Chemistry of Natural Compounds, Vol. 30, No. 5, 1994

FEATURES OF THE SYNTHESIS OF WATER-SOLUBLE CELLULOSE ACETATE-PHTHALATES

Sh. S. Arslanov and G. Rakhmanberdiev

UDC 547.458.81

The esterification of cellulose with phthaloyl dichloride leads to insoluble esters, and esterification with phthaloyl monochloride to partially soluble products [1]. The esterification of diacetylcellulose with phthalic anhydride has little effect on solubility, although the reaction gives mixed (acetate-phthalate) esters of cellulose [2]. It has remained unclear whether the solubility of the phthalate esters is affected by the degree of substitution (DP), the distribution of the substituents, and the presence of acetyl groups in the molecule, or whether, as a result of the reaction, cross-linked esters of cellulose and phthalic acid are obtained. In order to study this influence, we have synthesized cellulose acetate-phthalates (CAPs) by the direct esterification of sparingly substituted water-soluble acetylcelluloses (WSACs) with phthalic anhydride (PA) and also by the deep hydrolysis of highly substituted CAPs obtained by the phthaloylation of diacetylcellulose (γ_{ac} = 180-220).

Figure 1 shows kinetic curves of the esterification of WSAC with PA. A rise in the temperature of the reaction led to an increase in the DP of the cellulose with respect to phthalic acid. The use of sodium acetate as catalyst increased the rate of the reaction. At the same time, the DP of the cellulose with respect to phthalic acid changed only slightly. Thus, at 90°C, after reaction for 3 h, the DP was 0.70. On the use of the catalyst this value of the DP was reached after 45 min. In this case, the maximum DP was 0.79.

The DP could be varied by changing the reaction temperature. At 50°C and above, highly substituted products were obtained. CAPs with similar contents of phthalic acid groups have been obtained previously in glacial acetic acid [2]. These esters are soluble in organic solvents and insoluble in water.

The products of the phthaloylation of the WSACs have been tested for solubility in water and acetone. As the investigations showed, with an increase in the DP for phthalic acid the water solubility decreased. At the same time, the solubility in acetone increased. The CAPs obtained at a reaction temperature of 90°C dissolved practically completely in acetone and did not dissolve in water. The sodium salt of a CAP was more soluble in water than the acid form. Regardless of the DP for phthalic acid, the CAPs obtained by the phthaloylation of WSACs, dissolved completely in water at pH 7.5-8.8.

A CAP (DP for acetyl groups 2, and for phthaloyl groups 0.65) was subjected to hydrolysis under homogenous condition in the presence of perchloric acid. It was found that, as hydrolysis became deeper, both the acetyl and the phthaloyl

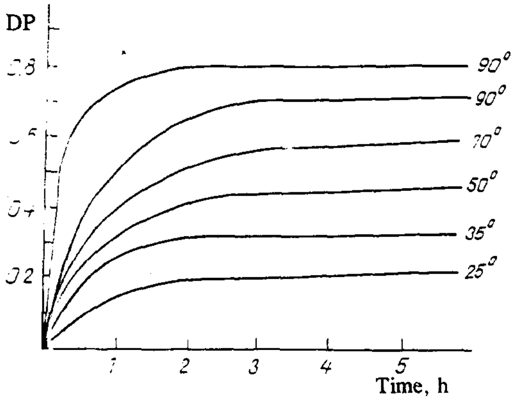

Fig. 1. Dependence on the reaction time of the degree of substitution of acetylcellulose with phthalic acid.

Scientific-Resarch Institute of the Chemistry and Technology of Cotton Cellulose, Republic of Uzbekistan, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 690-692, September-October, 1994. Original article submitted July 5, 1993.

0009-3130/94/3005-0642$12.50

groups were gradually saponified. The course of the reaction was monitored by testing for water solubility. At a reaction temperature of 50°C, water-soluble CAPs were obtained in 45-50 h. Analysis of the reaction products showed that the water-soluble CAPs had a DP for phthalic acid of 0.20-0.35. The DPs for acetyl groups in the water-soluble CAPs were similar to the DPs of the WSACs themselves, amounting to 0.60-0.85.

In the formation of water-soluble CAPs by hydrolyzing highly substituted CAPs, the pH interval of solubility extended from 5 to 9. Regardless of their DPs and other factors, all the CAPs synthesized had free carboxy groups. This shows that PA esterifies cellulose predominantly with the formation of the acid ester.

REFERENCES

1. N. I. Nikitin and I. M. Orlova, Zh. Prikl. Khim,., **8**, 1410 (1935).
2. V. N. Kryazhev and Yu. L. Pogosov, Plast. Massy, No. 10, 18 (1969).
3. G. A. Petropavlovskii and G. Rakhmanberdiev, Zh. Prikl. Khim., No. 2, 423 (1966).
4. V. N. Kryazhev and Yu. L. Pogosov, Vysokomol. Soedin., **12**, No. 9, 683 (1970).