

STRUCTURAL MODIFICATION OF POTATO STARCH BY SOLUTIONS OF NITROGEN(IV) OXIDE IN CCl₄

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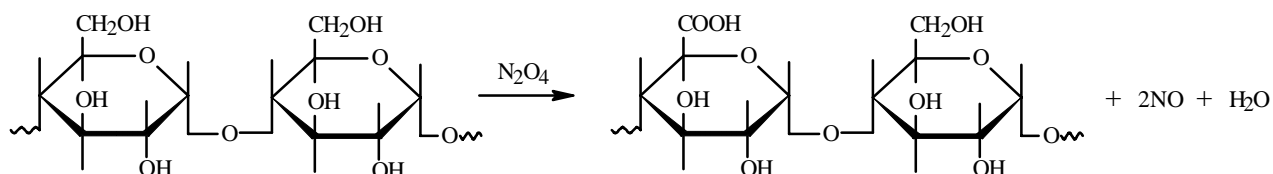
Structural transformations of potato starch by solutions of nitrogen(IV) oxide in CCl₄ were studied as a function of oxidant concentration, starch moisture content, reaction time, and molar ratio of reactants. Oxidized starches with various numbers of carboxylic acids were studied by x-ray phase analysis, ¹³C NMR, and IR spectroscopy. It was found that carboxylic acids were formed primarily on C₆ in starch oxidation products that were x-ray amorphous. The number of carboxyls increased slightly with increased oxidation time and oxidant concentration. It was shown that moisture must be present in the starch for oxidation by nitrogen(IV) oxide to be effective.

Key words: potato starch, oxidation, nitrogen(IV) oxide, functional composition, carboxylic and carbonyl groups, structure, ¹³C NMR and IR spectra.

Starch production has recently become more interesting [1-6] because modified starches have a unique set of physical chemical properties and the starting material can be constantly renewed.

The goal of the present work was to investigate the effect of various factors on oxidative transformations of starch by solutions of nitrogen(IV) oxide (N₂O₄) in CCl₄.

Starch oxidation by N₂O₄ follows mainly the following scheme:



A study of the effect of the glucopyranose unit (GPU):N₂O₄ mole ratio at constant N₂O₄ concentration (Fig. 1) on the rate of oxidative transformations of the polysaccharide revealed the effect of the reaction products (NO, H₂O, HNO₃, N₂O₃, HNO₂) on the reaction. The higher the mole ratio of reactants, the lower the oxidant concentration and the change of composition during the reaction. Increasing the amount of oxidant under otherwise equal conditions increased both the rate and the maximum degree of starch oxidation in the studied time interval. Further increasing (>10 moles) the excess of oxidant had no effect on the process. Therefore, all subsequent kinetic studies were carried out with a 10-fold excess of N₂O₄ relative to the stoichiometric amount required for full oxidation of the primary hydroxyls to carboxylic acids.

The results show (Table 1) that changing the N₂O₄ concentration from 5 to 20 mass % with a constant mole ratio of reactants increased the oxidation and the reaction rate to their upper limits. This can be explained by the activating action of N₂O₄, which can cleave intermolecular H-bonds and increase the rate of diffusion processes close to the quasihomogeneous value by penetrating into the starch granules. The activating action of N₂O₄ is quite consistent with the observed morphology change of the starch granules (Fig. 2). As the N₂O₄ solution concentration increased, the starch granules underwent greater changes.

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TABLE 1. Change of Nitrogen, Carbonyl, and Carboxylic Content in Carboxystarch upon Oxidation

t, h	Content, mass %			DS _{COOH}	DS _{CO}	Content, mass%			DS _{COOH}	DS _{CO}
	C=O	COOH	N			C=O	COOH	N		
	5 mass % N ₂ O ₄ in CCl ₄					20 mass % N ₂ O ₄ in CCl ₄				
1	0.21	1.3	0.04	0.047	0.012	0.23	4.3	0.06	0.16	0.013
3	0.57	3.5	0.04	0.13	0.033	0.84	8.2	0.05	0.30	0.050
5	0.86	8.8	0.05	0.33	0.051	1.46	14.2	0.06	0.53	0.088
7	1.27	11.8	0.05	0.44	0.076	1.95	18.9	0.07	0.72	0.12
24	2.16	22.7	0.04	0.88	0.13	3.10	26.5	0.06	1.04	0.20

T = 291 K, mole ratio GPU:N₂O₄ = 1:10.

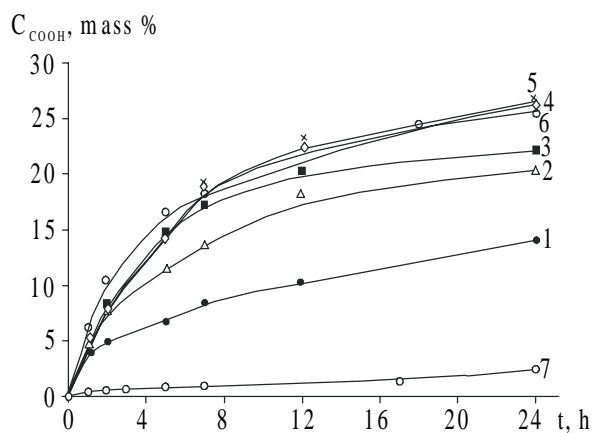


Fig. 1

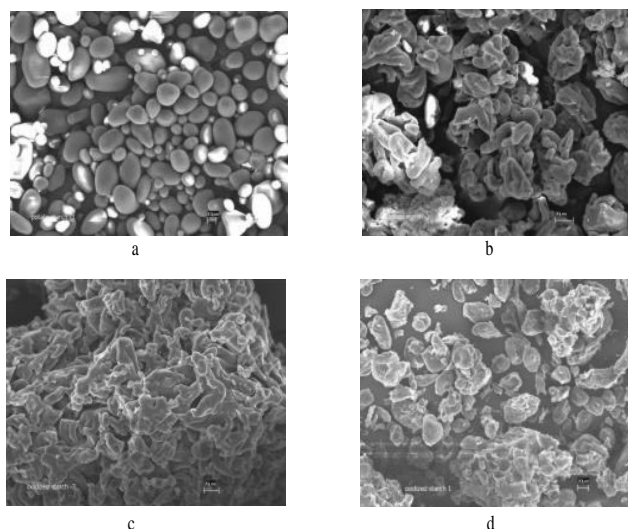


Fig. 2

Fig. 1. Increase of carboxylic groups as a function of starch oxidation time by 20 mass % N₂O₄ in CCl₄ at T = 291 K and various GPU:N₂O₄ ratios: 1:1 (1), 1:2.5 (2), 1:5 (3), 1:10 (4, 6, 7), 1:20 (5) and moisture content (ω) of native starch: ω = 12.5% (1-5), 19.5 (6), 0 (7) (starch was dried to constant mass before oxidation).

Fig. 2. Electron photomicrographs ($\times 1500$) of native potato starch granules (a) and carboxystarch (CS) (b, c, d) with various numbers of COOH groups (mass %): 10.4 (b), 15.9 (c), 0.7 (d). CS preparation conditions: t_{ox} = 6 h, T = 291 K, GPU:N₂O₄ = 1:10, 5 mass % N₂O₄ in CCl₄ (b) and 20 mass % N₂O₄ in CCl₄ (c, d); starch was dried to constant mass before oxidation (d).

Diffraction patterns (Fig. 3) indicated that the crystallinity of the starch decreased substantially after it was oxidized. These changes were more significant the higher the degree of transformation of the starch. The main reflections typical of native starch ($2\theta = 17.0, 19.5,$ and 22.1°) were absent in carboxystarch (CS).

The rate of starch oxidation by N₂O₄ and the limiting COOH content in CS (Fig. 1) depended substantially on the moisture content of the native starch. Even after 17 h of oxidizing native starch that was dried beforehand to constant mass with a solution of N₂O₄ in CCl₄, the number of COOH groups in it was only 1.4 mass %. This was probably due to the direct influence on one of the oxidation steps of water of hydration that facilitated the penetration of the oxidant to polysaccharide reaction centers and its rapid swelling. No visible changes in the reaction were observed during the whole reaction time for oxidation of starch that was dried to constant mass. However, increasing the moisture content from 12.5 to 19.5% increased the initial rate of oxidation of starch by N₂O₄. However, the maximum number of carboxylic groups attained after 24 h was practically constant.

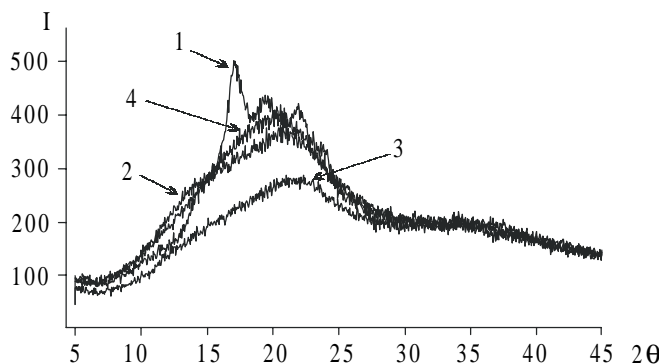


Fig. 3. Diffraction patterns of native starch (1) and CS (2-4) with various numbers of COOH groups (mass %): 10.4 (2), 15.9 (3), 0.7 (4). CS preparation conditions: $t_{\text{ox}} = 6$ h, $T = 291$ K, GPU:N₂O₄ = 1:10, 5 mass % N₂O₄ in CCl₄ (2) and 20 mass % N₂O₄ in CCl₄ (3, 4); starch was dried to constant mass before oxidation (4). I = relative intensity; 2θ = Bragg angle (deg).

Although starch dried to constant mass did not swell practically during the whole oxidation, electron microscopy and x-ray phase analysis (Fig. 2d and Fig. 3) indicated that the starch became amorphous and its granules were destroyed. Therefore, the insignificant increase of COOH groups cannot be due only to surface oxidation of starch granules.

Evidence for the formation of carboxylic groups was the appearance in the IR spectra of oxidized samples of strong C=O stretching bands at 1743 cm⁻¹ and an increase in strength of this band with increasing content of COOH groups. Oxidation of primary C₆ hydroxyls of the α -D-anhydroglucopyranose unit appeared as a decrease in strength of the deformation and wagging vibrations of CH₂ groups at 1420 cm⁻¹ and the band at 928 cm⁻¹ due mainly to COH vibrations on C₆.

Table 1 shows that the number of COOH groups in the highly oxidized sample is slightly greater than that theoretically possible (25.5 mass %) if all hydroxymethyls were oxidized. The number of carbonyl groups increased regularly as the reaction time and oxidant concentration increased. Regardless of the degree of CS oxidation, the number of aldehydes determined by iodometry [7] was very small (0.02-0.04 mass %). Thus, almost all carbonyls in CS were ketones. With respect to the content of bound nitrogen in CS, it decreased relative to native starch. No dependence of nitrogen content on N₂O₄ concentration and oxidation time was found. Starch was not etherified during oxidation by N₂O₄ in CCl₄ because characteristic absorption bands for ONO₂⁻ and ONO⁻ groups did not appear in IR spectra of CS. The nitrogen in both native starch and in its oxidized form may be due to a certain amount of protein, which is always present in starches of any origin [8].

The structure of the starch oxidation products was investigated by ¹³C NMR spectroscopy. The ¹³C NMR spectra of Na-CS contained a signal at weak field at δ 175.4 ppm that was assigned to a carboxylic C atom [9]. As the number of carboxylic groups increased, the intensity of this signal increased and that of the signal for C₆ at δ 60.3 ppm decreased. This unambiguously confirmed that primary hydroxyls were preferentially oxidized to carboxylic groups in the D-glucopyranose unit of the starch.

Thus, the results confirmed that oxidation of starch by N₂O₄ in CCl₄ is selective and made it possible to predict the direction and rate of the reaction as a function of various factors (oxidant concentration, GPU:N₂O₄ mole ratio, time, starch moisture content) and thereby determine the optimum conditions for preparing CS of a given composition.

EXPERIMENTAL

¹³C NMR spectra in D₂O were recorded at 50°C on an Avance-500 spectrometer (Bruker, Germany) in a quantitative regime with ¹³C-¹H decoupling (working frequency 125 MHz). IR spectra were recorded on a 3100 FT-IR IR-Fourier spectrometer (Varian) in the range 400-4000 cm⁻¹. Samples were prepared as pressed KBr disks (1:200 ratio) at $\sim 4.5 \cdot 10^8$ Pa. Diffraction patterns were recorded on an HZG-4A diffractometer (Carl Zeiss Jena) using Cu K α -radiation, Ni filter, and stepped recording. Samples were prepared by cold pressing polymer into monolithic round pellets 2 mm thick and 18 mm in diameter.

Starting material was GOST 7699-78 potato starch (amylose content 23.8 mass %, degree of polymerization $\bar{P}_n = 1760$, phosphorus content 0.23 %; N, 0.09; ash, 0.31; moisture, 12.5; acidity, 15.5. Analyses were performed as before [10]).

Starch oxidation used N_2O_4 (TU 113-03-11-80, OAO Azot, Dneproderzhinsk, Ukraine) containing at least 98.0% N_2O_4 . All other reagents were chemically pure or analytically pure.

Starch oxidation was carried out under heterogeneous conditions by 5 and 20 mass % N_2O_4 in CCl_4 at 291 ± 1 K and various GPU: N_2O_4 mole ratios. A weighed portion of starch was dispersed in a certain volume of reaction mixture and held at a fixed temperature for the required time. Then CS was separated from the solution on a porous glass filter, washed with water:isopropanol (1:1 v/v) until the rinsings were neutral, and dried in air at room temperature. The number of carboxylic acids was determined by the Ba-acetate method [11]; the number of carbonyls, by a modified hydroxylamine method [12]. The degree of substitution (DS) of the COOH groups was calculated using the formula

$$DS_{COOH} = (162.15 \times C_{COOH}) / (4500 - 14 \times C_{COOH})$$

where 162.15 is the molecular weight of the GPU and C_{COOH} is the number of carboxylic groups in mass %.

The content of bound N was determined by the Kjeldahl method [13].

The morphology of the structural units consisting of native potato starch particles and prepared samples of CS was studied using a scanning electron microscope LEO 1420 (Germany).

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