in the course of oxidation of cellulose with nitric acid.

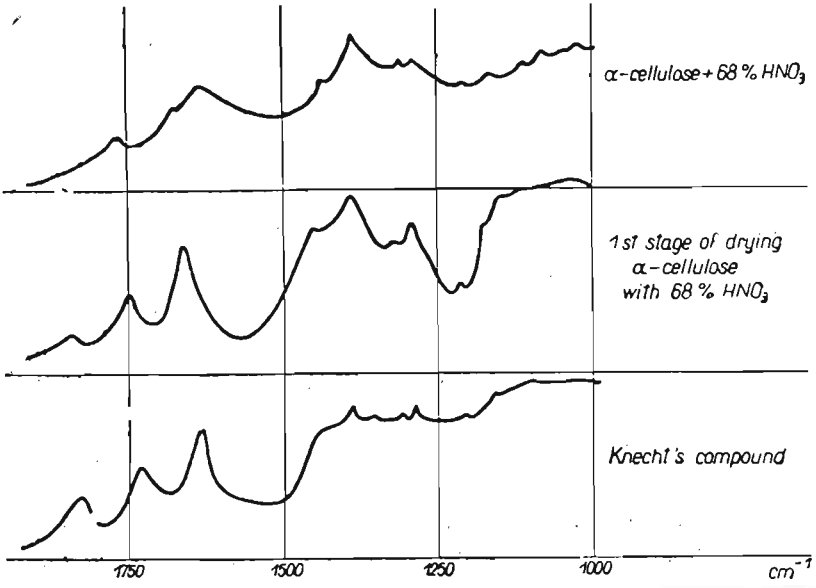
α-cellulose + 68 % HNO_3
1st stage of drying
α-cellulose
with 68 % HNO_3
Knecht's compound
1750
1500
1250
1000
cm^{-1}

Fig. 1

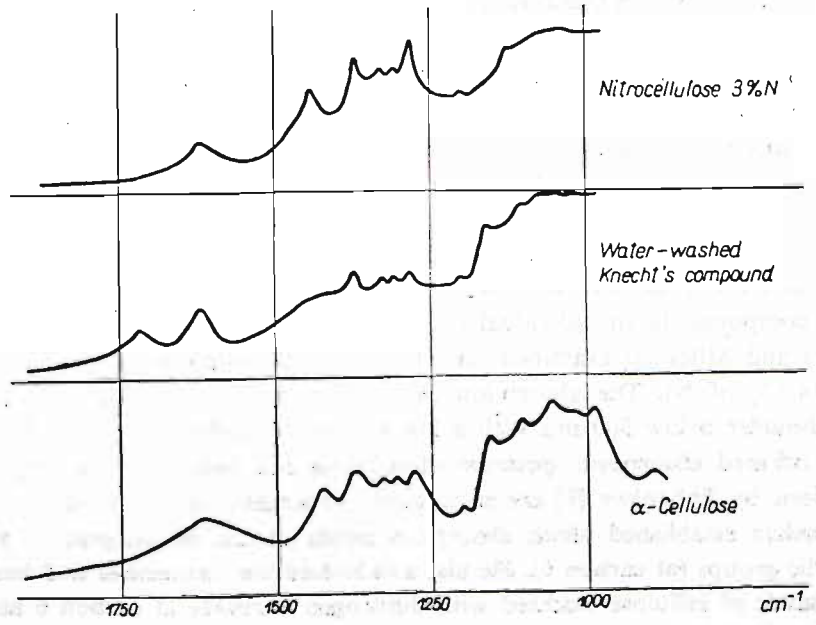
Nitrocellulose 3 %N
Water-washed
Knecht's compound
α-Cellulose
1750
1500
1250
1000
cm^{-1}

Fig. 2

Experimental

Cellulose samples were prepared from ramie or linters by boiling in solution of 1 per cent sodium hydroxide and 0.5 per cent sulphite followed by washing with water and treatment with sodium sulphite 0.5 per cent hydrochloric acid solution.

The Knecht compound was obtained by acting on α-cellulose with 68 per cent nitric acid. Cellulose swollen in this way was dried in a desiccator over calcium oxide. The Knecht compound contained 3.1—3.7 per cent of N (in nitrometer). This would correspond to the generally accepted formula

$$2C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O.$$

After being washed with water it yielded cellulose containing only a trace of nitrogen (*c.* 0.2% of N).

Nitrocellulose (12.6 % of N) was prepared by conventional nitration with mixed acid [1].

Nitrocellulose (3.0 % of N) was prepared according to Petropavlovskiĭ [12] by using a mixture containing 32 per cent nitric acid and 35 per cent sulphuric acid.

Oxidation of cellulose with dinitrogen tetroxide was carried out by passing gaseous N_2O_4 through a layer of cellulose.

Nitric acid (analytical grade) diluted to various concentrations was used.

TABLE I

Ultraviolet absorption spectra

	Absorption maximum mμ
Nitric acid, %	
94.1	262
68.6	267
32.3	295
1.9	309
Knecht compound	252—255 and
„ „	265
Mixture of α-cellulose and 68.6% HNO_3	267

Spectroscopy

Carbon tetrachloride mull UV-spectra were taken with a Unicam SP-500 spectrophotometer. Fluorolube FS5 mull and potassium chloride disc IR spectra were recorded with a Hilger H-800 spectrophotometer.

Discussion

Ultraviolet spectra

It is evident that the absorption spectrum of the Knecht compound differs from that of nitrocellulose prepared by the action of 69.8 per cent nitric acid on cellulose.

The spectrum of the Knecht compound does not appears to be composed of two superimposed spectra: of cellulose and of 68.6 per cent nitric acid, although one

of the two 265-mμ maxima in the Knecht compound spectrum corresponds to the absorption maximum in the 68.6 per cent nitric acid spectrum.

It should be, however, borne in mind that the maximum near 260 mμ can be produced by NO^+ [13] and this explanation would fit to our assignment of band 1870 cm.$^{-1}$ in the infrared spectrum.

Infrared spectra — 3700—2800 cm.$^{-1}$ region

The Knecht compound gives the OH band shifted to higher frequencies (3340 cm.$^{-1}$) by 40 cm.$^{-1}$ as compared with original cellulose (cellulose I). This would suggest that hydrogen bonds in the Knecht compound are somewhat weaker than those in original cellulose and close to those in mercerized cellulose (cellulose II) which was found to produce a band at 3400 cm.$^{-1}$. Still further shifting to higher frequencies is shown in the spectrum of nitrocellulose (12.6% of N), 3440 cm.$^{-1}$, where most hydrogen bonds are broken.

When comparing X-ray diagrams of the Knecht compound with those of cellulose I and II, we also reached the conclusion that the crystal lattice of the Knecht compound may be similar to that of cellulose II.

Region 1900—1200 cm.$^{-1}$

The assignments of the bands in the spectrum of cellulose are given in Table II.

The OH deformation frequencies differ slightly from those given by Zhbankov [8], (1360, 1340 and 1325 cm.$^{-1}$), but this may be due to a different technique of preparation of the samples.

Most of these bands disappear on oxidation of cellulose with N_2O_4 and are replaced by one strong band *c.* 1740 cm.$^{-1}$, obviously produced by C = O vibrations.

The following conclusions can be drawn from the comparison of the spectra of cellulose, (Tables I, II and Figs. 1, 2) 68 per cent nitric acid, the Knecht compound and of the cellulose recovered from the Knecht compound by washing with water:

(a) The 1870 cm.$^{-1}$ band present in the Knecht compound spectrum may well be assigned to nitrogen oxide [10], [11] bonded with the cellulose crystal lattice presumably through hydrogen bonds.

(b) The intensity of the 1430 cm.$^{-1}$ band is considerably lowered in the Knecht compound (as compared with cellulose).

This should most likely be ascribed to the oxidation of the greater part of the CH_2 groups.

(c) There is a shifting of the bands produced by bending vibrations of the OH groups attached to carbon 6: the frequencies 1335 and 1316 cm.$^{-1}$ (in cellulose) are altered to 1352 and 1307 cm.$^{-1}$, respectively. This is probably produced by changes around carbon 6 due to the attached molecule of nitric acid.

(d) Cellulose recovered from the Knecht compound regains the frequencies: 1339 and 1315 cm.$^{-1}$. The intensity 1430 cm.$^{-1}$ is much lower than in the cellulose before the action of nitric acid. The high intensity band of the carbonyl group at 1737 cm.$^{-1}$ persists.

(e) The Knecht compound shows frequencies which probably belong to nitric acid. These are the bands: at 2290 cm.$^{-1}$, noticed by a few authors in the spectra of nitric acid of various concentrations at 1640 and 1386 cm.$^{-1}$, assignable, respecti-

vely, to antisymmetrical and symmetrical stretching vibrations of the NO_2 group in the nitric acid molecule, the assignement being somewhat obscured by the fact that the 1644 cm.$^{-1}$ band is present in the spectrum of water. However, in the spectrum of water the intensity of this band is much lower than that in the Knecht compound spectrum.

Both bands are present in nitrocellulose of 12.6 and 3% N, viz. at 1650 and 1387 and at 1650 and 1386 cm.$^{-1}$, respectively. The 1650 cm.$^{-1}$ band subsisted in the spectrum of dried cellulose recovered from the Knecht compound by washing with water but its intensity was lower. This should be explained in terms of the presence of this band in the spectrum of water, as already pointed out.

One more band at 1382 cm.$^{-1}$ is present in the spectrum of the Knecht compound and is of the same frequency as the band of NO_3^- ion in nitric acid (1368—1385 cm.$^{-1}$). It was also present in the spectra of both the nitrocelluloses examined of 12.6 and 3% N as bands 1387 and 1386 cm.$^{-1}$, respectively. It is possible that the band is produced by vibrations of the ONO_2 group. This would explain why the weak band in question is due to the trace ONO_2 groups in cellulose recovered from the Knecht compound.

The following conclusion can be drawn from the results of spectroscopic examination described in the present paper:

(1) The cellulose moiety of the Knecht compound is partly oxidized and shown the presence of a carbonyl group similarly to oxycellulose.

(2) The part of nitric acid which was reduced to NO on oxidation of cellulose is probably also added to the molecule of oxycellulose.

This, however, may be a by-product which does not form part of the molecular of the Knecht compound.

(3) The formation of the Knecht compound seems to proceed through the following steps:

(a) oxidation of cellulose (mainly CH_2) group and

(b) addition of nitric acid to the partly oxidized cellulose.

Further work of one us was devoted to studying X-ray diagrams of the Knecht compound and of cellulose treated with nitric acid of various concentrations.

This paper is part of the doctoral thesis of S. Żyszczyński, Technical University, Warsaw.

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TABLE II

Infra-red absorption spectra, cm.$^{-1}$							
Cellulose I	Oxycellulose (oxidized with N_2O_4)	Knecht compound	Cellulose recovered from the Knecht compound by washing with water	Nitrocellulose (12.6% N)	Nitrocellulose (3% N)	68% Nitric acid	Assignment 8
1	2	3	4	5	6	7	8
3300 v.s.	3360 s.	3340 s.	3330 s.	3440 v.s.	3360 s.	3680 3580 w. 3460 v.s.	HNO_3; O—H (stretching)
2930 m. 2856 m.	—	2900 s.	2880 m.	2870 m.	2900 m.	2950 w.	C—H (stretching)
—	—	—	—	—	—	2650 m.	Nitric acid
2310 v.w.	2290 w.	2290 w.	—	—	—	2280 v.w.	Nitric acid
—	—	1850—70 m.	—	—	—	—	NO (stretching)
—	1745 m.	1737 m.	1737 m.	—	—	—	C = 0
1640±5 m.	1625 s.	1640 s.	1638 v.s.	1650 v.s.	1645 v.s.	1645 v.s.	H_2O and NO_2
1430±3 s.	—	1430 v.w.	1432 v.w.	1430 v.w.	1430 m.	—	CH_2
1368±2 w.	1387 v.s.	1382 v.s.	1381 s.	1387 m.	1386 w.	1370 v.s.	NO_2 (in $NO_3^{\ominus}$) OH (at carbon 6)
—	—	1352 v.w.	—	—	—	—	—
1335±2 w.	—	—	1339 w.	—	1336 w.	—	OH (at carbon 6)
1316±3 w.	—	1307 v.w.	1315 w.	—	1316 w.	—	OH (at carbon 6)
1281±2 m.	1286 w.	1283 m.	1280 s.	1286 m.	1286 m.	—	NO (in ONO_2)
1202±5 m.	—	1200 w.	1234 w. 1201 w.	1210 v.w.	—	—	—
1167±2 m.	1180—1000 b.	1167 m.	1168 s.	1184 w. 1165 w.	1167 w.	—	—
1112±3 m.	—	1110—1000 b.	1110—1000	1094 v.w.			
1058±4 m.	—	—	—	—	1102 w.	—	—
1030±2 w. 998±2 w.	—	—	—	—	—	—	—
900±2 m.	—	894 w.	896 m.	990 v.w.	—	942 w.	—
	830 s.	850 w.	—	831 s.	—	830 w.	—
		780 w.	—	750 w.	—	770 w.	—