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INVESTIGATION BY PMR SPECTROSCOPY OF THE REACTIVITIES OF THE ACETATE GROUPS IN THE SAPONIFICATION OF POLYSACCHARIDE TRIACETATES

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The reactivities of the acetate groups in the saponification of cellulose triacetate (CTA) and amylose triacetate (ATA) have been characterized for the first time by analyzing the structures of the reaction products by PMR spectroscopy in solution. To identify the signals of the acetate group protons we used the method of blocking the free OH groups with acetyl-d_3 chloride. The kinetic constants were evaluated: $K_6 = K_3 = K_2$ *for CTA, and* $K_6 > K_2 > K_3$ *for ATA in the saponification reaction.*

The specifics of polymer-analogous transformations in the chains of polymers and the reactivitities of the functional groups of polysaccharide macromolecules are attracting the attention of researchers in the modern physical chemistry of high-molecular-mass compounds [1].

In the present paper we give the results of an evaluation of the reactivities (*R*) of the acetate groups in the saponification of cellulose triacetate (CTA) and amylose triacetate (ATA) by analyzing the reaction mixtures with high-resolution PMR spectroscopy in solution.

Cellulose acetate with a degree of substitution γ (number of substituted OH groups calculated to one unit) of less than three per glucopyranose ring consists of polysaccharides with various units. In the general case the number of types of units is eight: one unsubstituted, three monosubstituted (2-, 3-, and 6-, according to the position of the substituent), three disubstituted (2, 3-, 2, 6-, and 3, 6-), and one trisubstituted (2, 3, 6-), containing twelve nonequivalent acetate groups.

In order to obtain quantitative information on the distribution of acetate groups in the elementary units of polysaccharide macromolecules from PMR spectra we made use of a method that we had developed previously, consisting in the acylation (blocking) of the free OH groups with acetyl-d_3 chloride. Such blocking can be achieved by the following scheme:

$$[C_6H_7O_2(OCOCH_3)_x(\underline{OH})_y]_n + CD_3COOCl \rightarrow [C_6H_7O_2(OCOCH_3)_x(OCO\underline{CD}_3)_y]_n$$

The $CD_3{-}C{=}O$ group introduced in this way creates the same environment as ordinary acetyl groups but these groups give no additional signals in the PMR spectrum in the region of acetate groups ($\delta = 1.8\text{-}2.2$ ppm). The assignment of the signals relating to the acetate groups positioned at C_2, C_3, and C_6 was based on the literature [2].

In an investigation of the saponification of CTA in NaOH we found a linear nature of the semilogarithmic anamorphosis (Fig. 1, *I*). The linearity of the kinetic curve was retained down to deep degrees of saponification, which showed that the distribution of acetate groups was independent of the conversion.

A similar effect has been observed in the synthesis of weakly substituted cellulose acetates by the saponification of cellulose diacetates [3], while it has also been observed in a study of the saponification of ATA in an alkaline medium [4].

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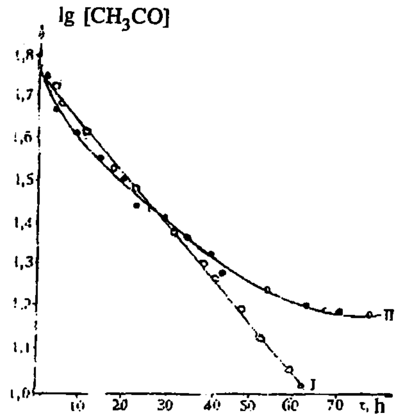


Fig. 1. Semilogarithmic anamorphoses of the saponifications of cellulose triacetate (*I*) and amylose triacetate (*II*) in NaOH solution at 25°C.

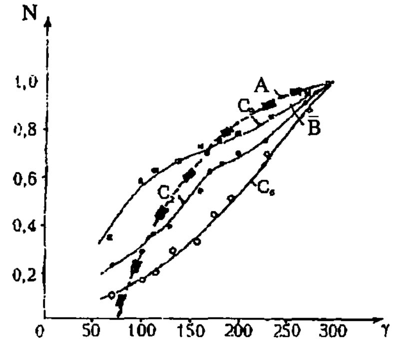


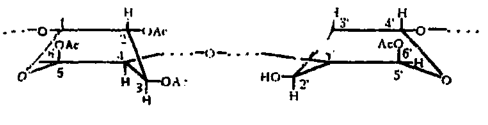
Fig. 2. Distribution of acetate groups at the C_6, C_2, and C_3 atoms in the saponification of cellulose triacetate (*A*) and amylose triacetate (*B*) according to the depth of reaction, found by PMR spectroscopy.

The distribution of acetate groups in the saponified CTAs was found by analyzing the reaction mixtures as a function of the depth of the reaction by PMR spectroscopy in solution (Fig. 2, *A*). As can be seen from the results obtained, up to deep degrees of reaction the numbers of acetate groups located at C_6, C_3, and C_2 were approximately equal; i.e. the *R* values for the acetate groups in the CTA saponification reaction had the relation $K_6 = K_3 = K_2$.

In this case, to calculate the distribution of the substituents it is possible to make use of the method of Bernouilli statistics, and it is then easy to calculate the amounts of unsubstituted (N_0) and of mono-, di- and trisubstituted (N_1, N_2, and N_3) units from the formulas: $N_0 = A^3$, $N_1 = 3A^2(1-A)$, $N_2 = 3A(1-A)^2$, $N_3 = (1-A)^3$, where A is the probability of finding acetate groups in an elementary unit.

Thus, the agreement of the kinetic results with those of a study of the distribution of the units once again fully confirms Suleimanov's suggestion [4] that, when it is difficult to find the distribution of the units experimentally, it is possible to use a linear nature of the semilogarithmic anamorphosis as a criterion of the synthesis of polymeric materials with a random distribution of the units.

In our study of the saponification of ATAs we found a nonlinear nature of the semilogarithmic anamorphoses, and an analysis of the kinetic results (Fig. 1, *II*) showed that the reaction took place with retardation, although, apparently, it should be accelerated because of the interaction of hydroxy and ester groups.



The effect observed may be connected both with steric hindrance and with a worsening of the accessibility of the acetate ester groups because of a convoluted macromolecular coil for ATA. Such a mechanism of the saponification of ATA, in contrast to that of CTA, may be due to several factors.

As is known, the macromolecules of cellulose derivatives consist of linear chains of cellobiose disaccharide units, while the chains of amylose derivatives consist of maltose units; moreover, the ATA macromolecule is more flexible in solution than that of CTA [5].

Analysis of the composition of the mixture of products from the saponification of ATA enabled us to evaluate the *R* values of the acetate groups (Fig. 2, *B*) and to establish that the highest *R* value was possessed by an acetate group at C_6, and then one at C_2, and, finally, the lowest *R* value was characteristic for an acetate group at C_3; i.e., $C_6 > C_2 > C_3$.

Thus it may be concluded that PMR spectroscopy can be used successfully for investigating the distribution of substituents in the saponification of polysaccharides.

EXPERIMENTAL

Synthesis of cellulose triacetate was performed as in [6]. Cotton cellulose (DP = 1350) previously dried at 105°C was treated with glacial acetic acid (100% of the weight of the cellulose) at 50°C for 2 h, after which an acetylating mixture consisting of acetic anhydride (350%), dioxane (700%) and 40% of sulfuric acid (on the weight of the cellulose) was added. Liquor ratio 10:1, time of acetylation 90 min, reaction temperature 38-40°C. The amount of bound acetic acid was determined by Berle's micro method [7]. The degree of polymerization was determined viscometrically in chloroform solution at 25°C from the formula [8]

$$|\eta|=2.51\cdot 10^{-4}\cdot M^{1.02}.$$

Amylose with the V-type of structure was obtained from potato starch by Husemann's method [9]. Its molecular mass, $M_w = 4.5\cdot 10^5$, at 20°C was determined from the formula [10]

$$|\eta|=1.51\cdot 10^{-2}\cdot \text{[illegible]}^{0.70} \quad \text{(in DMSO)}.$$

The amylose triacetate was synthesized by the method of [5], the amylose first being subjected to activation. For this purpose the amylose was dissolved in DMSO, and the solution was passed through glass filters to free it from impurities. The resulting solution was reprecipitated in butyl alcohol with constant stirring. The product was freed from DMSO by washing with glacial CH_3COOH. Yield 94%. The samples of ATA isolated were analyzed for their content of bound acetic acid [7], which, for ATA, amounted to 61.95%.

The saponification of CTA and of ATA was conducted by Suleimanov's procedure in NaOH solution at 25°C.

All the partially substituted cellulose and amylose acetates (PSCAs and PSAAs), which had various degrees of substitution, were subjected to deuteration with acetyl-d_3 chloride. The saponification products of 50-mg samples of CTA and ATA were subjected to esterification with a 25-fold excess of acetyl-d_3 chloride having the following indices: degree of deuteration — 98%; boiling point — 51°C; $n_D = 1.3895$. The reaction temperature was 45°C. Complete substitution of the OH groups in the PSCAs and the PSAAs was observed after 92 and 118 h, respectively.

The depth of the deuteration reaction was monitored by IR spectroscopy from the disappearance of the stretching vibrations of OH groups in the 3400-3600 cm^{-1} region. Then the products obtained, in which the OH groups had been substituted by CD_3COO groups, were dissolved in pyridine-d_5, and their PMR spectra were recorded and were analyzed for the distribution of acetate groups in the glucopyranose units of the polysaccharide macromolecules.

PMR Spectroscopy. The PMR spectra of the PSCAs and PSAAs deuterated with acetyl-d_3 chloride were recorded in methylene chloride on a Varian XL-200-15 spectrometer at a frequency of 200 MHz, a temperature of 50°C, and a concentration of the solution of 50-60 mg/ml. HMDS was used as external standard.

In order to obtain from the PMR spectra quantitative information on the distribution of the substituents in the deuterated PSCAs and PSAAs, we determined the intensities of the corresponding signals of the methyl protons in the region of acetate groups located at the C_2, C_3 and C_6 carbon atoms of the glucopyranose units of the polysaccharide macromolecules ($\nu = 1.8$-2.2 ppm).

REFERENCES

1. N. A. Platé, A. D. Litmanovich, and O. V. Noa, Macromolecular Reactions [in Russian], Khimiya, Moscow (1977), p. 255.
2. T. I. Usmanov, Vysokomol. Soedin., **33A**, No. 4, 698 (1991).
3. G. Rakhmanberdiev, Author's abstract of Dissertation, Doctor of Chemical Sciences [in Russian], Tashkent (1983).
4. R. T. Suleimanov, Dissertation, Candidate of Chemical Sciences [in Russian], Tashkent (1985).
5. U. G. Karimova, Dissertation, Candidate of Chemical Sciences [in Russian], Tashkent (1989).
6. R. Kh. Kaibusheva, E. I. Berenshtein, and B. I. Aikhodzhaev, Khim. Drev., No. 3, 35 (1985).
7. E. Berl, Chem. Ztg., **55**, 861 (1931).
8. N. V. Vostroilova and Kh. U. Usmanov, in: The Structure and Modification of Cotton Cellulose [in Russian], Tashkent, No. 3 (1966), p. 46.
9. E. Husemann and H. Bart, Macromol. Chem., **B25**, 147 (1957).
10. W. Banks and C. T. Ireenword, Polymer, **10**, No. 4, 257 (1969).