

Preparation of *O*-(3-chloro-2-hydroxypropyl)cellulose and its conversion to *O*-(3-iodo-2-hydroxypropyl) derivative

L. PETRUŠ and P. GEMEINER

*Institute of Chemistry, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 38 Bratislava*

Received 15 November 1982

Dioxan suspension is a suitable reaction medium for heterogeneous alkylation of bead, powdery, and fibrous types of cellulose with chloromethyloxirane under catalysis of perchloric acid. The prepared *O*-(3-chloro-2-hydroxypropyl)cellulose was quantitatively converted to *O*-(3-iodo-2-hydroxypropyl)-cellulose by treatment with sodium iodide in 2,4-pentanedione or acetone.

Суспензия в диоксане является подходящей реакционной средой для гетерогенного алкилирования сферического, порошкового и волокнистого типов целлюлозы действием хлорметилоксирана при катализе хлористой кислотой. Полученная *O*-(3-хлор-2-гидроксипропил)целлюлоза была количественно преобразована в *O*-(3-иод-2-гидроксипропил)-целлюлозу реакцией с иодистым натрием в 2,4-пентадионе или ацетоне.

O-(3-Chloro-2-hydroxypropyl)cellulose is an important reactive derivative of cellulose suitable for many transformations. It can be prepared by heterogeneous alkylation of cellulose with chloromethyloxirane in the presence of Lewis or Brønsted acids. It was prepared from viscose rayon [1] and crosslinked powdery cellulose [2] under catalysis of zinc fluoroborate, from crosslinked *O*-(2-hydroxypropyl)cellulose [3] and powdery cellulose [2] under catalysis of boron trifluoride etherate as well as from powdery, crosslinked powdery, and macroporous bead celluloses under catalysis of perchloric acid [4]. In the last case when alkylation was performed in a pasty reaction mixture composed of dried cellulose, alkylation agent, and catalytic amounts of perchloric acid and water, the process often could not be kept under control and even carbonization of cellulose occurred [4]. Moreover, application of the procedure to macroporous bead cellulose led to irreversible changes in the porous structure of the product due to drying of

cellulose. *O*-(3-Bromo-2-hydroxypropyl) derivative of crosslinked *O*-(2-hydroxypropyl)cellulose was also prepared under catalysis of boron trifluoride etherate [3].

Of iodo derivatives of cellulose with covalently bonded iodine only iododeoxycelluloses are known. They can be prepared by partial replacement of 4-toluenesulfonate, methanesulfonate, nitrate [5], and phosphate groups or chlorine [6] of the appropriate cellulose ester. Another procedure for their preparation might be the reaction of the iminium intermediate (isolable in the preparation of chlorodeoxycellulose by treatment with thionyl chloride in dimethylformamide) with potassium iodide in dimethylformamide at elevated temperature [7].

In the present work we have focused our attention on perfection of the alkylation reaction of cellulose with chloromethyloxirane under catalysis of perchloric acid. Further, we have examined the possibility of using *O*-(3-chloro-2-hydroxypropyl)cellulose for the preparation of *O*-(3-iodo-2-hydroxypropyl)cellulose which, regarding the higher reactivity of alkyl iodides in substitution reactions when compared to other alkyl halides, could find wider applications than the analogous chloro derivative.

In the experiments carried out for alkylation of cellulose with chloromethyloxirane under catalysis of perchloric acid the most suitable reaction medium was proved to be the suspension of cellulose in the mixture of chloromethyloxirane—1,4-dioxan—water (volume ratio 10:25:1). The inert solvent, dioxan, ensured homogeneous distribution of components in the reaction mixture and protected cellulose from carbonization by the effect of the catalyst. Alkylation of

Table 1

Alkylation of cellulose with chloromethyloxirane in dioxan under catalysis of perchloric acid in the presence of water

Starting cellulose		<i>O</i> -(3-Chloro-2-hydroxypropyl) derivative		
Type	Mass/g	Yield/g	w(chlorine)/mass %	DS _{CHP}
Bead ^a	2.0 ^c	2.2 ^d	4.6	0.24
Bead ^b	2.0 ^c	1.5	5.0	0.26
Viscose rayon ^a	1.0	1.0	2.3	0.11
Viscose rayon ^b	1.0	1.2	7.6	0.43
Viscose rayon ^b	2.0	2.4	7.2	0.41
Crosslinked microcrystalline ^b	4.0	5.1	10.8	0.69
Powdery ^a	1.0	1.0	3.1	0.15

a) Nonactivated, b) activated, c) water regain 5.22 cm³ g⁻¹, d) 4.76 cm³ g⁻¹.

cellulose proceeded at temperatures up to 100 °C without any darkening of the reaction mixture. After 4 h reaction at 95 to 97 °C the degree of substitution of bead macroporous cellulose by 3-chloro-2-hydroxypropyl groups (DS_{CHP}) was 0.2 to 0.3, of viscose rayon 0.4 to 0.45, and of crosslinked microcrystalline cellulose 0.55 to 0.7. Water present in the reaction mixture played an important role. At lower contents low DS_{CHP} (<0.1) were achieved, while in the presence of higher amount of water and/or catalyst degradation of cellulose to water-soluble products occurred. In order to ensure the proper amount of water and simultaneously retain the properties of cellulose, obtained by its activation, and the macroporous structure of bead cellulose, respectively, the celluloses employed in the reactions were freed from water by solvent exchange [8] through methanol displaced by dioxan. From this point of view the difference in conversion of activated (with 17 % aqueous solution of NaOH) and nonactivated viscose rayon to *O*-(3-chloro-2-hydroxypropyl) derivative (Table 1) was significant and so was the slight change in water regain of bead *O*-(3-chloro-2-hydroxypropyl)cellulose ($0.46 \text{ cm}^3 \text{ g}^{-1}$) when compared to the starting material. *O*-(3-Chloro-2-hydroxypropyl)cellulose prepared in such a way contained minimum 50 to 60 % of true α -halohydrine groups.

By treatment of *O*-(3-chloro-2-hydroxypropyl)cellulose with sodium iodide in 2,4-pentanedione or acetone at elevated temperatures total or only partial displacement of chlorine by iodine was achieved in dependence on the reaction conditions and type of cellulose employed. The most reactive materials were those with the retained activated structure. In bead macroporous *O*-(3-chloro-2-hydroxypropyl)cellulose, converted by solvent exchange into 2,4-pentanedione, all chlorine was displaced by iodine within 1 h at 140 °C, while in the same dry powdery derivative this displacement was complete only after 2 h at the same conditions (Table 2). The prepared bead *O*-(3-iodo-2-hydroxypropyl)cellulose

Table 2

Substitution of chlorine by iodine in *O*-(3-chloro-2-hydroxypropyl)cellulose by treatment with sodium iodide in 2,4-pentanedione at 140 °C

Reaction time/h	<i>O</i> -(3-Halo-2-hydroxypropyl)cellulose			
	Bead		Powdery	
	w(chlorine)/mass %	w(iodine)/mass %	w(chlorine)/mass %	w(iodine)/mass %
0	4.6	0	3.1	0
0.5	1.1	12.1	—	—
1	Traces	15.5	0.6	8.6
2	0	14.8	0.1	10.6
4	0	13.7	0	10.0

was white and retained bead shape of the particles and macroporous structure even at these extreme reaction conditions. When using boiling acetone as the reaction medium, only 40% of chlorine was displaced by iodine in the bead *O*-(3-chloro-2-hydroxypropyl)cellulose during 24 h.

The elaborated modified alkylation of cellulose with chloromethyloxirane catalyzed with perchloric acid enabled to obtain *O*-(3-chloro-2-hydroxypropyl) derivative from any type of cellulose. The prepared new iodo derivative of cellulose, *O*-(3-iodo-2-hydroxypropyl)cellulose, widens the assortment of reactive cellulose derivatives. One of its possible applications is demonstrated in the preparation of a new type of aldehyde derivative of cellulose [9].

Experimental

Bead macroporous cellulose was obtained from the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences, Prague; viscose rayon from J. Dimitrov Chemical Works, Bratislava; crosslinked microcrystalline cellulose was prepared according to [10], and powdery cellulose was purchased from Whatman, Maidstone. The water regain and dry mass, respectively, of the bead cellulose and its *O*-(3-chloro-2-hydroxypropyl) derivative were determined according to [11]. The degree of substitution by 3-chloro-2-hydroxypropyl (DS_{CHP}) and 3-iodo-2-hydroxypropyl (DS_{IHP}) groups was calculated from the relationship

$$DS = 162 / [(100 \% A_{r,i} / w_i) - M_{r,s}] \quad (1)$$

where $A_{r,i}$ is the relative atomic mass, w_i is the mass fraction of the determined halogen in mass %, and $M_{r,s}$ is the relative molecular mass of the *O*-substituent lessened by a unit. *O*-(3-Chloro-2-hydroxypropyl)cellulose was converted to *O*-(2,3-epoxypropyl)cellulose and the epoxy content in this derivative was determined by the reaction with sodium thiosulfate [4].

O-(3-Chloro-2-hydroxypropyl)cellulose

Activation of cellulose

Viscose rayon (1–2 g) and crosslinked microcrystalline cellulose (4 g), respectively, were stirred with 17 % aqueous solution of NaOH (20–50 cm³) and allowed to stand under nitrogen at 5 °C for 1 h. The mixture was neutralized with 10 % aqueous solution of acetic acid, sucked, and washed with methanol and dioxan (each 5 × 25 cm³).

Bead cellulose (12.4 g, $w(\text{dry}) = 16.1\%$, water regain 5.22 cm³ g⁻¹) was washed with methanol and dioxan (each 5 × 25 cm³) and used for alkylation or activated by the procedure mentioned above.

Alkylation of cellulose

Dry cellulose or that obtained after suction from dioxan (1—4 g dry cellulose) was suspended in dioxan (20 cm³). To this suspension chloromethyloxirane (10 cm³), water (1 cm³), and the mixture (5 cm³) of 70 % perchloric acid and dioxan in the volume ratio of 1:9 were added. The reaction mixture was heated at 95 to 97 °C for 4 h. Then the solid phase was filtered off and washed with methanol (5 × 25 cm³). The *O*-(3-chloro-2-hydroxypropyl) derivative (Table 1) prepared from viscose rayon and crosslinked microcrystalline cellulose was dried with ether, the derivative of bead cellulose was washed with water.

O-(3-Iodo-2-hydroxypropyl)cellulose

Bead *O*-(3-chloro-2-hydroxypropyl)cellulose (6 g, *w*(dry) = 17.4 %, *w*(chlorine) = 4.6 %, *DS*_{CHP} 0.24) washed with acetone and 2,4-pentanedione (each 5 × 10 cm³) and the similar derivative of powdery cellulose (1 g, *w*(chlorine) = 3.1 %, *DS*_{CHP} 0.15), respectively, were suspended in the solution of sodium iodide (2 g) in 2,4-pentanedione (10 cm³) and heated at 140 °C. In preset time intervals samples (ca. 0.2 g) were withdrawn, washed with acetone (5 × 2 cm³) and water till negative reaction for halides and the halogen content was established (Table 2).

In repeated experiments a white bead *O*-(3-iodo-2-hydroxypropyl)cellulose (5.3 g, *w*(dry) = 20.8 %, *w*(iodine) = 15.7 %, *DS*_{IHP} 0.26) was obtained after 50 min or a powdery derivative (1.0 g, *w*(iodine) = 11.3 %, *DS*_{IHP} 0.17) after 2 h reaction.

The same bead *O*-(3-chloro-2-hydroxypropyl) derivative (6 g) converted by solvent exchange into acetone afforded after 24 h reaction in a boiling solution of sodium iodide (2 g) in acetone (10 cm³) a miscellaneous derivative, *O*-(3-chloro-2-hydroxypropyl)-*O*-(3-iodo-2-hydroxypropyl)cellulose (5.3 g, *w*(dry) = 19.0 %, *w*(chlorine) = 2.8 %, *w*(iodine) = 6.1 %).

Acknowledgements. The authors thank Dr. M. Beneš (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague) for establishing the water regain in bead cellulose derivatives and O. Juríková for determination of halogens.

References

1. Sharkova, E. F., Virnik, A. D., and Rogovin, Z. A., *Vysokomol. Soedin.* 8, 1450 (1966).
2. Gemeiner, P. and Zemek, J., *Collect. Czech. Chem. Commun.* 46, 1693 (1981).
3. Ellingboe, J., Allmé, B., and Sjövall, J., *Acta Chem. Scand.* 24, 463 (1970).
4. Gemeiner, P. and Beneš, M., *Collect. Czech. Chem. Commun.* 48, 267 (1983).
5. Pacsu, E., *Methods Carbohydr. Chem.* 3, 259 (1963).
6. Reid, J. D., Mazzeno, L. W., Jr., and Buras, E. M., Jr., *Ind. Eng. Chem.* 41, 2831 (1949).
7. Vigo, T. L., Daigle, D. J., and Welch, C. M., *Polym. Lett.* 10, 397 (1972).
8. Green, J. W., *Methods Carbohydr. Chem.* 3, 95 (1963).

9. Petruš, L., Gemeiner, P., and Némethy, T., *Collect. Czech. Chem. Commun.*, in press.
10. Kuniak, L. and Alinče, B., *Czech.* 136062; *Chem. Abstr.* 75, 7664b (1971).
11. Peška, J., Štamberg, J., Hradil, J., and Ilavský, M., *J. Chromatogr.* 125, 455 (1976).

Translated by A. Kardošová