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Lignin aerobic oxidation promoted by molybdovanadophosphate polyanion $[PMo_7V_5O_{40}]^{8-}$. Study on the oxidative cleavage of β-O-4 aryl ether structures using model compounds

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Abstract

The lignin oxidative degradation in the reaction system $[PMo_7V_5O_{40}]^{8-}/O_2$ has been studied using guaiacyl and syringyl β-aryl ether dimeric lignin model compounds. The oxidation has been monitored by GC/MS and ESI/MS. Although the free phenolic and non-phenolic model compounds were both degraded under aerobic oxidation with $[PMo_7V_5O_{40}]^{8-}$, the reaction mechanisms involved are different. Oxidation routes leading to the cleavage of β-O-4 bonds have been proposed.

Keywords: Heteropolyanion; Lignin; Lignin model compound; Oxidation catalysis; Oxygen

1. Introduction

The pulp-and-paper industry, one of the biggest industries worldwide, deals with the transformation of wood into fibre material (chemical pulp), which is then used for paper-making. The destruction and elimination of the primary ''encrustant'' material (lignin) from wood tissues — delignification — is the major aim of the pulp industry [1]. The delignification of wood (or pulping) and the oxidation of the residual lignin in the pulp to acquire the necessary pulp brightness (bleaching) proceeds via several technological stages that involve toxic sulphur or chlorine based reagents and, thus, raises environmental concerns [1]. Recently, polyoxometalates (POM) were suggested as new regenerable oxidising reagents (anaerobic oxidation) for the delignification of lignocellulosics, which may replace the undesirable sulphur and chlorine based reagents [2,3]. Also, the possibility of using POM as effective catalysts in the oxygen delignification (aerobic oxidation) was proposed [4,5]. Promising results on practical aspects of the POM application on pulping and bleaching [2–5] stimulated the interest on the

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understanding of the reaction mechanisms involved in the delignification.

The results of the oxidative destruction of phenolic β-aryl ether and diarylmethane-type lignin structures using dimeric model compounds in anaerobic oxidation with heteropolyanion $[SiW_{11}VO_{40}]^5$ were previously reported [2,6]. Only the phenolic lignin structural units were suggested to be reactive in this reaction system. The use of a heteropolyanion $[PMo_7V_5O_{40}]^{8-}$ (HPA-5) as the catalyst in lignin aerobic oxidation allows to oxidise both phenolic and non-phenolic lignin structures [7,8]. However, the mechanisms that are responsible for that oxidative degradation remain unknown.

The aim of this paper is to evaluate the oxidation routes and the reaction mechanisms involved in the cleavage of the β-aryl ether bonds of lignin in the reaction system $[PMo_7V_5O_{40}]^{8-}/O_2$ using phenolic and non-phenolic dimeric lignin model compounds.

2. Oxidative delignification catalysed by heteropolyanions

2.1. Lignin

Lignin is a complex natural aromatic polymer (Fig. 1), a product of random radical polymerisation of oxyphenylpropane monomeric precursors (coniferylic, sinapylic and *p*-coumarylic alcohols). Lignin is chemically bonded to polysaccharides in the cell wall, forming a three-dimensional network [9]. The basic structural units (so-called guaiacyl, syringyl and *p*-hydroxyphenyl) are linked by different types of linkage that depend on the chemical nature of precursors and on the phase of physiological evolution of the cell wall. Also, the frequency of occurrence of lignin structural units in the cell wall depends on the genetic origin of plants. Thus, the lignin of gymnosperms consists essentially of guaiacyl units, whereas lignin of angiosperms is constituted by guaiacyl, syringyl and a minor proportion of *p*-hydroxyphenyl monomer units [9].

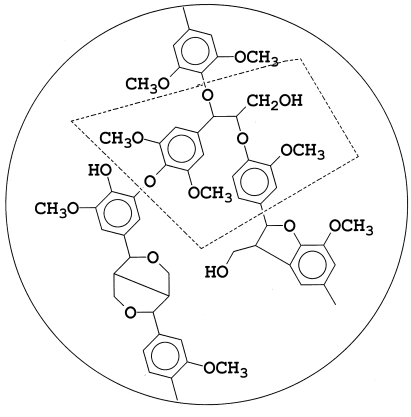

Fig. 1. Schematic representation of the fragment of hardwood lignin. The arylglycerol-β-arylether (β-O-4) linkages representing 40–55% of all lignin inter-unit links are indicated in dashed lines.

The structural complexity of lignin in wood tissues seriously hinders the studies of its reaction mechanisms. The common way for the elucidation of lignin reaction pathways is the use of oligomeric (mostly dimeric) phenylpropane structures as lignin models. The dimeric structures modelling phenolic (terminal) and non-phenolic lignin β-aryl ether structures (representing 40–55% of inter-unit linkages in lignin [9]) are those mostly used for these investigations.

2.2. Oxidative delignification with heteropolyanions

Molybdovanadophosphate heteropolyanions (HPA), polyoxometalates with the Keggin structure, are highly selective catalysts in oxidative organic syntheses and in oxidative delignification [10]. The oxidation of organic substrates in the presence of HPA occurs via oxidation by V(V) in HPA and by VO_2^+ ions released from HPA-*n* (where *n* is the number of vanadium atoms) under partial dissociation in acidic media [10]: HPA-$n \leftrightarrow$ HPA-$(n-x) + xVO_2^+$. VO_2^+ ions play an extremely important role in the oxygen delignification catalysed by HPA-*n* [11]. HPA-*n* containing four to six vanadium atoms were suggested to be the most suitable for the delignification catalysis.

HPA containing more than one vanadium atom in their composition (HPA-*n*, $n \geq 2$) are considered as multi-electron oxidants and, after the reduction in reaction with an organic substrate, may be easy re-oxidised in the same process step when the reaction is performed under aerobic conditions [10]:

$$\text{HPA-}n + \text{Red} + m\text{H}^+ \rightarrow \text{H}_m(\text{HPA-}n) + \text{Ox} \quad (1)$$

$$\text{H}_m(\text{HPA-}n) + (m/4)\text{O}_2 \rightarrow \text{HPA-}n + (m/2)\text{H}_2\text{O} \quad (2)$$

where **Red** is a substrate and **Ox** is an oxidised form of the substrate. The thermodynamic condition for the occurrence of reactions (1) and (2) may be formulated using redox potentials: $E°(\text{substrate}) \leq E°(\text{HPA-}n) \leq E°(O_2) = 1.23$ V (at pH 1) [10,12].

Under anaerobic conditions, the lignin oxidation (Eq. (1)) and the catalyst re-oxidation (Eq. (2)) are performed in separate process stages [2,6]. In the aerobic lignin oxidation with HPA-*n*, the reaction steps (1) and (2) occur simultaneously [11]. The conditions normally applied for the HPA-5 catalysed oxygen delignification (aerobic approach) are as follows [4,5,11]: temperature 90–100°C; pH 2–3; catalyst concentration 2–4 mmol/l. This was the reason to run experiments with lignin model compounds at 90°C, pH 2 and the catalyst concentration 2 mmol/l.

3. Experimental

3.1. Materials

1-(3-Methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol (**I**), 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (**Ia**) and 1-(3,5-dimethoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol (**II**) were 98% purity compounds and synthesised following a known method [13].

The aqueous solution of $Na_{8-x}H_x[PMo_7V_5O_{40}]$ (0.2 mol/l) was prepared according to a previously published procedure [11].

3.1.1. 1-(3-Methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol (*I*)

^{1}H NMR ($CDCl_3$): 3.46 (1-OH, s); 3.90 (2″-OCH_3,s); 3.91 (3′-OCH_3, s); 3.95 (H-2, 1H t, J 9.9 Hz); 4.16 (H-2, 1H, dd J 10.0 end 2.7 Hz); 5.04 (H-1, d, J 9.6 Hz); 5.61 (4′-OH, s); 6.89–7.01 (H-2′, H-5′, H-6′, H-3″, H-4″, H-5″, H-6″, m). EI-MS (*m*/*z*) (rel. int.): 290 (M^+, 7); 289 (37); 165 (34); 153 (21); 152 (90); 150 (12); 139 (11); 138 (60); 137 (51); 125 (27); 124 (56); 123 (13); 122 (19); 109 (32); 107 (14); 93 (43); 92 (11); 91 (12); 86 (25); 84 (71); 82 (100); 81 (13); 77 (32); 65 (24).

3.1.2. 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (*Ia*)

^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): 3.62 (1-OH, s); 3.58 (4′-OCH_3, s); 3.88 (2″-OCH_3,s); 3.90 (3′-OCH_3, s); 3.96 (H-2, 1H, t, J 9.6 Hz); 4.14 (H-2, 1H, dd J 10.0 and 3.0 Hz); 5.04 (H-1, dd, J 9.3 and 2.7 Hz); 6.85–6.98 (H-2′, H-5′, H-6′, H-3″, H-4″, H-5″, H-6″, m).

3.1.3. 1-(3,5-Dimethoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)ethanol (*II*)

^{1}H NMR ($CDCl_3$): 3.82 (1-OH, s); 3.90 (2″-OCH_3, 3′OCH_3 and 5′-OCH_3, s); 3.97 (H-2, 1H t, J 10.2 Hz); 4.17 (H-2, 1H, dd J 10.5 and 2.7 Hz); 5.03 (H-1, dd, J 9.3 and 3.0 Hz); 5.55 (4′-OH, s); 6.91–7.01 (H-2′, H-6′, H-3″, H-4″, H-5″, H-6″, m). EI-MS (*m*/*z*) (rel. int.): 320 (M^+, 16); 319 (50); 317 (19); 195 (41); 183 (26); 182 (100); 181 (17); 180 (49); 166 (48); 155 (28); 140 (19); 138 (44); 137 (36); 124 (44); 123 (49); 122 (27); 109 (32); 95 (30); 82 (22); 81 (13); 77 (31); 65 (13).

3.2. Oxidation procedure

Thirty milligrams of each model compound were dissolved in 20 ml of acetone–water

(30:70, v/v) solution and placed in a 100 ml Berghof Model BAR 845 Teflon reactor equipped with temperature and pressure control systems and magnetic stirring. After the addition of 200 μl of catalyst (final pH of solution about 2), the reactor was quickly closed, charged with oxygen (0.5 MPa) and introduced in the preheated oven. The time of oxidation at 90°C was 20 min. After the reaction, the reactor was quickly cooled during 15 min being placed in a iced water bath. The reaction mixture was extracted three times with chloroform (3 × 50 ml). The final organic phase was dried over anhydrous sodium sulphate and the solvent evaporated. The oxidation products, after the addition of internal standard (2-methoxynaphthalene), were dissolved in 200 μl of pyridine and treated with BSTFA to prepare trimethylsilyl (TMS) derivatives. The TMS derivatives of oxidation products were analysed by GC/MS.

In the experiments monitored by Electrospray Ionisation Mass Spectrometry (ESI/MS) 1.0 mg of model compound was dissolved in 1 ml of acetonitrile–water (30:70, v/v) solution and injected 5 min after the addition of 20 μl of catalyst solution (room temperature). The time to reach the MS detector was 2–3 min.

3.3. Analyses

GC/MS analyses were performed on a Hewlett Packard 5890 chromatograph equipped with a Mass Selective Detector MDS series II using helium as carrier gas (linear velocity: 35 cm/s). The chromatographic conditions (fused silica J&W column DB-5, 30 m × 0.32 mm i.d.; 0.25 μm film thickness;) were as follows: initial temperature 100°C; temperature rate 5°/min; final temperature 270°C; injector temperature 270°C; detector temperature 290°C. The identification of oxidation products (as TMS derivatives) was made based on comparison of their retention times and mass spectra with those of pure compounds commercially available (Aldrich and Merck Chem., Madrid) or synthesised in the laboratory.

Positive mode ESI mass spectra were acquired with a VG AutoSpecQ (VG Analytical Manchester, UK). The instrument of EBEqQ geometry was equipped with a Micromass ESI source. Solutions of model compound with catalyst were freshly prepared as described above. 10 μl of sample solution were injected to the needle, using methanol as the eluent continuously infused at a flow rate 20 μl/min by means of a Fisons model Phoenix 20CU syringe pump.

4. Results and discussion

4.1. Oxidation of phenolic model compounds

The oxidation of phenolic arylglycol β-aryl ethers **I** and **II** by $Na_{8-x}H_x[PMo_7V_5O_{40}]$ under oxygen atmosphere at pH 2 and 90°C showed 100% conversion for both model compounds and yielded 2-methoxyphenol (guaiacol) (**III**), 2-(2-methoxyphenoxy)ethanal (**IV**) and 2-(2-methoxyphenoxy)ethanoic acid (**V**) as predominant products (total yield about 90%) derived from aromatic ring B (Fig. 2). For this reason, the yield of other reaction products was evaluated in molar percentage to the total amount of products **III–V**. 1,4-Dihydroxy-2-methoxyben-

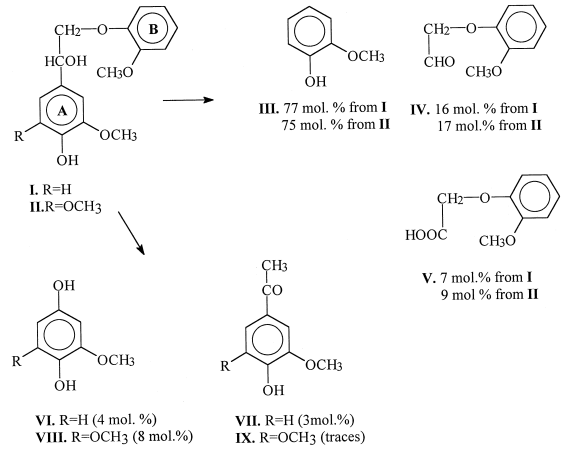

Fig. 2. Reaction products of phenolic arylglycol β-aryl ether model compounds.

zene (**VI**), 4-hydroxy-3-methoxyacetophenone (acetoguaiacone) (**VII**) were derived from dimeric compound **I** and 1,4-dihydroxy-2,6-dimethoxybenzene (**VIII**) and 4-hydroxy-3,5-dimethoxyacetophenone (acetosyringone) (**IX**) from the dimeric compound **II**. Both compounds **I** and **II** have yielded fumaric acid in the oxidation process.

The nature of the reaction products **III–IX** clearly suggests two principal reaction pathways for β-aryl ether structure degradation: (i) cleavage of the alkyl–phenyl linkage between the phenolic guaiacyl/syringyl groups and glycolic side chain and, (ii) cleavage of β-O-4 ether linkage. The last reaction pathway deals with the acid catalysed cleavage of β-O-4 ether, because **VII** and **IX** are typical products for the acidolytic splitting of these linkages [14]. Moreover, the products **VII** and **IX** were detected in test experiments after treatment of **I** and **II** in a nitrogen atmosphere at pH 2 without addition of the catalyst. The cleavage of the alkyl–phenyl linkages is a consequence of the phenolic group oxidation with catalyst species coupled with hydrolysis reactions (Fig. 3). Such mechanism for the splitting of the alkyl–phenyl linkages, including two consecutive one-electron oxidations of the aromatic ring with catalyst followed by hydrolytic degradation of the formed cyclohexadienyl cation, was proposed previously based on wood lignin [11] and monomeric model compound studies [7,8]. Based on the study of the oxidation of different lignin model compounds, the same mechanism was proposed for the cleavage of the alkyl–phenyl linkages with $[SiW_{11}VO_{40}]^{5-}$ heteropolyanions under anaerobic conditions [2,3,6].

Vanillin and syringaldehyde are well-known lignin oxidation products released in the homolytic reaction stages. These products were detected in the oxidation of lignin [15] and model compounds [16] with oxygen in acidic media via an autooxidation mechanism. These products are also formed in the oxidation of the phenolic arylglycerol β-aryl ether lignin model compounds with manganese peroxidase (MnP),

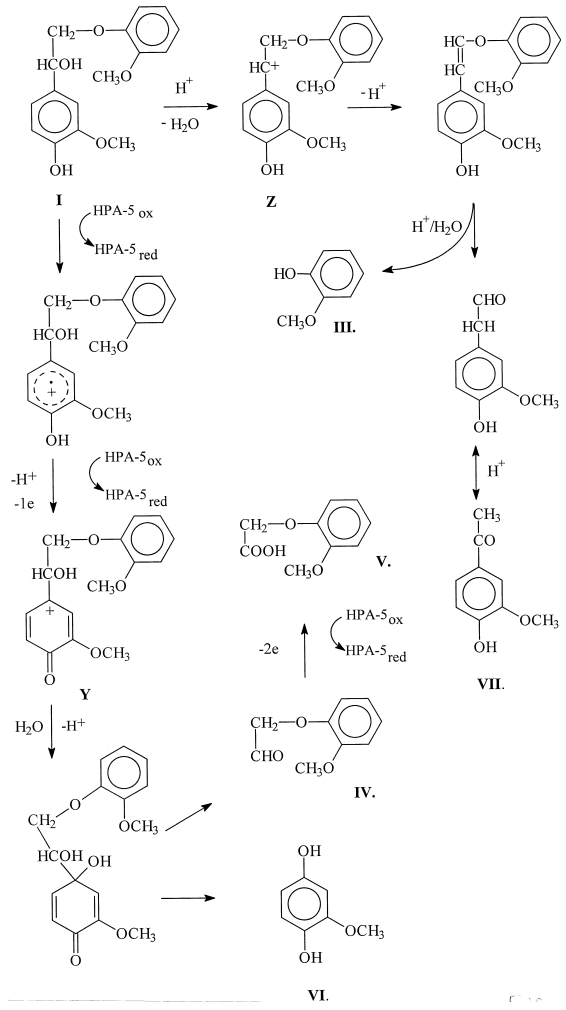

Fig. 3. Reaction scheme of dimer **I** oxidation in the presence of HPA-5.

as an evidence for the Cα–Cβ linkage cleavage through the homolytic mechanism [17]. The absence of vanillin and syringaldehyde in the oxidation products mixture of compounds **I** and **II** indicate a predominant heterolytic mechanism of β-O-4 oxidative cleavage of the phenolic structural units in the aerobic oxidation with HPA-5.

It must be noted that, under the acidic conditions used, HPA-5 suffers a partial hydrolytic degradation with release of VO_2^+ ions from its coordination sphere. Actually, in the solution, at pH 2, different positional isomers of HPA-*n*

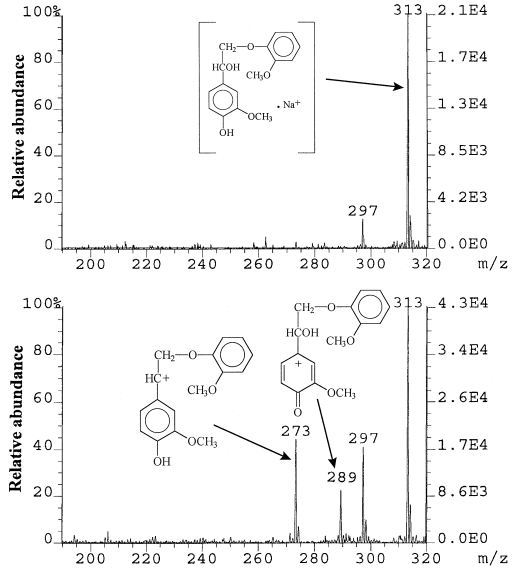

Fig. 4. Positive mode ESI/MS spectra of compound **I** without the catalyst (upper image) and after the catalyst addition (lower image).

with less than five vanadium atoms ($n = 1–4$) are detected [11]. In addition, the reduced V(IV) appearing in the lignin oxidation step (Eq. (1)) has a tendency to be partially released from the HPA structure as VO^{2+} ions leading to the formation of HPA species with lower numbers of vanadium atoms than that in initial solution before the reaction [11]. All these HPA-*n* ($n = 1–5$) species existing simultaneously in the solution, as well as the VO_2^+ ions, may be considered as oxidising agents for the lignin model compounds **I** and **II**. The oxidation peaks in the anodic scan (E_{pa}) of free phenolic guaiacyl and syringyl structural units containing non-etherified benzylic hydroxyls are 0.58 and 0.45 V vs. NHE (pH 2), respectively [7,8]. This is lower than the E_p of HPA-5 estimated for the same conditions (0.60 V vs. NHE). Thus, oxidation of **I** and **II** both with HPA-*n* ($n \leq 5$) and with VO_2^+ ions ($E_p = 0.90$ V at pH 2, 20°C [7,8]) dissociated from the HPA-5 under acidic conditions is thermodynamically favourable.

The feasibility of the pathways drawn in Fig. 3 was supported by monitoring the initial phase of the reaction with compound **I** using electrospray ionization mass spectrometry (ESI/MS). Five minutes after the catalyst addition (room temperature), the reaction mixture was injected in the electrospray system working in positive mode. Fig. 4 shows the ESI/MS spectra of initial dimeric compound **I** in neutral solution in the presence of sodium sulphate without the catalyst addition (top image) and after the catalyst introduction (bottom image). The m/z 313 peak corresponds to compound **I** with an electrostatically attached sodium cation in the gaseous phase. Abstraction of two electrons from **I** by the catalyst and the proton elimination leads to the formation of an intermediate cyclohexadienyl cation **Y** (Fig. 3) that, attending to the coulombic repulsion with positively charged sodium cation, appears on the ESI/MS spectrum in a cationless form as m/z 289 peak (Fig. 4). The formation of the benzyl cation intermediate **Z** (Fig. 3) is represented by m/z 273 peak (290 u–17 u) on ESI/MS spectrum (Fig. 4).

4.2. Oxidation of non-phenolic model compound

The aerobic oxidation of the non-phenolic β-aryl ether lignin model compound **Ia** in the presence of HPA-5 showed a low conversion degree (~20%) and yielded 3,4- dimethoxy-

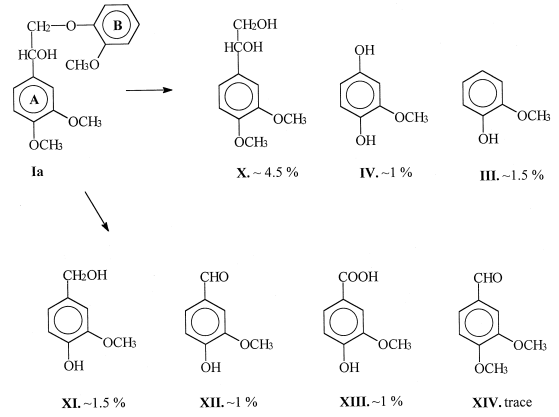

Fig. 5. Reaction products of the non-phenolic arylglycol β-aryl ether compound **Ia**.

phenylglycol (**X**) as the most abundant reaction product (Fig. 5). Compounds **III**, **VI** and **XII–XIII** were also detected. The formation of **X** in the oxidation of **Ia** clearly indicates a direct cleavage of the β-O-4 linkage via an one-electron oxidation mechanism (Fig. 6). Such a mechanism for the subsequent β-ether bond cleavage through an one-electron oxidation of the adjacent B-ring in the non-phenolic lignin model compounds was suggested previously in oxidation experiments with lignin peroxidase (LiP) [18]. The formation of vanillyl alcohol (**XI**) may be considered as the result of a one-electron oxidation of the A-ring with catalyst species followed by homolytic cleavage of the Cα–Cβ bond. The homolytic cleavage of Cα–Cβ bond was previously suggested in the oxidation of non-phenolic arylglycerol β-aryl ether structures by LiP [19]. Vanillin (**XII**) and 3,4-dihydroxybenzoic acid (**XIII**) are derived from **XI** by further oxidation with the catalyst. The active catalyst form in the oxidation of non-phenolic structures is V(V) in VO_2^+ ions ($E_p = 0.90$ V at pH 2, 20°C) released via destructive dissociation from the HPA-5 structure [7,8]. This fact explains the predominance of one-electron oxidation mechanisms with **Ia.** Unlike to phenolic β-aryl ether structures **I** and **II**, the acidolytic cleavage of β-O-4 bond for the non-phenolic compound **Ia** is not an important reaction pathway. This follows from the absence of 3,4-dimethoxyacetophenone (acetoveratrone) among the reaction products of **Ia** oxidation. However, the small amounts of **XIV** detected in the **Ia** oxidation indicate a possible formation of an enol ether type intermediate. Thus, the participation of acydolytic stages in **Ia** degradation is not completely excluded.

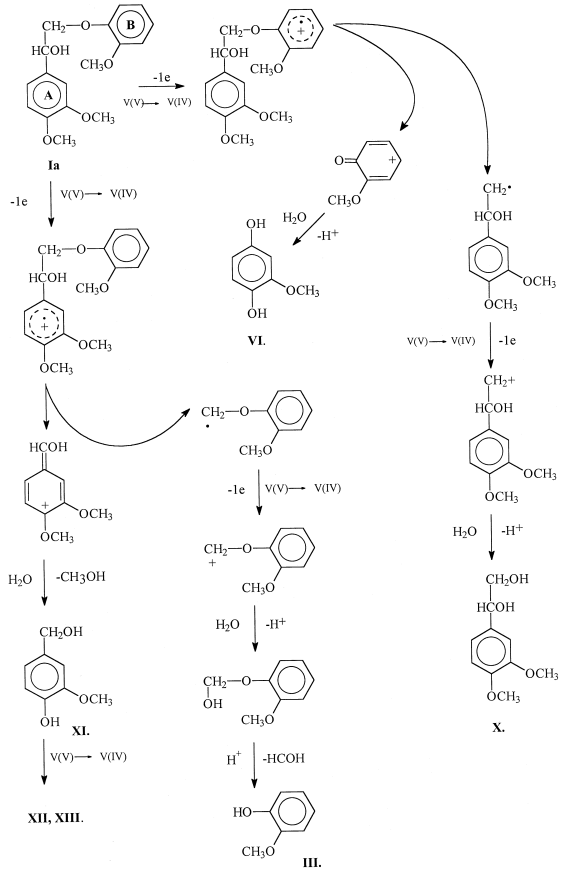

Fig. 6. HPA-5 catalysed oxidative cleavage of β-O-4 bonds in the non-phenolic lignin model compound (V(V) and V(IV) are in the composition of VO_2^+ and VO^{2+} ions, respectively).

5. Conclusions

The study on lignin model compounds showed oxidative destruction of both phenolic and non-phenolic β-aryl ether structures in the reaction system $[PMo_7V_5O_{40}]^{8-}/O_2$. Phenolic β-aryl ether structures have a conversion, at least, five-times higher than it is estimated for the non-phenolic structures. The cleavage of β-O-4 bonds in the phenolic structures occurs predominantly through heterolytic mechanisms. These include the hydrolytic cleavage of the alkyl–phenyl bonds in the phenolic structural units oxidised by $[PMo_7V_5O_{40}]^{8-}$ and the acidolytic splitting of the β-O-4 linkages. The oxidative cleavage of non-phenolic β-aryl ether structures is determined by one-electron oxidation of aromatic groups with VO_2^+ ions released from the $[PMo_7V_5O_{40}]^{8-}$ followed by homolytic cleavage of β-O-4 ether and Cα–Cβ linkages.

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