NOTE

Significance of benzylic hydroxymethylene group in the reaction of lignin side-chain with active oxygen species under oxygen bleaching conditions

Satoshi Ohmura · Tomoya Yokoyama · Yuji Matsumoto

Abstract To examine the effect of the presence of benzylic hydroxyl group on the reaction of β-O-4 type lignin moiety with active oxygen species (AOS) under oxygen bleaching conditions, a specially designed β-O-4 type model compound carrying the benzylic methoxyl group, 2-(3,5-difluorophenoxy)-3-methoxy-3-(3,4-dimethoxyphenyl) propan-1-ol (IV), was treated together with a phenolic compound, 4-hydroxy-3-methoxybenzyl alcohol (II), under oxygen bleaching conditions. In this reaction system, AOS were generated by reactions of compound II with dioxygen and attacked compound IV. Compound IV was rather stable, while an analogous model compound carrying the benzylic hydroxyl group, 2-(3,5-difluorophenoxy)-1-(3, 4-dimethoxyphenyl)propane-1,3-diol (I), was rather degraded. This result and the previous knowledge on the relatively high stability of 3,4-dimethoxybenzyl alcohol carrying only the hydroxymethyl group as side-chain under the identical reaction conditions suggested that the existence of benzylic hydroxymethylene group is essential in the extensive reaction of side-chain of β-O-4 type lignin moiety with AOS. To compare the reactivity of AOS toward different types of hydroxyl and aryloxyl carbons, 2-(3,5-difluorophenoxy)propane-1,3-diol (VI) or 3-(3,5-difluorophenoxy)propane-1,2-diol (VII) was also subjected to this reaction system. Compound VII was degraded by AOS more extensively than compound VI.

Keywords Alkyl-aryl ether · Benzylic position · Delignification · Phenol

Introduction

Dioxygen reacts only with electron-rich substructures in pulp components, such as dissociated phenolic hydroxyl groups in lignin without α-carbonyl group [1, 2] and reducing end groups in carbohydrates [3], under oxygen bleaching conditions. These reactions generate active oxygen species (AOS), which attack carbohydrates resulting in the serious problem in an oxygen bleaching process, their depolymerization [3–6].

It has basically been considered that only phenolic lignin moieties are oxidized in an oxygen bleaching process, and on the other hand, non-phenolic analogues are inert. Several oxidation products were isolated and characterized in an oxygen-alkali treatment of simple phenolic lignin model compounds [5, 7]. The number of dioxygen can be calculated to be up to 1.5 molecules to afford 1.0 molecule of the oxidation products. On the other hand, Tong et al. [8]. and Imai et al. [9]. showed that about 3 mol of dioxygen are consumed by 1.0 molar equivalent aromatic nucleus in a prolonged oxygen oxidation of kraft and isolated residual lignin samples as well as various lignin model compounds although many of aromatic nuclei in these lignin samples are not phenolic but non-phenolic. These results were considered to suggest that not only phenolic but also non-phenolic lignin moieties are extensively oxidized in an oxygen bleaching process and general reaction products obtained from phenolic lignin moieties are further

S. Ohmura · T. Yokoyama (✉) · Y. Matsumoto
Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan
e-mail: yokoyama@woodchem.fp.a.u-tokyo.ac.jp

oxidized. Two possible mechanisms were considered to explain the extensive oxidation of non-phenolic lignin moieties in an oxygen bleaching process: hydroxylation of a non-phenolic aromatic nucleus to convert it to a new phenolic analogue, and cleavage of an aryl ether bond to liberate the aryl portion as the new phenolic aromatic nucleus. The latter mechanism seemed to be more plausible on the basis of the previous information on the reactivity of AOS [4, 6, 8, 10]. Therefore, the cleavage of an aryl ether bond should be a key in the extensive oxidation of non-phenolic lignin moieties in an oxygen bleaching process.

In our previous study, it was confirmed that a non-phenolic aromatic nucleus consisting of a β-O-4 linkage is liberated as the new phenolic aromatic nucleus under oxygen bleaching conditions, when a specially designed non-phenolic β-O-4 type lignin model compound, 2-(3,5-difluorophenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (I in Fig. 1), was treated together with a phenolic compound, 4-hydroxy-3-methoxybenzyl alcohol (II in Fig. 1), under oxygen bleaching conditions [10]. In this reaction, AOS were generated by reactions of compound II with dioxygen, and attacked the side-chain of compound I resulting in the β-O-4 bond cleavage and liberation of the non-phenolic 3,5-difluorophenoxyl aromatic nucleus as the new phenolic compound, 3,5-difluorophenol (III in Fig. 1). Compound I itself does not directly react with dioxygen. Because of the resistance of compound III under oxygen bleaching conditions even where AOS are operative, compound III was quantitatively detected when it was liberated from compound I, which made it possible to quantitatively confirm the β-O-4 bond cleavage and liberation of compound III. Since the attack of AOS on the side-chain was considered to result in the liberation of compound III, the reactivity of AOS toward side-chain should be examined in detail.

In this study, it was examined how the presence of benzylic hydroxyl group influences the reaction between side-chain of β-O-4 type lignin moiety and AOS. Another specially designed β-O-4 type model compound, 2-(3,5-difluorophenoxy)-3-methoxy-3-(3,4-dimethoxyphenyl)propan-1-ol (IV in Fig. 1), was treated together with compound II under oxygen bleaching conditions. The degradation of compound IV was caused by the attack of AOS generated from compound II, and the liberation of compound III were quantitatively examined. Compound IV does not have the benzylic hydroxyl but methoxyl group, and hence, the comparison between the results obtained from compounds IV and I can evaluate the effect of the presence of benzylic hydroxyl group on the reaction with AOS. Furthermore, the significance of benzylic hydroxymethylene group in the reaction of β-O-4 type lignin moiety with AOS was discussed based on the obtained results and the previous knowledge on the relatively high stability of 3,4-dimethoxybenzyl alcohol (V in Fig. 1) under oxygen bleaching conditions where AOS are operative [6].

To examine the reactivity of AOS toward different types of hydroxyl and aryloxyl carbons in side-chain, 2-(3,5-difluorophenoxy)propane-1,3-diol (VI, Fig. 1) or 3-(3,5-difluorophenoxy)propane-1,2-diol (VII, Fig. 1) was also treated under the same conditions as those for compound IV. Compound VI consists of hydroxymethyl and aryloxymethylene groups, while hydroxymethyl, hydroxymethylene, and aryloxymethyl groups are the substructures of compound VII. These structural differences can make it possible to evaluate the reactivity of AOS toward these substructures.

Materials and methods

Materials

Compound IV was prepared from compound I, which had been synthesized according to the method of Adler et al. [11]. Compound I was dissolved in methanol containing sulfuric acid. The mixture was kept over night at 50 °C with stirring, which afforded compound IV. Compound VI was synthesized from diethyl bromomalonate (diethyl bromopropandionate). This compound was reacted with the sodium salt of compound III in dry acetone at 40 °C, which afforded diethyl 3,5-difluorophenoxymalonate (diethyl 3,5-difluorophenoxypropandionate). The reaction product was reduced with lithium aluminum hydride in dry tetrahydrofuran (THF), which gave compound VI. Compound VII was synthesized from bromomethyloxirane. This compound was dissolved in dry THF containing compound III and potassium carbonate. The mixture was refluxed for
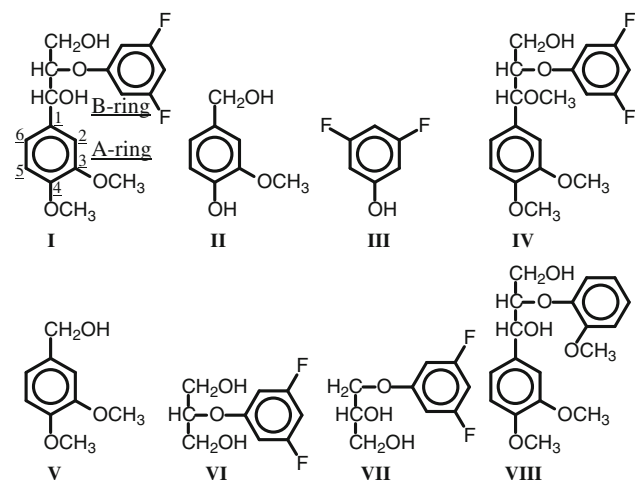
Fig. 1 Chemical structure of the model compounds used and referred to in this study

3 days in dry THF, which gave 3,5-difluorophenoxymethyloxirane. The reaction product was hydrolyzed in aqueous 20 % 1,4-dioxane containing sulfuric acid for 2 days at room temperature, which afforded compound VII. The structures of these compounds were confirmed by ^{1}H- and ^{13}C-NMR (JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) and GC/MS (GC2010/PARVUM2, Shimadzu Co., Kyoto, Japan).

Compound IV (mixture of the *erythro* and *threo* isomers) ^{1}H-NMR ((CD$_3$)$_2$CO) δ 3.28, (s, 3H, *erythro* or *threo* Cα-OC$\underline{H}_3$), 3.30 (s, 3H, *erythro* or *threo* Cα-OC$\underline{H}_3$), 3.60–3.62 (m, 1H, *erythro* or *threo* Cγ-$\underline{H}_a$), 3.71-3.77 (m, 1H, *erythro* or *threo* Cγ-$\underline{H}_a$), 3.86 (s, 3H, *erythro* or *threo*-OC$\underline{H}_3$), 3.88 (s, 3H, *erythro* or *threo*-OC$\underline{H}_3$), 3.93–3.98 (m, 1H, *erythro* or *threo* Cγ-$\underline{H}_b$), 4.01–4.08 (m, 1H, *erythro* or *threo* Cγ-$\underline{H}_b$), 4.48–4.50 (d, 1H, *erythro* or *threo* Cα-$\underline{H}$), 4.51–4.54 (d, 1H, *erythro* or *threo* Cα-$\underline{H}$), 4.61–4.67 (m, 1H, *erythro* or *threo* Cβ-$\underline{H}$), 6.53–7.14 (m, 6H, aromatic); ^{13}C-NMR ((CD$_3$)$_2$CO) δ 56.1 (2-OCH$_3$), 57.0 (*erythro* or *threo* Cα-OC$\underline{H}_3$), 57.1 (*erythro* or *threo* Cα-OC$\underline{H}_3$), 62.1 (*erythro* or *threo* Cγ), 62.2 (*erythro* or *threo* Cγ), 83.2 (*erythro* or *threo* Cα), 83.9 (*erythro* or *threo* Cβ), 84.0 (*erythro* or *threo* Cβ), 84.7 (*erythro* or *threo* Cα), 96.3-96.9 (B1), 100.7–101.0 (B3 and B5), 112.1–112.5 (A2 and A5), 121.2–121.6 (A6), 131.6-131.7 (A1), 150.4–150.6 (A4 and A3), 163.2–163.4 (B4), 165.2–165.5 (B2 and B6) (see Fig. 1 for how to number the carbons in the model compounds. A1 shows the number 1 carbon of the A-ring.); MS *m/z* (rel. int.): 354 (M$^+$, 1), 292 (1), 217 (1), 182 (14), 181 (100), 166 (14), 165 (5), 151 (7), 133 (2), 132 (2), 127 (1), 95 (1), 91 (1), 77 (1).

Compound VI (meso compound) ^{1}H-NMR ((CD$_3$)$_2$CO) δ 3.71–3.76 (dd, 2H, *J* = 5.5, *J* = 11.5, -C$\underline{H}_aH_b$OH), 3.76–3.81 (dd, 2H, *J* = 4.5, *J* = 11.5, -CH$_a\underline{H}_b$OH), 4.40–4.45 (dd, 1H, *J* = 4.5, *J* = 5.5, -C$\underline{H}$(OAr)-), 6.50–6.69 (3H, aromatic); ^{13}C-NMR ((CD$_3$)$_2$CO) δ 61.9 (primary carbon), 82.1 (secondary carbon), 96.5–96.9 (B1), 100.5–100.7 (B3 and B5), 162.3–165.6 (B2, B4, and B6) (The carbons of the aromatic ring are numbered in the same order as those of the B aromatic ring of compound IV.); MS *m/z* (rel. int.): 204 (M$^+$, 4), 155 (5), 131 (14), 130 (100), 127 (13), 113 (4), 102 (13), 101 (9), 74 (11), 54 (9).

Compound VII: ^{1}H-NMR ((CD$_3$)$_2$CO) δ 3.84 (1H, dd, *J* = 6.0, *J* = 8.5, -C$\underline{H}_aH_b$OH), 4.06–4.12 (2H, m, -C$\underline{H}_2$OAr), 4.14 (1H, dd, *J* = 6.5, *J* = 8.5, -CH$_a\underline{H}_b$OH), 4.43–4.48 (1H, m, -C$\underline{H}$(OH)-), 6.56–6.66 (3H, m, aromatic); ^{13}C-NMR ((CD$_3$)$_2$CO) δ 67.0 (primary carbon of hydroxymethyl group), 70.6 and 74.8 (primary carbon of phenoxymethyl group and secondary carbon), 96.7–97.2 (B1), 99.3–99.6 (B3 and B5), 162.0–165.7 (B2, B4, and B6) (The carbons of the aromatic ring are numbered in the same order as those of the B aromatic ring of compound IV.); MS *m/z* (rel. int.): 204 (M$^+$, 7), 155 (10), 144

(10), 143 (6), 131 (34), 130 (100), 127 (13), 115 (7), 114 (13), 113 (12), 102 (10), 101 (7), 75 (11), 74 (42), 61 (32), 57 (18).

Semiconductor grades (99.99 + %) of NaOH and FeCl$_3$ (Sigma-Aldrich Japan K. K., Tokyo, Japan) were used without further purification. All the other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) or Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and used without further purification. Ultra-high-purity water produced by reverse osmosis filtration (Puric-Z, Organo Co., Tokyo, Japan) was used in all the experiments.

Oxygen- or nitrogen-alkali treatment

The reaction solution (300 ml) contained NaOH (0.50 mol/l), FeCl$_3$ (0.36 mmol/l), one of the model compounds (1.0 mmol/l), and compound II (0 or 10 mmol/l). The solution was transferred into a Teflon-coated stainless steel vessel (Taiatsu Techno® Co., Tokyo, Japan), and O$_2$ or N$_2$ was pressurized to 1.1 MPa. The vessel was heated to 95 °C for 10 min, which was maintained for 360 min with stirring. Reaction time was defined as 0 when the temperature reached 95 °C.

FeCl$_3$ was added to stably produce AOS and overshadow effects of transition metal ions possibly present in the reaction system. FeCl$_3$ is commonly known as an oxidizing agent and can oxidize phenolic compounds. It was confirmed, however, that phenolic compound II is not oxidized at all by FeCl$_3$, when it was subjected to a nitrogen-alkali treatment under the conditions employed in this study where the pH was high.

Quantification of the model compounds

At prescribed times, a portion of the reaction solution (1.0 ml) was withdrawn for the quantification of the model compounds. It was acidified with acetic acid, and 1.0 ml of methanol containing an internal standard compound, 2,3-dichlorophenol, was added. After filtration, the resulting mixture was injected into HPLC (LC-10A, Shimadzu Co., Kyoto, Japan) equipped with an SPD-M10A detector (254 nm, Shimadzu Co.).

Conditions for HPLC analysis were as follows. Column: Luna 5 u C18(2) 100 A (150 mm × 4.6 mm, Phenomenex, Inc.). For the analysis of compound IV: oven temperature, 40 °C; flow rate, 1.0 ml/min; solvent system, CH$_3$OH/H$_2$O = 10/90 (v/v) for 10 min, gradient to 80/20 for 30 min and maintained for 5 min; total time, 45 min. For the analyses of compounds VI and VII: oven temperature, 40 °C; flow rate, 1.0 ml/min; solvent system, CH$_3$OH/H$_2$O = 25/75 (v/v) for 5 min, gradient to 60/40 for 20 min and maintained for 10 min; total time, 35 min.

Results and discussion

Significance of benzylic hydroxymethylene group in the reaction with AOS

Figure 2 shows the results obtained in our previous paper, where compound I was treated under the same conditions as those employed in this study [10]. The β-O-4 bond cleavage of compound I liberated compound III as a phenolic compound from the non-phenolic 3,5-difluorophenoxyl group of compound I. The degradation of compound I and liberation of compound III were observed even in the nitrogen-alkali treatment without the presence of compound II, which confirmed the progress of the general alkali-induced β-O-4 bond cleavage without any contribution of oxidation reactions. The mechanism of this cleavage should be the dissociation of the benzylic α-hydroxyl group and successive intramolecular S_N2 type attack of the generated α-alkoxide on the β-carbon. This type of cleavage is not expected to proceed with a detectable degree under the conditions employed in this study, when the common non-phenolic β-O-4 type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (VIII in Fig. 1), is used. The higher lability of the β-O-4 bond of compound I under alkaline conditions can be basically attributed to the fact that the leaving ability of the 3,5-difluorophenoxyl group of
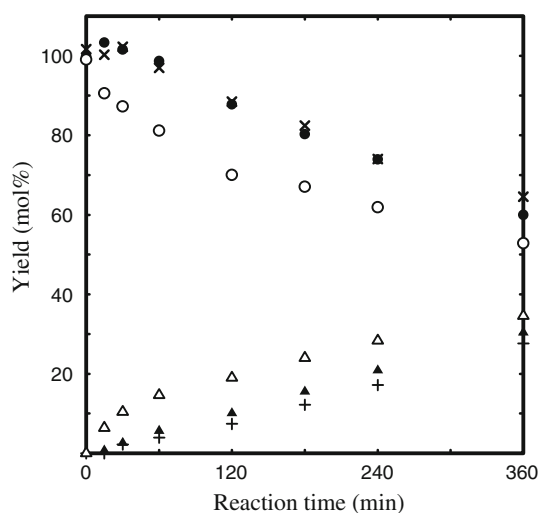
compound I is much higher than that of the 2-methoxyphenoxyl group of compound VIII.

When compound I was subjected to the oxygen-alkali treatment without the presence of compound II, the degradation of compound I and liberation of compound III were almost the same as those in the nitrogen-alkali treatment (Fig. 2). This result shows that only the alkali-induced β-O-4 bond cleavage without any contribution of oxidation reactions occurs even in the oxygen-alkali treatment when AOS are not operative. The degradation of compound I and liberation of compound III were enhanced when compound II was treated together (Fig. 2), which suggests that AOS generated from reactions between compound II and dioxygen attack the side-chain of compound I resulting in the β-O-4 bond cleavage and liberation of compound III. The side-chain of compound I rather than the non-phenolic aromatic 3,4-dimethoxyl aromatic nucleus should be attacked by the AOS, because it is known that compound V is rather stable under the conditions identical to those employed in this study even in the reaction together with compound II where AOS are operative [6].

Figure 3 shows the results obtained in the oxygen-alkali treatments of compound IV with and without the presence of compound II. The liberation of compound III was not observed in either case. Compound IV was not degraded in the absence of compound II, which indicates that the alkali-induced β-O-4 bond cleavage is completely suppressed and compound IV has the high resistance to the attack of dioxygen. It was also confirmed that the β-O-4 bond cleavage caused by the attack of the γ-alkoxide on the β-carbon, which is analogous to the general alkali-induced mechanism, does not occur under the conditions employed. Compound IV was expected to undergo the β-O-4 bond

Fig. 2 Change in the yields of compounds I and III when compound I was treated in the nitrogen- or oxygen-alkali treatment in the absence or presence of compound II, which was conducted in our previous paper [10]. The data points were the averages of the results obtained by two runs. ×●○ Compound I, +▲△ Compound III, ×+ N_2 in the absence of compound II, ●▲ O_2 in the absence of compound II, ○△ O_2 in the presence of compound II. Reaction conditions: 0.5 mol/l NaOH, 95 °C, 0.36 mmol/l FeCl₃, 1.0 mmol/l compound I (initial conc.), 10 mmol/l compound II (initial conc.), 1.1 MPa of N_2 and O_2
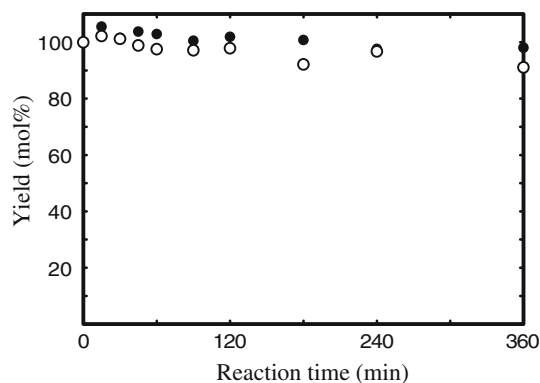
Fig. 3 Change in the yield of compound IV in the oxygen-alkali treatment in the absence or presence of compound II. ● O_2 in the absence of compound II, ○ O_2 in the presence of compound II. Reaction conditions: 0.5 mol/l NaOH, 95 °C, 0.36 mmol/l FeCl₃, 1.0 mmol/l compound IV (initial conc.), 10 mmol/l compound II (initial conc.), 1.1 MPa of O_2

cleavage via this γ-alkoxide mechanism more significantly than compound I, because the γ-alkoxide of compound I forms as the secondary in the molecule due to the higher acidity of the α-hydroxyl group while the primary anion generated in the alkaline solution is the γ-alkoxide for compound IV.

The presence of compound II resulted in the slight degradation of compound IV. Therefore, it can be stated that AOS generated from compound II slightly degraded compound IV. On the other hand, as shown in Fig. 2 the AOS degraded compound I more severely than compound IV. Furthermore, the degradation of compound IV caused by AOS was not accompanied by the liberation of compound III, while compound III was liberated with the degradation of compound I (Fig. 2). These results suggest that the presence of benzylic hydroxyl group is quite important in the reaction between side-chain of β-O-4 type lignin moiety and AOS under oxygen bleaching conditions and that an etherification of benzylic hydroxyl group makes the side-chain resistant to the attack of AOS. It is known that compound V, which has only the hydroxymethyl group as side-chain, is relatively stable under the conditions identical to those employed in this study even where AOS are operative [6]. This suggests the resistance of hydroxymethyl group on the attack of AOS. Based on these considerations, the significance of benzylic hydroxymethylene group is suggested in the extensive reaction of side-chain of β-O-4 type lignin moiety with AOS. The mechanism of the reaction between the side-chain and AOS should also be changed by the etherification.

It is generally considered that the hydrogen of a carbon–hydrogen bond is abstracted from a hydroxyl carbon by an AOS. On the basis of this consideration, it seems that etherification of a hydroxyl group does not largely influence the hydrogen abstraction reaction, and compound IV is degraded by AOS liberating compound III similarly to compound I. The above result is not in accordance with this consideration and possibly suggests that the hydrogen of a hydroxyl group is abstracted by AOS.

Reactivity of AOS toward different types of hydroxyl and aryloxyl carbon groups

It has been suggested, as described above, that presence of benzylic hydroxyl group is important in the reaction of side-chain of β-O-4 type lignin moiety with AOS under oxygen bleaching conditions. To further examine the effect of side-chain structure on the reaction with AOS, compound VI or VII was subjected to the nitrogen- or oxygen-alkali treatment with or without the presence of compound II. Compounds VI and VII do not have benzylic position owing to the lack of aryl group directly linked to the propyl chains. Compound VI consists of
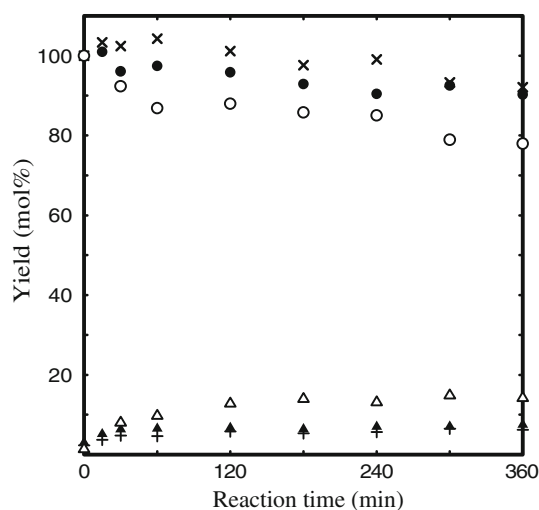

Fig. 4 Change in the yields of compounds VI and III when compound VI was treated in the nitrogen- or oxygen-alkali treatment in the absence or presence of compound II. The data points were the averages of the results obtained by two runs. ×●○ Compound VI, +▲△ Compound III, × + : N₂ in the absence of compound II, ●▲ O₂ in the absence of compound II, ○△ O₂ in the presence of compound II. Reaction conditions: 0.5 mol/l NaOH, 95 °C, 0.36 mmol/l FeCl₃, 1.0 mmol/l compound VI (initial conc.), 10 mmol/l compound II (initial conc.), 1.1 MPa of N₂ and O₂

hydroxymethyl and aryloxymethylene groups, while hydroxymethyl, hydroxymethylene, and aryloxymethyl groups constitute compound VII. It is considered that the comparison between the results obtained from these compounds can suggest the difference in the reactivity of AOS between these groups.

Figure 4 shows the degradation of compound VI and liberation of compound III in the nitrogen- or oxygen-alkali treatment with or without the presence of compound II. Compound III was liberated from compound VI in the nitrogen-alkali treatment, which suggests that the alkali-induced β-O-4 bond cleavage proceeds without any contribution of oxidation reactions. The amount of the degradation of compound VI was fairly smaller than that of compound I in their nitrogen-alkali treatments (Figs. 1, 4). This result should suggest that the acidity of the benzylic hydroxyl group in compound I is higher than that of the primary hydroxyl group in compound VI and consequently the β-O-4 bond cleavage of compound I proceeds more frequently than that of compound VI in the nitrogen-alkali treatment. The degradation of compound VI in the oxygen-alkali treatment without the presence of compound II seems to be slightly greater than that in the nitrogen-alkali treatment. The degradations of the other compounds in the nitrogen-alkali treatments were almost the same as those in the oxygen-alkali treatments in the absence of compound II. Compound VI would slightly be degraded by the action of dioxygen in spite of the absence of reaction site

on compound VI with dioxygen. However, this phenomenon cannot be rationally explained.

The difference in the amount of the degradation of model compound between the oxygen-alkali treatments with and without the presence of compound II should correspond to the amount of model compound degraded by AOS. Although this difference observed for compound VI or I was not constant during their reactions (Figs. 2, 4), the difference observed for compound VI seems to be smaller than that observed for compound I. This result suggests that the presence of the 3,4-dimethoxyphenyl aromatic ring slightly activates the side-chain in the reaction with AOS partly due to the presence of the benzylic position.

Figure 5 shows the degradation of compound VII and liberation of compound III in the nitrogen- or oxygen-alkali treatment with or without the presence of compound II. Although the degradation of compound VII was not clearly observed in the nitrogen-alkali treatment, the small amount of compound III was liberated. This result shows the slight occurrence of the general alkali-induced alkyl-aryl ether bond cleavage without any contribution of oxidation reactions. Compound VII underwent the general alkali-induced alkyl-aryl ether bond cleavage less extensively than compound VI, which suggests that the acidity of the secondary hydroxyl group in compound VII is lower than that of the primary hydroxyl group in compound VI. The degradation of compound VII in the oxygen-alkali treatment in the absence of compound II was not clearly observed from Fig. 5. The amount of liberated compound III from compound VII in the oxygen-alkali treatment in the absence of compound II seems to be similar to that in the nitrogen-alkali treatment (Fig. 5). Therefore, compound VII should be resistant to the action of dioxygen.

It should be pointed out that the difference in the amount of the degradation of compound VII between the oxygen-alkali treatments with and without the presence of compound II is fairly larger than that of compound VI. Although this result cannot clearly be related to the reactivity of AOS toward the different substructures between compounds VI and VII, there can be a possible interpretation. AOS attack hydroxymethylene group more preferentially than hydroxymethyl group, which was suggested in our previous study in the reaction of AOS with some alditols [12]. The reactivity of AOS toward the aryloxyl carbons cannot be clarified in this study.

Conclusion

Compound IV was almost inert in the reaction with AOS, although the benzylic methoxyl group had been expected to have only a small influence on the reaction with AOS on
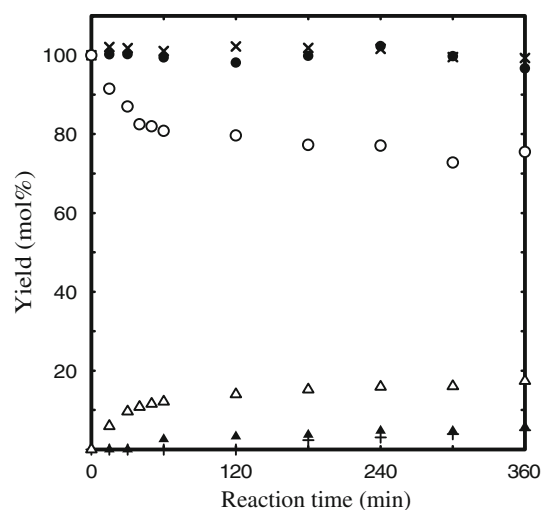

Fig. 5 Change in the yields of compounds VII and III when compound VII was treated in the nitrogen- or oxygen-alkali treatment in the absence or presence of compound II. The data points were the averages of the results obtained by two runs. $\times \bullet \circ$ Compound VII, $+ \blacktriangle \triangle$ Compound III, $\times +$ N_2 in the absence of compound II, $\bullet \blacktriangle$ O_2 in the absence of compound II, $\circ \triangle$ O_2 in the presence of compound II. Reaction conditions: 0.5 mol/l NaOH, 95 °C, 0.36 mmol/l $FeCl_3$, 1.0 mmol/l compound VII (initial conc.), 10 mmol/l compound II (initial conc.), 1.1 MPa of N_2 and O_2

the basis of the general mechanism for the hydrogen abstraction reaction by a radical species like AOS. The results obtained in this study combined with the previous information on the stability of compound V under the conditions identical to those employed in this study suggested the significance of benzylic hydroxymethylene group in the reaction of side-chain of β-O-4 type lignin portion with AOS.

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