



Note

New iodination of cellulose in phosphoric acid

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Received 19 September 1998; revised 2 January 1999; accepted 15 January 1999

Abstract

Microcrystalline cellulose was dissolved at ambient temperature in 85% H_3PO_4 , and KIO_3 was added together with KI to the solution thereby obtained. After 24 h, a white product was isolated by adding cold ethanol. The product has a large specific weight and a high content of iodine. On the basis of IR and NMR spectroscopy data, it is suggested that the polymer is the cellulose triester of the unstable acid HOI. A reaction mechanism for the ester formation is proposed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose; Ester; Autocatalytic; Iodination; Phosphoric acid

1. Introduction

Halogens and oxyhalogen species are widely used in carbohydrate chemistry, mainly as oxidative agents [1]. Alkaline hypochlorites [2] and hypobromites [3] are used for the oxidation and molecular mass reduction of large-scale available polysaccharides, while bromine is used for the oxidation of anomericly protected mono- and oligosaccharides to aldonic acids [4]. Oxidative reaction mechanisms vary depending on the halogen species and on the reaction conditions [4,5]. Since selectivity in carbohydrate oxidations is a desirable property, the reaction conditions (typically, the pH) must be controlled [2–5].

Iodine also finds use in carbohydrate chemistry. Thus, alkaline hypoiodite is a good oxidising agent for the conversion of aldoses into aldonic acids, whereas free iodine does not act as an oxidant [1]. The periodate ion selectively oxidises adjacent hydroxyls cleaving the glycolic bond. Apart from its older use as an

analytical tool [6], periodate oxidation is nowadays used in the carbohydrate industry for the conversion of polysaccharides into the corresponding 2,3-dialdehyde derivatives [7].

At neutral pH, the iodic ion is unreactive toward sugars whereas in acid solution and at high temperature, iodic acid oxidises carbohydrates to carbon dioxide [1]. On the other hand, the acidic iodate/iodide reaction system is a well-known oxidant system for several substrates, including alcohols [8]. This is interesting, since cellulose can be dissolved in concentrated (85% w/w) phosphoric acid with very limited hydrolysis [9]. Solubility is not very high ($\sim 3\%$ w/w at 20 °C), but the homogeneous conditions allow cellulose derivatisations with higher selectivity and lower degradation in comparison to similar reactions carried out in heterogeneous conditions. In fact, new selective oxidations of cellulose primary alcohols with nitrogen [10] and halogen oxides [11] were recently reported, in which the oxidising oxides are generated in situ by the addition of the corresponding an-

hydrides. We now report that by treating cellulose dissolved in 85% phosphoric acid with potassium iodate and potassium iodide, the polysaccharide is converted into the triester of hypoiodous acid.

2. Results and discussion

Addition of a finely powdered mixture of potassium iodate and potassium iodide to a solution of microcrystalline cellulose in 85% phosphoric acid immediately resulted in a purple–black mixture due to release of molecular iodine. In contrast, with analogous cellulose reactions in phosphoric acid with bromate and chlorate [11], very little heat was released upon the addition of the iodate/iodide mixture, and the reaction could be carried out at ambient temperature. After 24 h, a white–grey powder was isolated by adding cold

(–20 °C) ethanol followed by a mild heat treatment at 40 °C. A product of high specific weight was isolated, which contained a high percentage of iodine, i.e., 3.20 g of product from 1.0 g of starting cellulose with I content of 70.5%. The product was insoluble in water while moderate heating in dimethyl sulfoxide yielded a pale yellow solution. Surprisingly, the hydrolysis of the polymer was very slow even in concentrated sulfuric acid (96%), and release of iodine was observed only after stirring for several hours.

Apart from C, H and O, only iodine was present in the product with a percentage corresponding to the complete substitution of the hydrogen hydroxyls with iodine residues. As seen from the ^{13}C NMR spectrum in Fig. 1, the poly(1→4- β -glucose) structure was retained and practically no ring cleavage between C-2 and C-3 had occurred. Signals at 102.33, 79.56 and 60.19 ppm were assigned to

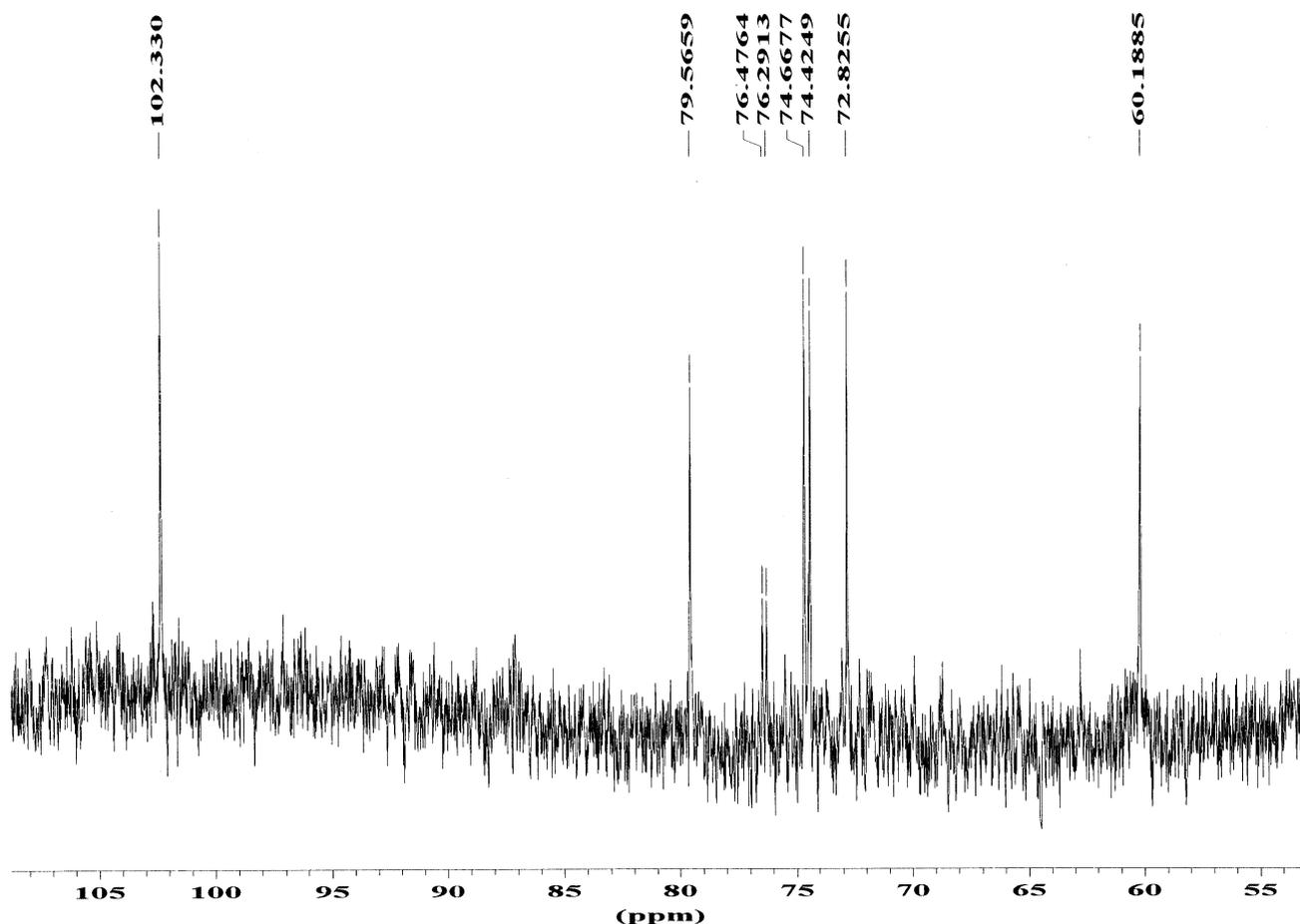
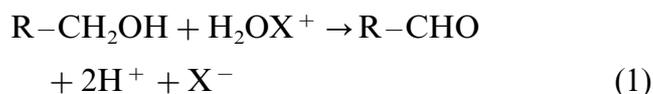


Fig. 1. ^{13}C NMR spectrum in Me_2SO of the product obtained by treating cellulose dissolved in 85% H_3PO_4 with KIO_3 and KI . Reaction conditions were as described in Section 3.

C-1, C-4 and C-6, while signals at 74.67, 74.42 and 72.82 ppm could reasonably be assigned to C-5, C-3 and C-2 based on analogy with literature data of cellohexaose. The absence of signal around 177 ppm suggests the absence of primary alcohol oxidation into carboxylic acids. The FT-IR spectrum in KBr showed a strong absorption band at 530 cm^{-1} assigned to the stretching mode of I–O bond [12]. In contrast to the stability of other cellulose esters in the presence of protic solvents, such as in the case of the cellulose triester of the unstable nitrous acid [13], the hypoiodite triester is stable enough to prevent its hydrolysis upon the addition of ethanol in order to precipitate the product from the reaction mixture.

We recently reported that the treatment of cellulose dissolved in phosphoric acid with sodium bromate or sodium chlorate in the presence of catalytic amounts of sodium bromide and sodium chloride yields 6-carboxy-cellulose with different degrees of depolymerisation [11]. The oxidation mechanism there proposed involves the formation of the protonated ester via attack of glucopyranosyl primary hydroxyl groups by H_2OX^+ , followed by the slow elimination of H–X, according to Eq. (1).



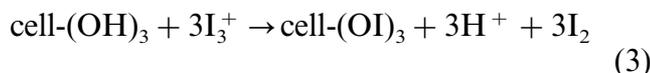
This reaction mechanism is analogous to the mechanism of aromatic electrophilic halogenations, in which the aromatic ring is attacked by the electrophilic halonium ions X^+ [14]. It might indeed be noted that cellulose esters are prepared in acidic media by enhancing the concentration of X^+ by addition of a strong mineral acid, e.g., in the case of the commercially important nitrocellulose synthesis, sulfuric acid is used along with nitric acid to promote the formation of NO_2^+ [15].

Among halogens, molecular iodine is the least powerful halogenating agent and organic iodinations are generally conducted in the presence of a strong oxidising acid (typically HNO_3) [16]. Interestingly, iodinations carried out with iodine in the presence of HIO_3 have been ascribed to the species I_3^+ [17]. As mentioned above, the iodate/iodide reaction sys-

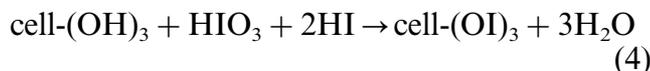
tem is the source of well-known chemical oscillators, autocatalytic reactions where the oxidant (H_2OI^+) is regenerated by HIO_3 in a feedback cycle in which I^- ions are re-oxidised by iodic acid [8], according to Eq. (2).



On the basis of these previous findings, we propose that in the case of the cellulose iodination in concentrated phosphoric acid here described, reaction may proceed through the attack of cellulose glucosyl –OH groups on I_3^+ followed by iodine elimination and the formation of cellulose hypoiodite, according to Eq. (3).



The overall stoichiometry of the reaction is easily written as Eq. (4),



By using a 10% excess of iodate/iodide, we isolated a sample with a degree of substitution (DS) of 2.9. In conclusion, a new cellulose ester of hypoiodous acid has been isolated. The physical and chemical properties of the material remain to be studied. Considering its chemical stability and the wide range of utilisation and commercial importance of other cellulose esters [15], this novel hydrophobic material might find applications.

3. Experimental

Materials and methods.—Microcrystalline cellulose (DS0) and all chemicals used were obtained from Fluka (Buchs, Switzerland). All products were of analytical grade and were used without prior purification. Elemental analysis was performed with a Carlo Erba automated analyser. The ^{13}C NMR spectrum was recorded on a Varian spectrometer operating at a proton frequency of 500 MHz by dissolving the product in deuterated Me_2SO . The IR spectrum was recorded on a Bruker FTIR spectrometer by prior dispersion of a product sample in potassium bromide.

Iodination method.—Cellulose (1.0 g) was dissolved at ambient temperature in H_3PO_4 (20 mL, 85% w/w) by thoroughly adding the polymer to a 250 mL glass cylinder containing the acid under fast stirring. Stirring was then set at low speed until a viscous solution was obtained (about 3 h). Then a mixture of finely powdered potassium iodide and potassium iodate (KIO_3 , 4.35 g; KI, 6.40 g, i.e., 1.1 mol IO_3^- /2.1 mol I^- /3 Glc residues) was rapidly added in a fumehood. After 24 h, a polymer was precipitated by adding cold EtOH (-20°C , 200 mL) followed by vigorous stirring with a spatula. The precipitate was filtered and washed several times with 96% EtOH. Mild drying at 40°C yielded 3.20 g of amorphous material. Anal. C, 13.34; H, 1.30; I, 70.5.

Acknowledgements

This work is dedicated to Flore and Alexander Murard, two with a common love for the sea and the trees. I wish to thank Monsieur Michel Vignon (Grenoble) for the elemental analysis, Giuseppe Impallomeni (Catania) and Bas Leeflang (Utrecht) for the NMR spectroscopy measurements and their comments. Thanks are due to Professor Giulio Deganello

who allowed me the freedom to follow personal lines of investigation.

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