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Alkoxylation of Cellulose Nitrates

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Abstract—Reactions of high nitrogen-containing cellulose nitrate with a series of aliphatic alcohols are studied. In the course of physicochemical studies most probable pathways of chemical reaction were established. They include substitution of nitrate groups by alkoxy group, opening of glucopyranose ring with the addition of the fragment of alcohol by the free bonds formed and formation of the carbonyl group, and also saponification of nitrate groups while studying the process in alkaline medium.

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Regeneration of obsolete gunpowder is nowadays one of the most important problems of gunpowder production because large amount of out-of-date gunpowder were released as well as the gunpowder charges going out of the armament.

Out-of-date gunpowders and cartridges with the powder charges are potentially dangerous. They are liquidated mainly by burning what is ecologically unsuitable. That is why in the last years great attention is attracted to utilization of powders based on cellulose nitrate by chemical modification with the purpose of obtaining useful products [1–6].

Modification of polymers is one of the ways of synthesis of high molecular compounds with new structural fragments. This process is based on the transformation of one polymer to another by exposing the starting polymer to physical or chemical action in the course of which it transforms to the polymer of another chemical structure. Hence, modification of polymers is a universal method permitting to vary physical or chemical properties of polymer in the broad range or to transform them in the desired direction [7].

The goal of this study is the development of methods of chemical modification of cellulose nitrates using nucleophilic reagents like aliphatic alcohols and establishing the rules of chemical reactions under different conditions. This is the research aimed to evaluate the further applications of methods of cellulose nitrate modification to obtain practically interesting polymer materials.

Reported data [1–6] show that usually under treating of cellulose nitrate with chemical reagents and also under thermal treating of its solutions three types of reactions are observed more or less simultaneously. They include the reactions at the nitrate groups, at the free hydroxyls, and at the glycoside bonds always leading to destruction of the polymer chain. Reactivity of each center directly depends on its surrounding in the elementary unit altering in the course of the reaction.

In the present study ethanol, 2-propanol, butanol, and pentanol were chosen as modifying agents of cellulose nitrate. Alcohols exhibit low acidic and basic properties, and as weak nucleophiles (weak Lewis bases) in the reactions of nucleophilic substitution require proton acceptors. Just due to that the chemical transformation of cellulose nitrate was carried out homogeneously in pyridine.

Both starting components are well soluble in it and pyridine also acts as nucleophilic catalyst [8].

High nitrogen-containing cellulose nitrate with the empirical formula $C_6H_7O_2(OH)_{0.87}(ONO_2)_{2.13}$ (nitrogen content 11.56%) was used as starting polymer subjected to chemical transformation.

Among the reaction products solid polymeric products were isolated as fine yellow orange powder well soluble in DMF, DMSO, acetone, and the other polar solvents. Besides, water-soluble yellowish crystals of monomer products precipitated from the solution in the course of removing the solvent and water.

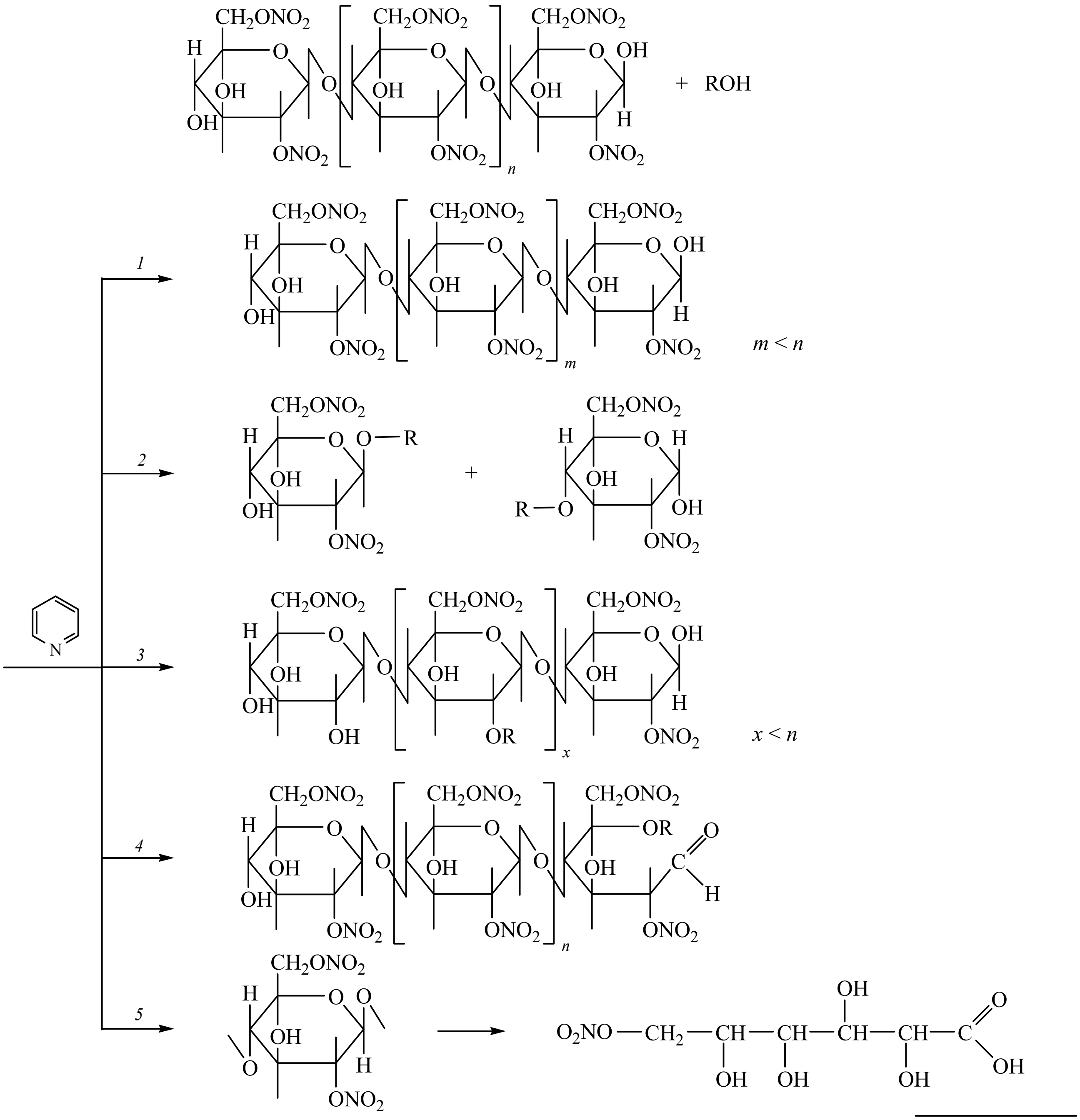
Results of the reaction of $C_6H_7O_2(OH)_{0.87}(ONO_2)_{2.13}$ with ROH at 50°C

R	Reaction time, τ, h	Intrinsic viscosity, η	Yield, %	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
Nitro-cellulose		1.25		27.72	3.08	11.74	$C_6H_{7.87}O_{9.26}N_{2.13}$	27.92	3.05	11.56
Polymer reaction products										
C_2H_5	1	0.82	77	49.62	7.49	2.00	$C_{9.54}H_{17.05}O_{5.87}N_{0.3}$	49.84	7.42	1.83
	2	0.78	68	51.03	7.66	1.19	$C_{9.9}H_{18.02}O_{5.85}N_{0.21}$	50.91	7.72	1.26
	4	0.71	55	51.62	7.99	0.90	$C_{10.2}H_{18.83}O_{5.88}N_{0.15}$	51.56	7.93	0.88
	6	0.67	36	52.15	8.17	0.53	$C_{10.42}H_{19.44}O_{5.9}N_{0.1}$	52.04	8.09	0.60
i-C_3H_7	1	1.12	84	36.24	4.51	7.88	$C_{7.17}H_{11.05}O_{7.61}N_{1.30}$	36,30	4.66	7.68
	2	0.97	79	38.49	5.16	6.62	$C_{7.5}H_{11.86}O_{7.28}N_{1.14}$	38.41	5.06	6.81
	4	0.94	63	44.13	6.31	4.18	$C_{8.4}H_{14.1}O_{6.4}N_{0.7}$	44.36	6.21	4.32
	6	0.90	44	46.47	6.70	3.12	$C_9H_{15.6}O_{6.1}N_{0.5}$	46.58	6.56	3.23
C_4H_9	1	0.88	80	56.24	8.61	1.76	$C_{12.88}H_{23.4}O_{5.75}N_{0.37}$	56.16	8.50	1.89
	2	0.83	72	56.67	8.53	1.67	$C_{13.24}H_{24.28}O_{5.79}N_{0.33}$	56.66	8.66	1.65
	4	0.74	59	57.73	9.03	1.18	$C_{13.92}H_{25.89}O_{5.77}N_{0.24}$	57.88	8.97	1.16
	6	0.69	38	58.16	9.17	1.00	$C_{14.04}H_{26.19}O_{5.77}N_{0.22}$	58.08	9.03	1.07
C_5H_{11}	1	1.01	81	55.51	8.42	1.99	$C_{12.55}H_{22.7}O_{5.8}N_{0.4}$	55.43	8.35	2.06
	2	0.93	74	56.76	8.61	1.71	$C_{12.85}H_{23.38}O_{5.64}N_{0.32}$	56.63	8.58	1.65
	4	0.85	67	57.49	8.97	1.29	$C_{13.45}H_{24.71}O_{5.65}N_{0.28}$	57.55	8.81	1.40
	6	0.80	40	59.32	9.59	1.12	$C_{15.65}H_{29.63}O_{6.08}N_{0.25}$	59.02	9.31	1.10
Water-soluble low molecular reaction products										
C_2H_5	6	–	27	28.19	4.55	5.20	$C_{5.8}H_{11.5}O_{9.5}N_{0.97}$	28.33	4.68	5.13
i-C_3H_7	6	–	25	19.5	2.5	12.4	$C_{5.9}H_{9.1}O_{14.5}N_{3.2}$	19.85	2.55	12.56
C_4H_9	6	–	22	26.87	4.62	6.41	$C_{5.6}H_{11}O_{9.4}N_{1.1}$	27.19	4.8	6.76
C_5H_{11}	6	–	22	22.97	3.27	9.70	$C_{5.75}H_{10}O_{11.5}N_{2.05}$	23.65	3.43	9.84

On the basis of elemental analysis data empirical formulas of the reaction products were calculated (see the table).

From the elemental analysis data of the compounds obtained, in particular, from the fact that increase in the reaction time causes the decrease in nitrogen content,it can be concluded that the degree of nucleophilic substitution of the nitrate groups with alkoxy ones increases in time.

From the data of experiments listed in the table it also follows that the lowest content of nitrogen and highest content of carbon were achieved in the course of modification of polymer with ethanol. It may be due to the fact that the reaction proceeds according to the mechanism of nucleophilic substitution, alkoxyl ion being the attacking particle. Alcohols are weak nucleophiles, while alkoxyl ions are strong ones. The ionizing ability of alcohols decreases with the increase in the degree of branching and the increase in the molecular mass in the series $C_5H_{11}OH < (CH_3)_2CHOH < C_4H_9OH < C_2H_5OH$. The structure of elementary unit for all the final products of substitution of nitrate groups with ethoxy, propoxy, butoxy, and pentoxy groups may be represented as it is shown in the scheme. These data are confirmed with the IR and ^1H NMR spectroscopic data.



IR spectra of synthesized polymers contained the characteristic absorption bands of cellulose nitrates at 840, 1250, and 1660 cm^{-1} (NO_2), a series of bonds in the range 1060–1160 cm^{-1} (glucopyranosyl ring), a band at 1070 cm^{-1} (C–O–C), the bands at 2930 and 2980 cm^{-1} (C–H), and the band at 3500–3800 cm^{-1} (OH). Furthermore IR spectra of modified polymers contained the characteristic bands of stretching and bending vibrations of bonds belonging to the molecules of modifying alcohols at 1375, 1460, and 2960 cm^{-1}, (C–H, CH_3), 1430, 1465, and 2925 cm^{-1} (C–H, CH_2) [11]. The observed deformation of the absorption band that corresponds to the glucopyranoside bond in the IR spectra of all water-soluble samples suggests the openning of the ring.

^{1}H NMR spectra of polymers agree with the assumed formulas of cellulose nitrate derivatives containing CH_3 groups of alcohols and carbonyl groups formed by opening of glucopyranosyl ring. The spectrum of starting cellulose nitrate contains the signals corresponding to the protons of $–CH_2ONO_2$ fragment of glucopyranosyl ring at 4.1 ($H^{1,5}$), 4.8 (H^6), 5.15 ($H^{2,4}$), and 5.65 (H^3). In the ^1H NMR spectra of reaction products besides the above-mentioned signals additional ones are observed at 0.87 and 0.86 ppm (CH_3), 2.08 and 1.28 ppm (CH_2), and at 7.4, 7.8, and 8.6 ppm (CH=O) [12,13].

These data show that substitution of nitrate groups with alkoxy ones in one of the probable directions of the process.

For the evaluation of the degree of the processes causing the decrease in the molecular mass the flow times of acetone solutions of modified polymers and starting cellulose nitrate were evaluated, and values of intrinsic viscosity were calculated. The results of these analyses show that in all cases the viscosity of solutions of the products decreases as compared to the solutions of starting cellulose nitrate. As known, the intrinsic viscosity directly depends on the molecular mass of polymer according to the Mark–Kun–Hauvink equation [9]. Its lowest value is observed for the polymers obtained at the chemical modification of cellulose nitrate with ethanol. The flow times of acetone solutions of water-soluble compounds and of pure acetone were the same. That means that they are low molecular products.

At the increase in time of the process the yield of water-insoluble polymer decreases because partial destruction of cellulose nitrate takes place. The procedure of isolation of water-soluble products is described in the Experimental. On the basis of physicochemical studies and elemental analysis data it was found that water-soluble yellowish crystals isolated from filtrate are formed by opening of the pyrane ring and contain nitrate groups at C^2, C^3, and C^6 carbon atoms.

Results obtained in the course of physicochemical studies agree with the reported data [10].

Hence, it can be concluded that the monomer units with greater degree of substitution with nitrate groups are more easily exposed to destruction and hydrolysis with the formation of low molecular products. In the units where esterification is not complete the nucleophilic substitution of nitrate groups with alkoxy ones takes place.

Analysis of the performed investigations shows that in the course of the reaction of cellulose nitrate with the chosen alcohols four pathways are observed. They include substitution of nitrate groups with alkoxy ones, hydrolysis, opening of glucopyranose ring, and destruction of macromolecular chain of modified cellulose nitrate with the formation of water-soluble organic products.

On the basis of these results it can be concluded that chemical modification of cellulose nitrate with lower aliphatic alcohols is possible. Purposeful variation of reaction conditions permits to obtain modified polymers with different physicochemical characteristics. The obtained products contain smaller amount of nitrate groups, they are less combustible and can be recommended as plasticizers of polymers which can change their physicochemical properties.

EXPERIMENTAL

IR spectra of reaction products were recorded on a UR-20 two-beam spectrometer for the dispersions in mineral oil and for the films prepared from 1% ethyl acetate solutions. Accuracy of evaluation of absorption band frequencies was ±3 cm^{-1}. ^1H NMR spectra were taken on a Bruker CPX-100 spectrometer (200 MHz) in DMSO-d_6, internal reference TMS. Intrinsic viscosity was evaluated on an Ubbelohde viscometer in acetone at 25°C.

Reactions of cellulose nitrate with 2-propanol, butanol, and pentanol were carried out as follows. To a solution of 1 g of cellulose nitrate in 20 ml of pyridine placed in a 100 ml tree-neck flask equipped with a stirrer, a reflux condenser, and a calcium chloride protective tube, 6 moles of alcohol per each nitrate group of polymer were added, and the resulting mixture was stirred for a desired time at 50°C (see the table). After the completion of the treatment the solution obtained was poured in 100 ml of distilled water. The solid formed was filtered on a glass frit filter, washed with hot water for removing admixtures, and dried in a vacuum desiccator over calcium chloride until the constant mass.

The filtrate obtained after removing of polymer was evaporated in a vacuum (20 mm Hg) to remove water and pyridine. The evaporation was completed when no more liquid was distilled on a boiling water bath. Yellowish brown oily residue was washed with anhydrous ethanol until the formation of yellowish crystals which were filtered on a glass frit filter and dried in the desiccator over calcium chloride until the constant mass.

For the microscopic studies of optically active anisotropic elements, phase structures, and phase transfer such as melting and crystallization thermal polarization microscopy was used. Microscopic studies were carried out with the help of MIN-8 polarization microscope.

Thermal polarization microscopy data show that in the temperature range 190–220°C the products begin to darken independent of the modifying agent and at 230°C their carbonization is observed.

REFERENCES

1. Sarybaeva, R.I. and Schchelokova, L.S., *Khimiya azotnokislykh efirov tsellulozy* (Chemistry of Cellulose nitrates), Frunze: Ilim, 1985.
2. Moisak, M.E., *Khimiya i tekhnologiya nitrotsellulosy* (Chemistry and Technology of Cellulose Nitrate), Moscow: Oborongiz, 1941.
3. Romanova, S.M., Nurgatin, V.V., and Fridland, S.V., *Izv. Vys. Ucheb. Zaved., Ser. Khim. Khim. Tekhnol.*, 2003, vol. 46, no. 8, p. 134.
4. Romanova, S.M. and Fridland, S.V., *Vest. Kazan. Gos. Tekh. Univ.*, 2010, no. 7, p. 79.
5. Romanova, S.M., Mukhutdinova, A.M., and Fridland, S.V., *Vest. Kazan. Gos. Tekh. Univ.*, 2010, no. 9, p. 124.
6. Romanova, S.M., Mukhutdinova, A.M., and Fridland, S.V., *Vest. Kazan. Gos. Tekh. Univ.*, 2010, no. 10. p. 555.
7. Korshak, V.V., *Usp. Khim*., 1980, no. 12, p. 2286.
8. Smith, M.B. and March, J., *March's Advanced Organic Chemistry*, New York: Wiley–Interscience, 2007, p. 576, 6 ed.
9. Avvakumova, N.I., Budarina, L.A., Divgun, S.M., Zaikin, A.E., and Kurenkov, V.F.*, Praktikum po khimii i fizike polimerov* (Practical Course of Chemistry and Physics of Polymers), Moscow: Khimiya, 1995.
10. Zakoshchikov, A.P., *Nitrotselluloza* (Cellulose Nitrate) Moscow: Oborongiz, 1950.
11. Bellami, L., *Infrakrasnye spectry slozhnykh molekul* (IR Spectra of Comlex Molecules), Moscow: Inostrannaya Literatura, 1963.
12. Roberts, D., *Yadernyi magnitnyi rezonans.Primenenie v organicheskoi khimii* (Nuclear Magnetic Resonanse. Application in Organic Chemistry), Moscow: Inostrannaya Literatura, 1961.
13. Baikls, N. and Segal, L., *Tselluloza i ee proizvodnye* (Cellulose and Its Derivatives), Moscow: Mir, 1974, vol. 1.