SPECTROSCOPIC INVESTIGATION OF THE LOSS OF HYDROXY GROUPS OF CELLULOSE UNDER THE ACTION OF NITROGEN DIOXIDE

I. N. Ermolenko, R. G. Zhbankov, N. Ia. Lenshina, V. S. Ivanova and V. I. Ivanov

The chemistry and mechanism of the oxidative reactions of cellulose are of importance in treatments of vegetable tissues and cellulose. The transformations of cellulose due to the oxidation of hydroxy groups constitute a very important process for the modification of the chemical properties of cellulose as a macromolecular substance [1]. However, the separate determination of the secondary and primary hydroxy groups participating in the reaction has not been worked out. The existing methods (tosylation, iodination, tritylation) possess all the defects of indirect methods [2]. Methods of determining hydroxy groups by the action of specific oxidizing agents are also unreliable because of occurrence of side reactions [3, 4].

This paper reports an investigation on the transformations of the hydroxy groups of cellulose when it is oxidized with nitrogen dioxide vapor. The oxidation of cotton cellulose in the form of gauze was carried out under static conditions [5]. Products of reaction were washed out with water. To determine the change in the content of hydroxy groups in the course of the reaction we used infrared spectroscopy. The absorption spectra were determined on an IKS-11 recording infrared spectrograph with a rock salt prism by the method described previously [6].

In the spectra of cellulose materials the symmetrical valence vibration of hydrogen-bonded groups lies at 3330 cm\(^{-1}\), and that of free hydroxy groups lies nearby at 3570 cm\(^{-1}\). Fall in the intensity of absorption in these regions characterizes reduction in the total content of hydroxy groups. Absorption bands at 1360, 1340 and 1325 cm\(^{-1}\) correspond to the vibration of primary hydroxy groups, as in the case of alcohols [7]. An indirect method of determining the loss of hydroxy groups in cellulose is based on our observation [4] of the reduction in the intensity of the band at 1430 cm\(^{-1}\), which corresponds to the internal deformational vibration of CH groups. The reduction in the total number of hydroxy groups in the course of the oxidation of cellulose with NO\(_2\) was calculated from the fall in intensity of the absorption band at 3330 cm\(^{-1}\). Fig. 1 shows a considerable fall in the intensities of the bands of the primary hydroxy groups at 1360, 1340, and 1325 cm\(^{-1}\) with increase in the degree of oxidation of the sample, which indicates oxidation of the hydroxy groups. Curve 1, Fig. 2, shows the relation of the loss of hydroxy groups to the accumulation of carboxy groups, as determined by the calcium acetate method. This curve shows that the loss in hydroxy groups is proportional to the gain in carboxy groups. Curve 2, Fig. 2, which was plotted from the spectrum data of Fig. 1, shows the loss in primary hydroxy groups in its relation to the gain in the number of carboxy groups in the products. The increase in the intensity of the band at 1290 cm\(^{-1}\), which characterizes the accumulation of nitric ester groupings, will be considered separately.

![Absorption spectra in the range 7-8.5 μm: o—unoxidized cellulose and products of the oxidation of cellulose with oxides of nitrogen and having the following COOH contents: o—7.6%; e—12%; x—16%; Δ—21%.](image-url)
When we compare the loss of primary hydroxy groups with total loss of hydroxy groups in the reaction for the formation of a given amount of carboxy groups, we find that, if we take the ratio of these losses as 1 at the beginning of the process, then at the end of the reaction it is 0.52. As will be seen from Curve 1, Fig. 2, the total loss of hydroxy groups corresponding to the formation of unit amount of carboxy groups remains approximately constant. Hence, at the start of the process (until about 12% of COOH groups are formed) the formation of carboxy groups proceeds mainly at the expense of primary hydroxy groups (I). The rate at which they react then falls, and as the rate at which hydroxy groups of both kinds react scarcely changes, in the next stage the accumulation of carboxy groups must proceed also at the expense of secondary hydroxy groups (II). Hence, uronic carboxyls are formed mainly in the early stages of the oxidation. This is again evidence of quasihomogeneous oxidation by oxides of nitrogen. If the reaction was heterogeneous, oxidation of primary and secondary hydroxy groups would be observed already in the early stages in the more accessible regions of the cellulose, working inward from the surface; and then, as the oxidizing agent diffused, the same process would be observed in the compact regions. Hence, in this case the primary factors are the differences in reactivity of the hydroxyls of cellulose and the specificity of the oxidizing agent, and the differences in the densities of packing of the different region of the cellulose have only secondary effects.

The process studied in this investigation may be represented as follows:

![Chemical structure](image)

The results are in good agreement with those of investigations [1,4] in which it was shown by chemical methods that part of the carboxy groups are formed by oxidative cleavage of the pyran ring.

**SUMMARY**

1. The loss of hydroxy groups in the oxidation of cotton cellulose with nitrogen dioxide vapor was studied with the aid of infrared spectra.

2. The reaction is quasihomogeneous; in the first stage products are formed mainly by the oxidation of primary hydroxy groups, and in the second stage by the oxidation of primary and secondary hydroxy groups.

**LITERATURE CITED**


* Original Russian pagination. See C. B. Translation.