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Cellulose degradation in the reaction system O_2/heteropolyanions of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$

A.A. Shatalov[1], D.V. Evtuguin, C. Pascoal Neto*

[a]Department of Chemistry, University of Aveiro, 3810 Aveiro, Portugal

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Abstract

The degradation reactions of cellulose under conditions of dioxygen oxidation in acidic aqueous and organic solvent–water medium in the presence of molybdovanadophosphate heteropolyanions of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$ have been investigated. The medium acidity and the heteropolyanions action were found to be the factors causing cellulose chain scission by solvolytic and oxidative degradation reactions, respectively. The cellulose oxidative depolymerisation was associated mainly with the action of VO_2^+ ions released from heteropolyanions via their partial dissociation under acidic conditions. The scheme reflecting the main pathways of cellulose degradation in the reaction system dioxygen/heteropolyanions is proposed. The effect of the medium ionic strength on cellulose depolymerisation is discussed in the context of possibilities to minimise the negative action of medium acidity and of VO_2^+ ions on cellulose. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose degradation; Oxygen; Heteropolyanions

1. Introduction

Metal–oxygen anion clusters (polyoxometalates) are a large and rapidly growing class of synthetic inorganic compounds (Hill, 1998). Polyoxometalates (POM) are composed primarily of the early transition metal cations in their high oxidation states (most commonly W^{IV}, Mo^{VI} and V^{V}) and oxoanions with a variety of structures and sizes. There are two classes of POM, the isopolyoxometalates, that are binary oxides of formula $[M_mO_y]^{n-}$ (M—metal cation), and the heteropolyoxometalates, that contain heteroatoms X (X = P, Si, B, …) in addition to the metal cations and oxoanions, $[X_xM_mO_y]^{n-}$ (Pope, 1983).

Heteropolyoxometalates (free acids and salts of heteropolyanions) possessing the properties, on the one hand, of strong acids with extremely high Brönsted acidity (Kozhevnikov & Matveev, 1982a; Misono, 1985) and, on the other, of very efficient oxidants (Pope & Muller, 1991; Kozhevnikov, 1998) are of great interest as bifunctional catalysts in homogeneous and heterogeneous systems (Hill & Prosser-McCartha, 1995; Okuhara, Mizuno & Misono, 1996). Such remarkable features of some heteropolyanions as high solubility in water and oxygen containing organic solvents, high stability over a wide temperature and pH range and, finally, the ability to regenerate using molecular dioxygen have made their use as oxidative reagents under anaerobic conditions possible (Weinstock, Attala, Agarwal & Minor, 1993; Weinstock, Attala, Reiner, Moen & Hammel, 1996a,b; Weinstock et al., 1997). They are also effective catalysts under aerobic conditions (Evtuguin & Pascoal Neto, 1997; Evtuguin & Pascal Neto, 1998; Evtuguin, Pascoal Neto Rocha & Pedrose deJesus, 1998a; Evtuguin, Pascoal Neto & Pedrose deJesus, 1998b) for selective delignification of wood and pulp in aqueous and organic solvent–water medium. Heteropolyanions having the Keggin structure (Fig. 1), such as molybdovanadophosphates of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$ (HPA-*n*, where *n* denotes the number of vanadium atoms in HPA composition) were recognised as perfectly suitable as the above-mentioned catalysts (Evtuguin et al., 1998a).

Nowadays, most attention has been concentrated on the use of POM in combination with dioxygen to develop effluent-free kraft pulp bleaching technologies as possible alternatives to chlorine based processes currently in use (Weinstock et al., 1996a,b; Evtuguin & Pascoal Neto, 1997). The main goal of pulp bleaching is to remove selectively the residual lignin without cellulose damage. Cellulose is the main component

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* Corresponding author. Tel.: +351-34-370-693; fax: +351-34-370-084.
E-mail address: cneto@dq.ua.pt (C. Pascoal Neto).

[1] On leave from Department of Wood Chemistry, St.-Petersburg Forest Technical Academy, 194021 St.-Petersburg, Russian Federation.

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of pulps and determined all the properties and quality parameters of paper commercially produced. In thus the study on cellulose reactions, especially those leading to its degradation under the bleaching with POM, is of prime importance. Up to now, there is a lack of information on the cellulose behaviour in the presence of POM under pulp bleaching conditions (Weinstock et al., 1997; Evtuguin & Pascoal Neto, 1997). This limits the interpretation of experimental results and makes it difficult to define future research strategies to overcome undesirable polysaccharide degradation.

In this paper we present the results on studies of cellulose degradation reactions in the reaction system dioxygen/molybdovanadophosphate heteropolyanions of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$ (HPA-*n*) under acidic conditions.

2. Materials and methods

2.1. Materials

Purified cotton cellulose (α-cellulose—95%; pentosans—1.4%; residual lignin—0.3%;) as a model of pulp cellulose was used in all oxidative experiments.

Vanillyl alcohol, acetovanillone and cellobiose, used as model compounds, were purchased from Sigma Chemical Co as high purity reagents.

HPA of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$ were prepared as previously reported (Evtuguin et al., 1998a). The pH of solutions was adjusted using sulfuric acid (9 M). The partially reduced form of heteropolyanion (0.2–0.5 e/mol HPA) was obtained by reaction of the sodium salt of heteropolyacid with an equivalent quantity of hydrazine sulfate, in the presence of sodium hydrogenosulfate.

2.2. Methods

2.2.1. Oxidation experiments and analysis of oxidised cellulose

The experimental conditions selected were those normally used for kraft pulp bleaching (90°C, pH 1.8–2.0, HPA concentration 2 mmol/l, initial oxygen pressure 0.5 MPa). Cotton cellulose 1% consistency was treated in a 0.35 l PARR reactor Model 4843 equipped with mechanical stirring, temperature and pressure control. The extent of cellulose destruction was evaluated by changes in cellulose viscosity and by the content of aldehyde groups. The intrinsic viscosity of cellulose was measured in cupri-ethylenediamine solution according to SCAN-CM 15:88 standard. The analysis of aldehyde groups in treated cellulose was carried out spectrophotometrically following reaction with 2,3,5-triphenil-2H-tetrazolium chloride (Aldrich reagent), as previously reported (Obolenskaya, Elnitskaya & Leonovitch, 1991).

2.2.2. NMR spectra

^{51}V NMR spectra were recorded at 105.2 MHz on a Bruker MSL 400 (9.4 T) spectrometer (293 K). The field frequency stabilisation was locked to deuterium by placing a coaxial inner tube with D_2O into 10 mm tube containing the sample. The chemical shifts are quoted in ppm from $VOCl_3$. The downfield shift was taken as positive. A 45° pulse and a recycle delay of 2 s were used in all experiments. The number of scans varied in the range 18 000–22 000.

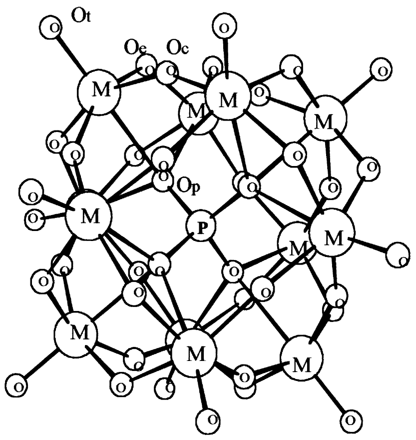


Fig. 1. The Keggin structure of $[PM_{12}O_{40}]^{3-}$ anion in ball-and-stick representation (the central PO_4 tetrahedron is surrounded by 12 MO_6 octaedra). The terminal (O_t), corner-sharing (O_c), edge-sharing (O_e) and phosphorous-linked (O_p) oxygen atoms and the metal atoms (primarily W, Mo, V) are depicted by small and big colourless balls, respectively.

2.2.3. GPC-analysis

The GPC-analysis of oxidised cellulose, dissolved in *N,N*-dimethylacetamide (DMAC) containing 0.5% (w/v) LiCl, was performed on two Plgel 10 μm MIXED B 300 × 7.5 mm columns protected by a Plgel 10 μm Pre-Column (Polymer laboratories Ltd, UK) using a PL-GPC 110 system (Polymer Laboratories Ltd, UK) (Kennedy, Rivera, White, Lloyd & Warner, 1990). The columns, guard column and injection system were maintained at 70°C. The eluent (0.5% (w/v) LiCl in DMAC) was pumped at flow rate of 0.9 ml/min. The GPC columns were calibrated using pullulan reference materials (Polymer Laboratories Ltd, UK).

2.2.4. HPLC-analysis

The HPLC-analysis of low molecular weight products of cellobiose degradation was performed on a PL Hi-PlexH 300 × 7.7 i.d. mm ion-exchange column (Polymer laboratories Ltd., UK) using GILSON HPLC system (France), equipped with RI-detector model 131 GILSON (France). The column was maintained at 65°C. The eluent (0.005 M H_2SO_4) was pumped at flow rate of 0.6 ml/min. The identification of oxidation products was done by comparing their retention time with those of model compounds and by joint injection of models and reaction mixture.

Table 1
Results of cotton cellulose oxidation in aqueous medium (90°C, 2 h, 1% consistency)

Oxidation conditions	Intrinsic viscosity $[\eta]$ (cm^3/g)	CHO groups (mmol/100 g)	Rate constant of chains scission ($K \times 10^{-6}$ min^{-1})	Peak molecular (Mw)
Oxygen atmosphere, pH = 6.0	1570[a]	0.2	0.1[b]	600 665[c]
Nitrogen atmosphere, pH = 1.8	450	1.9	5.6	133 740
Oxygen atmosphere, pH = 1.8	430	2.2	6.0	–
Oxygen atmosphere, pH = 1.8, $[HPA - 5]_{ox} = 2$ mmol/l	420	2.6	6.3	130 800
Oxygen atmosphere, pH = 1.8, $[HPA - 5]_{ox} = 2$ mmol/l, vanillyl alcohol 2 mmol/l	350	3.5	7.7	–
Oxygen atmosphere, pH = 1.8, $[HPA - 5]_{red} = 2$ mmol/l	340	3.9	8.2	–

[a] The intrinsic viscosity of initial cottol cellulose $[\eta]_0$ was 1620.

[b] Rate constants of chains scission (K) were calculated from the equation: $K_t = 1/DP_t - 1/DP_0$, where the degree of cellulose depolymerisation (DP) was calculated from the equation: $[\eta] = 0.42DP^{1.0}$.

[c] Peak molecular weight of initial cotton cellulose $(Mw)_0$ was 808 700.

3. Results and discussion

3.1. Background

The catalytic action of POM as reversible oxidants in liquid-phase oxidation electron transfer or redox type oxidations is usually represented according to the simplified reaction scheme (Pope & Muller, 1991):

$$\text{Substrate} + POM_{ox} \rightarrow \text{Substrate}^* + POM_{red} + H^+ \qquad (1)$$

$$POM_{red} + 2H^+ + 1/2O2 \rightarrow POM_{ox} + H_2O \qquad (2)$$

where POM_{ox} and POM_{red} are the oxidised and the reduced forms of POM, respectively, and Substrate* is the oxidised form of the substrate.

The oxidation of organic compounds in the presence of molybdovanadophosphates occurs due to the ability of V(V) to accept electrons from the substrate (Eq. (1)). The reduced V(IV) can be oxidised back to V(V) via reaction with molecular oxygen (Eq. (2)). This redox cycle is continuously repeated. All POM of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$ (HPA-n) with $n > 1$ have the property of easy reversible oxidation with dioxygen and can be considered as multi-electron oxidants (Kozhevnikov & Matveev, 1982b). During the pulp bleaching the residual lignin plays the role of the substrate. The selective delignification in the presence of POM is possible due to the lower lignin oxidation potential as compared to polysaccharides (Weinstock et al., 1993). According to the anaerobic approach (Weinstock et al., 1997) the pulp may be bleached with POM (Eq. (1)) under inert atmosphere, followed by the alkaline extraction stage to remove oxidised residual lignin. The regeneration of reduced POM by dioxygen (Eq. (2)) occurs in a separate stage at temperatures higher than those applied in the bleaching stage. In the aerobic approach (Evtuguin & Pascoal Neto, 1997) the lignin oxidation and reduced POM re-oxidation occur in the same stage. In this case POM plays the role of catalyst as reactions (1) and (2) runs simultaneously. This approach enables low concentrations of the catalyst (1–3 mmol/l) be used and the bleaching to be run in one stage. However, in this case the cellulose is also subjected to the oxidative action of the catalyst causing cellulose degradation which is undesirable (Evtuguin & Pascoal Neto, 1997).

The molybdovanadophosphate heteropolyanions (HPA-n) reported in this work, which uses the aerobic approach, are stable under moderate acidic conditions, pH 1.0–4.0 (Kozhevnikov & Matveev, 1982a,b). It has been shown elsewhere (Weinstock et al., 1996b; Evtuguin et al., 1998b) that the best bleaching results can be obtained at pH values 1.5–2.0 and in the temperature range 90–120°C. That is the reason for the using of pH 2.0 and temperature 90°C in the cellulose oxidative experiments discussed in this paper. Following previously found optimal conditions for HPA-n supported pulp bleaching (Evtuguin & Pascoal Neto, 1997), the HPA-n concentration of 2.0 mmol/l and dioxygen pressure of 0.5 MPa is kept in all experiments performed in aqueous as well as in the organic solvent–water medium.

It may be assumed that three factors in the selected reaction system (O_2/HPA) may contribute to cellulose degradation, namely: (i) medium acidity; (ii) dioxygen; and (iii) the catalyst. To estimate the contribution of these factors on cellulose degradation, a series of experiments have been carried out varying the treatment conditions. The cellulose degradation was monitored by determination of intrinsic viscosity, aldehyde group content and by analysis of molecular weight using GPC.

3.2. Effect of medium acidity and molecular oxygen on cellulose degradation

Trials on delignification of unbleached kraft pulps using HPA under both anaerobic (HPA-2 as oxidative reagent)

Table 2
Results of cotton cellulose oxidation in ethanol–water medium (90°C, 2 h, 1% consistency, EtOH/$H_2O = 1/1$)

Oxidation conditions	Intrinsic viscosity $[\eta]$ (cm^3/g)	CHO groups (mmol/100 g)	Rate constant of chain scission ($K \times 10^{-6}\ min^{-1}$)	Peak molecular weight (Mw)
Nitrogen atmosphere, pH = 1.8	420	1.8	6.2	130 760
Oxygen atmosphere, pH = 1.8, $[HPA - 5]_{ox} = 2$ mmol/l	420	2.0	6.2	130 780
Oxygen atmosphere, pH = 1.8, acetovanillone 2 mmol/l	400	2.3	6.0	–
Oxygen atmosphere, pH = 1.8, $[HPA - 5]_{ox} = 2$ mmol/l, acetovanillone 2 mmol/l	410	2.2	6.1	–

and aerobic (HPA-n, $n = 2$–5, as catalyst) conditions showed that the medium acidity, coupled with the elevated temperature, provides favourable conditions for occurrence of acid-catalysed solvolytic reactions of cellulose resulting in a decrease of pulp viscosity (Weinstock et al., 1996a; Weinstock et al., 1997; Evtuguin & Pascoal Neto, 1997; Evtuguin et al., 1998b). It was also proposed that during the pulp bleaching under oxygen atmosphere, other oxygen-containing species are formed, which can react with cellulose giving undesirable cellulose degradation (Sonnen, Reiner, Attala & Weinstock, 1997). The loss of pulp viscosity, in studies of kraft pulp bleaching by $[PMo_{10}V_2O_40]^{5-}$ (HPA-2) under aerobic conditions, has been assigned to autoxidation processes by the action of dioxygen through the generation of unselective oxygen-centered radicals (Weinstock et al., 1997).

To evaluate the contribution of acid-catalysed (solvolysis) and oxidative reactions on cellulose degradation in the reaction system O_2/HPA in aqueous and organic solvent–water medium, a series of experiments have been performed using varying treatment conditions (Tables 1 and 2).

The results obtained in aqueous medium under an oxygen atmosphere without catalyst at pH 6.0 show the absence of any significant impact of molecular oxygen on cellulose. In contrast, a dramatic increasing in cellulose chains scission is observed at pH 1.8 under a nitrogen atmosphere. Similar decreases in cellulose viscosity under aerobic conditions at the same pH value are observed in the presence and absence of catalyst. Thus, the acidity of the reaction medium is considered to be the main factor, responsible for cellulose degradation in an aqueous medium.

In an ethanol–water medium, the major decrease in cellulose viscosity also occurs at low pHs (Table 2), indicating again that the medium acidity makes the main contribution to cellulose degradation. Moreover, the rate of the acid-catalysed solvolysis reaction of cellulose in the organic solvent medium is higher than the hydrolysis reaction in aqueous medium. This can be explained by the increase of protons activity towards cleavage of glycosidic linkages with the addition of organic solvents (Young & Rowell, 1986). This effect, which is particularly strong in the case of aprotic solvents, was attributed previously to poor proton hydration and to the decreasing enthalpy of protons solvation with increasing proportion of organic solvent in solution (Seliverstova, Matusevich, Kushner & Reznikov, 1985).

3.3. Effect of HPA on cellulose degradation

It is evident from the data shown in Tables 1 and 2 that when HPA-5 is inserted into the reaction mixture there is some negative action on the quality parameters of cellulose. As can be seen from Eqs. (1) and (2), at least two forms of catalyst (the initial oxidised (POM_{ox}) and partially reduced, so-called “blue”, (POM_{red})) are present in the reaction mixture, under the conditions of pulp bleaching process by dioxygen with POM. So, the degradative action of catalyst on cellulose should be examined from the points of joint action of all the catalyst’s structural modifications, which exist simultaneously. The degradation action of POM on carbohydrates during the aerobic bleaching of kraft pulps was explained by an affect of active oxygen-centred radicals (hydroperoxy and hydroxyl radicals) formed in the catalyst re-oxidation step (Eq. (2)) through the interaction of partially reduced POM with dioxygen (Weinstock et al., 1997). The experiments with addition of vanillyl alcohol as lignin model compound into reaction mixture cellulose/HPA-5/O_2 showed the increase in cellulose depolymerisation (Table 1). The same negative effect on cellulose was observed with the partial reduction of HPA-5 by hydrazine (0.5 e/mol) before involvement in the oxidation. Thus, the partial reduction of HPA-5 by lignin during the pulp bleaching leads to an increase in cellulose degradation. However, it is difficult to explain the decrease in cellulose viscosity in the presence of reduced HPA-5 only by auto-oxidation, due to appearance in the solution of radicals formed during the oxidation of the reduced catalyst by dioxygen. It has been observed (Kozhevnikov & Matveev, 1982a), that no hydroxyl radicals were detected during the oxidation of reduced HPA-n containing more than three vanadium atoms ($n > 3$). Moreover, experiments on phendics and tetralin oxidation by dioxygen using heteropolyoxomolybdates $PMo_{10}V_2O_{40}^{5-}$ (HPA-2) as catalyst (Lissel & Jansen, 1992; Neumann & Levin, 1992) showed complete suppression of auto-oxidation.

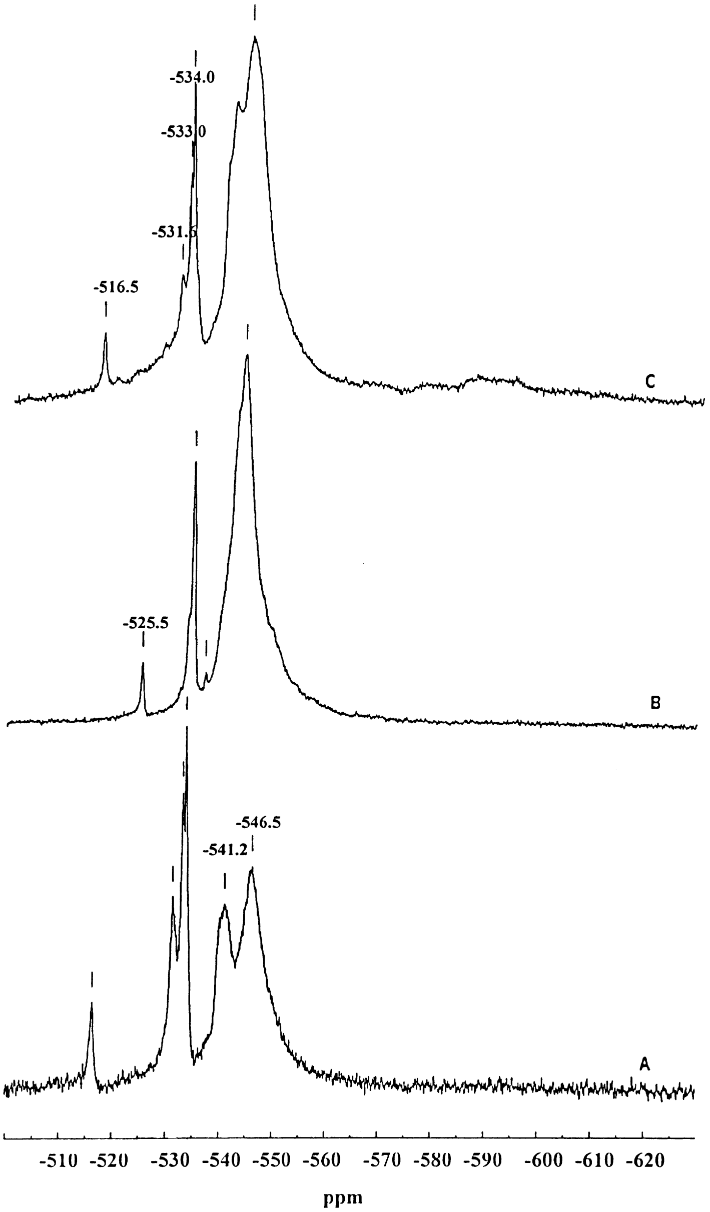


Fig. 2. ^{51}V NMR spectra of aqueous HPA-5 (4 mmol/l) solutions at pH 2.0: A. Partially (0.2 e/mol) reduced HPA-5; B. Oxidised HPA-5; C. Oxidised HPA-5 in 0.25 M solution of Na_2SO_4. Assignments of vanadium resonances were done based on previously reported data (Pettersson et al., 1994; Evtuguin et al., 1998a). The spectra reflects the variety of HPA-*n* isometric forms in solution. The peak at −533.0 ppm is assigned to HPA-1. The group of peaks at −516.5, −525.5, −531.6, −534.0 and −537.4 ppm are assigned to different positional isomers of HPA-2. The groups of non resolved peaks from −540.0 to −554.0 ppm are attributed to different positional isomers of HPA-3. The different positional isomers of HPA-4 and HPA-5 give the groups of peaks overlapping between −570.0 and −600.0 ppm. The high number of vanadium atoms in the coordination sphere is considered as an indication of weak dissociation of HPA-5 with VO_2^+ ions release. As practically all V(IV) in partially reduced HPA is presented in the form of VO^{2+} ions at pH 2.0 (e.g. out of sphere of HPA-5) this partial reduction should not insert suspicion in NMR spectra.

Hence, the free radical reactions can not be accepted as the main cause of HPA-*n* action on cellulose. The decrease in cellulose viscosity under aerobic bleaching in the presence of HPA-*n* can be explained only from the viewpoint of structural changes and the redox properties of the catalyst under the experimental conditions used.

In dilute acid solutions (<0.001 M) molybdovanadophosphates containing few vanadium atoms in their composition (HPA-*n*, $1 < n < 6$) updergo degradative dissociation with VO_2^+ ions released from the coordination sphere of HPA-*n* and formation of so-called “defect” or “lacunary” hetepoly species with fewer vanadium atoms than the parent polyanion (Courtin, 1971):

$$\text{HPA} - n \rightarrow \text{VO}_2^+ + \text{HPA} - (n - 1) \quad (3)$$

The free VO_2^+ ions have a reduction potential ($E° = 0.90$ V at pH = 2) higher than that of the parent HPA-*n* ($E° \leq 0.60$ V at pH = 2) (Evtuguin et al., 1998a) and

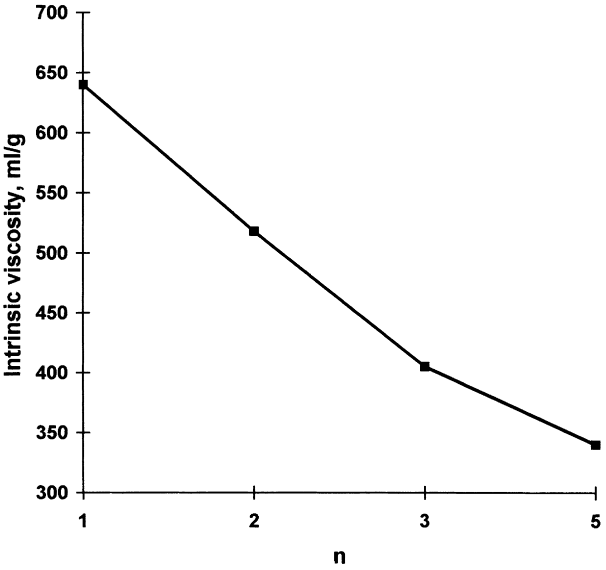


Fig. 3. Effect of partially (0.2 e/mol) reduced HPA-*n* on the cellulose viscosity (90°C; 2 h; $[HPA - n] = 2.0$ mmol/l; oxygen atmosphere).

exhibits stronger catalytic activity in the aerobic oxidative reactions of organic compounds (Gorodetskaya, Kozhevnikov, Matveev, Sidelnikov & Maksimovskaya, 1984; El Ali, Bregeault, Martin & Martin, 1989; Kholdeeva, Golovin, Maksimovskaya & Kozhevnikov, 1992). It has been shown that during dioxygen delignification of wood and pulps in the presence of molybdovanadophosphates the free VO_2^+ generated via dissociation of the parent HPA-*n* plays a determinant role in the catalytic oxidation of lignin (Evtuguin et al., 1998a). Thus, the VO_2^+ ions can be considered as catalyst species more active than the parent HPA-*n* and may have a pronounced effect on the cellulose oxidation during molybdovanadophosphates catalysed dioxygen pulp bleaching. Partial reduction of HPA-*n*, with formation of heteropolyblues or mixed-valence complexes containing V(IV), like for instance $[PMo^{6+}_{12-n}V^{5+}_{n-m}V^{4+}_{m}]^{(3+n)-}$ leads to increase of HPA-*n* degradative dissociation with release of VO_2^+ ions (Kuznetsova, Yurchenko, Maksimovskaya, Kirik & Matveev, 1977; Kuznetsova, Maksimovskaya, & Matveev, 1986; Evtuguin et al., 1998a). This is supported by data of ^{51}V NMR spectroscopy of oxidised and reduced HPA-5 in aqueous solution (Fig. 2). It is evident from Fig. 2, that partial reduction of HPA-5 results in increasing amounts of HPA-*n* species with a lower number of vanadium atoms than in the parent HPA-5 and, consequently, leads to increasing quantities of free VO_2^+ ions in solution. Thus, the decrease in cellulose viscosity in the presence of lignin model compounds can be explained through the partial reduction of HPA-5 with increasing levels of VO_2^+ ions released into solution.

To confirm the negative action of VO_2^+ ions on cellulose, experiments with partially (0.2 e/mol) reduced heteropolyanions of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$, HPA-*n* where $n = 1, 2, 3, 5$, have been carried out (Fig. 3). The stability of HPA-*n* in aqueous solutions decreases with increasing numbers of vanadium atoms in their composition (Kozhevnikov & Matveev, 1982a). Hence, changing the type of catalyst to be used and keeping constant other parameters of the process, we can control the concentration of VO_2^+ ions in solution. It can be seen from Fig. 3, that increasing the number of vanadium atoms (n) in the HPA-*n* composition from 1 to 5 leads to significant cellulose depolymerisation, showing the negative influence of free VO_2^+ on cellulose degradation.

The destructive action of VO_2^+ on cellulose has been shown also using sodium metavanadate ($NaVO_3$) solutions in acidic conditions under nitrogen atmosphere without HPA-*n* (Table 3). In acid medium metavanadate-ions (VO_3^-) exist in the form of free VO_2 :

$$VO_3^- + 2H^+ \rightarrow VO_2^+ + H_2O \qquad (4)$$

The high concentration of metavanadate-ions in solution favours the formation of more complex structures of three-, four- and up to decavanadate-anions ($[V_{10}O_{28}]^{6-}$) in equilibrium with lower oxidative potential than free VO_2^+ ions (Pope, 1983). Thus, the high proportion of metavanadate-ions (and consequently of VO_2^+ ions) may be observed only with low metavanadates concentration and $pH < 1$. It is evident from the data presented in Table 3, that increase in the concentration of metavanadates from 0.001 to 0.1 mol/l results in a decrease in cellulose depolymerisation,

Table 3
Effect of sodium metavanadate addition on cellulose depolymerisation (90°C, 2 h., 1% consistency, pH = 1.8)

Oxidation conditions	Intrinsic Viscosity $[\eta]$ (cm^3/g)	CHO groups (mmol/100 g)	Rate constant of chain scission ($K \times 10^{-6} min^{-1}$)
Nitrogen atmosphere, $[NaVO_3] = 0.1$ mol/l	615	1.0	3.5
Nitrogen atmosphere, $[NaVO_3] = 0.01$ mol/l	535	1.6	4.4
Nitrogen atmosphere, $[NaVO_3] = 0.001$ mol/l	430	2.0	5.9
Nitrogen atmosphere, $[NaVO_3] = 0.001$ mol/l	425	2.2	6.0

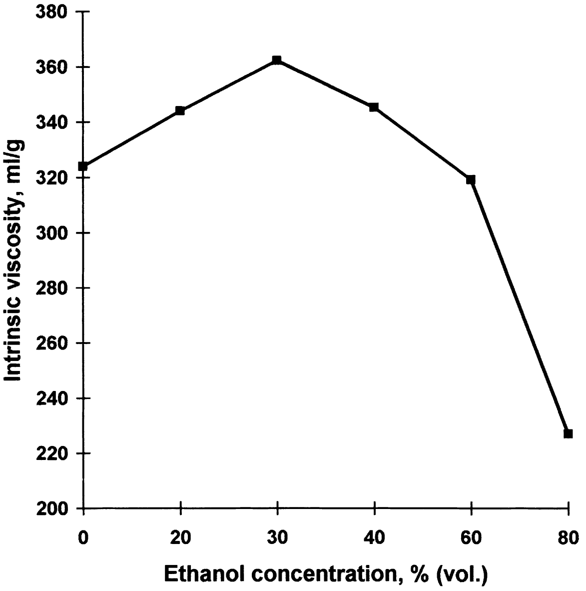


Fig. 4. Effect of ethanol–water medium composition on intrinsic viscosity of cotton cellulose under aerobic oxidation in the presence of partially reduced HPA-5 (90°C; 2 h, 1% consistency, $P(O_2) = 0.5$ MPa. $[HPA - 5]_{red} = 2$ mmol/l).

reflecting the involvement of free VO_2^+ ions in the cellulose degradation process.

In ethanol–water medium (50/50, v/v), the introduction of HPA-5 into the reaction mixture does not lead to cellulose degradation showing a viscosity increase compared with aqueous solutions (Table 2). Moreover, the progressive increase in the proportion of ethanol in the reaction mixture in the presence of partially reduced HPA-5 affects cellulose degradation. It can be seen from Fig. 4, that the dependence of cellulose viscosity on the composition of the ethanol–water reaction mixture, during the oxidation with partially reduced HPA-5 (simulating the reduction of catalyst by lignin during the pulp bleaching), is complex, showing a maximum at an $EtOH/H_2O$ ratio of 30/70 (v/v). The viscosity results were confirmed by GPC (Fig. 5). The displacement of maximum in GPC-curves of oxidised cellulose to the direction of high molecular weights (lower elution volumes) occurs with increasing ethanol content up to 30% (vol.). A further increase in ethanol concentration leads to displacement of the maximum in the GPC-curves in the direction of low molecular weights. Such cellulose behaviour can be explained by HPA-5 structural changes with addition of organic solvents. It has been established by conductometry (Kulikov & Kozhevnikov, 1981) and ^{51}V NMR (Evtuguin et al., 1998a) that the addition of ethanol to aqueous solutions of molybdovanadophosphates increases their stability in acidic solutions, e.g. increases the resistance of HPA-*n* towards degradative dissociation with the release of VO_2^+ ions in solution. Considering that VO_2^+ is the active catalytic species responsible for cellulose degradation, it is evident that the decrease in concentration of free VO_2^+ ions in the organic solvent medium leads to decrease of cellulose degradation compared to aqueous solutions. On the other hand, the increase in ethanol concentration in the reaction mixture raises the rate of degradative solvolytic reactions. This behaviour was observed in experiments with cellobiose as a model compound for cellulose (Fig. 6). Thus, the observed behaviour of cellulose with increasing ethanol content in the reaction mixture in the presence of partially reduced HPA-5 can be explained as a result of two competitive processes: (i) increase in cellulose solvolytic degradation with increase of ethanol concentration and (ii) decrease in cellulose oxidative destruction (by VO_2^+ ions released from HPA-5) with increasing ethanol concentration. The maximum in the plot of cellulose viscosity vs ethanol concentration (30% ethanol), (Fig. 4) corresponds to the composition of $EtOH/H_2O$ solution where the degradative solvolytic processes of cellulose starts to dominate.

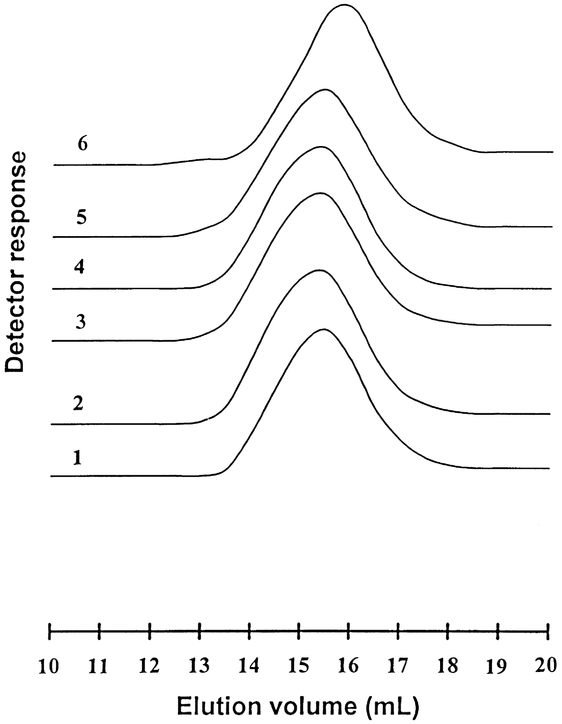


Fig. 5. GPC-curves of cotton cellulose after aerobic oxidation in the presence of partially reduced HPA-5 (90°C, 2 h, 1% consistency, $[HPA - 5]_{red} = 2.0$ mmol/l) with different composition of ethanol–water medium. $EtOH/H_2O$: 1—0/100, 2—20/80; 3—30/70; 4—40/60; 5—60/40; 6—80/20.

3.4. Effect of medium ionic strength on cellulose degradation

Changing the ionic strength of the reaction medium is one possible way to minimise the degradative effect of medium acidity and VO_2^+ ions on cellulose during oxidation in the presence of HPA. The increase in ionic strength favours the decrease of protons activity in solution ($a_{H^+} = \gamma[H^+]$), preserving the cellulose against hydrolysis and degradative

Table 4
Effect of sodium sulfate addition on cellulose depolymerisation (90°C, 2 h, 0.25 M Na_2SO_4)

Oxidation conditions	Intrinsic viscosity $[\eta]$ (cm^3/g)	CHO groups (mmol/100 g)	Rate constant of chain scission ($K \times 10^{-6}$ min^{-1})
Oxygen atmosphere, pH = 1.8	820	0.8	2.0
Oxygen atmosphere, $[HPA-5]_{red} = 2.0$ mmol/l, pH = 2.2	960	0.8	1.4

action of VO_2^+ ions through the decrease in their reduction potential:

$$VO_2^+ + 2H^+ \rightarrow VO^{2+} + H_2O \quad (5)$$

Moreover, the increase in medium ionic strength favours stability of HPA-*n* in solution and partially suppresses VO_2^+ release (Pettersson, Andersson, Selling & Grate, 1994). This is demonstrated by the ^{51}V NMR spectra of HPA in distilled water and in 0.25 M sodium sulphate solution (Fig. 2), showing the appearance of HPA isomers enriched in vanadium atoms with the addition of sodium sulphate in solution.

The experiments on cellulose oxidation with the addition of 0.25 M sodium sulphate solution to the reaction mixture confirmed the conclusions concerning the positive action of medium ionic strength on cellulose protection towards the acid hydrolysis and VO_2^+ ions action (Table 4).

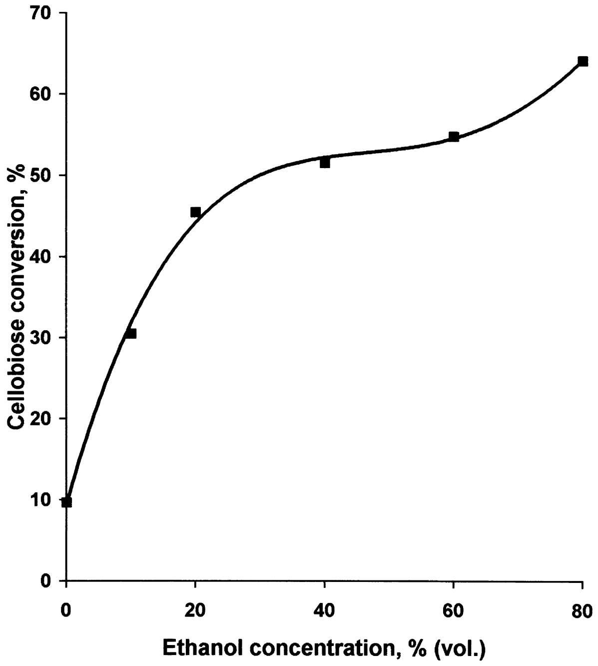


Fig. 6. Effect of ethanol–water medium composition on solvolytic cellobiose degradation (100°C, 2 h, 0.01 M H_2SO_4, initial cellobiose concentration 0.03 mol/l).

3.5. Analysis of low molecular weight products of cellobiose oxidative degradation

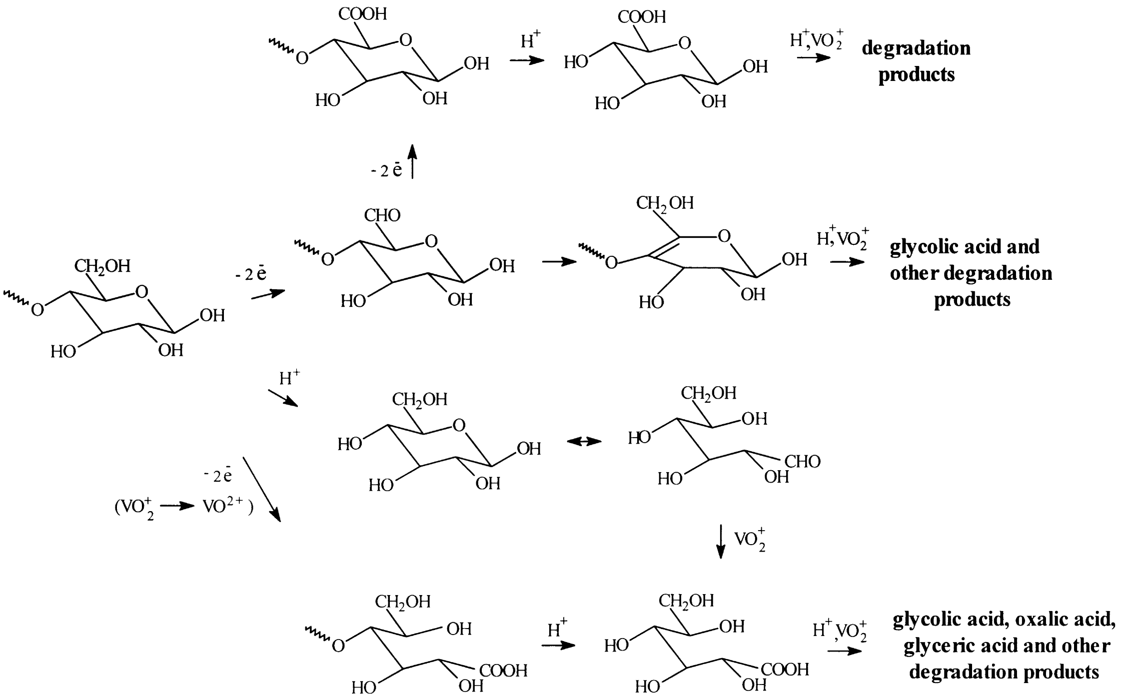
To establish the main directions and possible mechanism of cellulose degradation by dioxygen in the presence of HPA-5 the oxidative experiments with cellobiose as model compound of cellulose have been carried out. The degree of cellobiose conversion to glucose, estimated by HPLC analysis of reaction mixture after oxidation experiments (90°C, 2 h, 1% consistency, $[HPA-5]_{red} =$ 2 mmol/l) was 45%.

In Table 5 the results of the analysis of low molecular weight products of cellobiose oxidative degradation in the presence of partially reduced HPA-5 are summarised. The proposed mechanism of cellobiose degradation in the system O_2/HPA, based on the data in Table 5, are shown in Scheme 1.

The high proportion of glucuronic acid and its lactone in the reaction mixture (more than 50% of the total oxidation products) means that the oxidation at C-6 position of glucopyranosic units is the predominant oxidation route. Apparently, the oxidation at the C-6 position up to carboxyl groups passes through primary formation of aldehyde groups as the intermediates. This proposition is supported by the high amount of aldehyde groups detected in the cellulose samples after treatment with partially reduced HPA-5 (Table 1). The appearance of the carboxyl groups at the C-6 position leads to a decay of adjacent glycosidic linkages and accelerates hydrolytic degradation (Young & Rowell, 1986). This pathway reflects the weakening of cellulose glucosidic bonds induced by the oxidative action of HPA-*n*. With the appearance of the aldehyde groups at

Table 5
Low molecular weight products of celloboise oxidation by dioxygen in the presence of HPA-5 (90°C, 2 h, 1% consistency, $[HPA-5]_{red} = 2$ mmol/l)

Compound	(%)
Oxalic acid	5.9
Glucuronic acid	41.7
Malic acid	8.4
Glucuronic acid (lacton)	11.4
Glycolic acid	6.1
Glyceric acid	12.1
Gluconic acid	< 0.5
Non-identified	14.0



Scheme 1. Proposed mechanics of cellulose degradation under aerobic oxidation in the presence of HPA.

the C-6 position, the isomerisation with formation of unsaturated structures takes place with further rapid degradation to glycolic acid and other degradation products.

The other direction of cellulose oxidative degradation in the presence of HPA-5 is the oxidation in C-1 position of the reducing end units with the closing of the pyranose ring. Such a proposition is supported by the gluconic acid detected in the reaction mixture (Table 5). Oxalic and glyceric acids formed can be considered as the products of the fast stepwise oxidation of gluconic acid, unstable under acidic conditions (Scheme 1).

4. Conclusions

During aerobic oxidation of cellulose in the presence of $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ (HPA-*n*) heteropolyanions under acidic conditions in aqueous and organic solvent–water media the solvolytic and oxidative degradation reactions of cellulose take place, leading to a large decrease in cellulose viscosity. The cellulose oxidative depolymerisation was associated mainly with the action of VO_2^+ ions released from heteropolyanions via their partial dissociation under acidic conditions. The main directions of oxidative action of VO_2^+ ions on cellulose are C-6 and C-1 positions of glucopyranosic units followed by solvolysis of oxidised cellulose chains and further formation of low molecular weight oxidation products. The presence of organic solvents, such as ethanol, has a notable influence on cellulose degradation in reaction system O_2/HPA. Ethanol addition up to 30–50% (v/v) decreases cellulose oxidative depolymerisation through the partial suppression of VO_2^+ release from HPA-*n*. The increase in ionic strength of reaction medium reduces the negative action of medium acidity and VO_2^+ ions on cellulose through a decrease in protons activity and a decrease in the reduction potential of VO_2^+ ions.

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