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NOTE

Stereo-preference in the degradation of the *erythro* and *threo* isomers of *β*-*O*-4-type lignin model compounds in oxidation processes III: in the reaction with chlorine- and manganese-based oxidants

Pattaraporn Posoknistakul[1,2] · Satoru Akiho[1,3] · Takuya Akiyama[1] · Tomoya Yokoyama[1] · Yuji Matsumoto[1]

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Abstract

We examined which isomer, the *erythro* or *threo*, of a non-phenolic *β*-*O*-4-type lignin model compound is stereo-preferentially oxidized in hypochlorite, chlorite, manganese dioxide, or permanganate systems. No clear stereo-preference was observed in the hypochlorite or chlorite systems at alkaline, neutral, or acidic pH except for a slight *threo* stereo-preference that appeared after the step-wise addition of the oxidizing reagent had been terminated in the neutral or acidic chlorite systems. A clear *threo* stereo-preference was observed in the manganese dioxide or permanganate systems.

Keywords Chlorine dioxide · Chlorite · Hypochlorite · Manganese dioxide · Permanganate

Introduction

Because the *β*-*O*-4-type is the most abundant substructure in lignin, cleavage of the *β*-*O*-4 bond always controls the delignification and depolymerization of lignin in chemical processes. The diastereomeric *erythro* (***E***) and *threo* (***T***) isomers exist in the side chain of the *β*-*O*-4-type substructure (Fig. 1). These isomers show different reactivities in various chemical reactions. An example reaction is the *β*-*O*-4 bond cleavage under alkaline pulping conditions, where the *β*-*O*-4 bond of the ***E*** isomer cleaves more rapidly than that of the ***T*** isomer [1–6]. However, only a few papers have examined stereo-preferential degradation in oxidation processes [7–10]. Some of them reported stereo-preferential degradation of the ***T*** isomer [7, 8], while no clear stereo-preference was observed in the others [9, 10].

Our previous reports examined the stereo-preferential degradation of the ***E*** or ***T*** isomer, when each isomer of non-phenolic *β*-*O*-4-type lignin model compounds was individually oxidized by various radical species generated as active oxygen species under oxygen bleaching conditions [11] or by hydroxyl radical and/or its conjugate base, oxyl anion radical, under alkaline hydrogen peroxide bleaching conditions [12]. A slight stereo-preferential degradation of the ***T*** isomer was observed at a high pH (> 13). When the electric repulsion between the side chains of the lignin model compounds and a negatively charged active oxygen species, oxyl anion radical, working at high pH, was quenched by lowering the pH (< 13) or structurally modifying the lignin model compounds, a slight stereo-preferential degradation of the ***E*** isomer was observed. We concluded, therefore, that the essential stereo-preference of oxyl anion radical is slightly in favor of the ***E*** isomer although the reverse stereo-preference can appear depending on the reaction conditions.

In this paper, the stereo-preferential degradation of the ***E*** or ***T*** isomer was examined when each isomer of the most general non-phenolic *β*-*O*-4-type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (***1E*** or ***1T***, respectively, Fig. 1), was oxidized in hypochlorite, chlorite, manganese dioxide, or permanganate systems.

✉ Tomoya Yokoyama
yokoyama@woodchem.fp.a.u-tokyo.ac.jp

[1] 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

[2] Present Address: Department of Chemical Engineering, Faculty of Engineering, Mahidol University, 25/25 Phutthamonthon 4 Road, Salaya, Phutthamonthon, Nakhon Pathom 73170, Thailand

[3] Present Address: Tsukuba Research Center, Kuraray Co., Ltd., 41 Miyukigaoka, Tsukuba, Ibaraki 305-0841, Japan

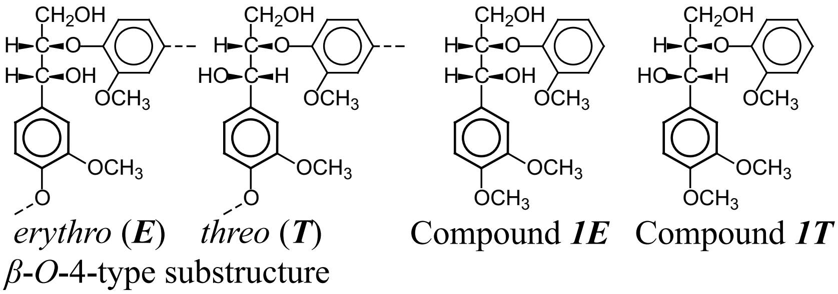

Fig. 1 Structures of the *β*-*O*-4-type lignin subunit, compound ***1E***, and compound ***1T***

Materials and methods

Materials

All chemicals except compounds ***1E*** and ***1T*** were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and Sigma-Aldrich Co. LLC. (St. Louis, MO, USA), and used without further purification. Ultrapure water (Puric-Z, Organo Co., Tokyo, Japan) was used in all the experiments.

The synthesis of compounds ***1E*** and ***1T*** and their separation were described in our previous reports [11–13]. The structures and purities were confirmed by nuclear magnetic resonance spectroscopy (^{1}H-NMR and ^{13}C-NMR, JNM-A500, JEOL Ltd., Tokyo, Japan). The spectral peaks were indicated in our previous report [11].

Oxidation in hypochlorite systems

Either compound ***1E*** or ***1T*** (30 μmol) or both (15 μmol each) were dissolved in 30 mL of water at an alkaline pH of 13.3, neutral pH of 6.3, or acidic pH of 1.0, adjusted by sodium hydroxide, no reagent, or sulfuric acid (H_2SO_4), respectively, in a round-bottom glass flask (50 mL volume). The flask was placed in a water bath and heated to 70 °C in the alkaline or neutral reaction, while the acidic reaction was conducted at room temperature. Sodium hypochlorite (NaClO, 0.30 mmol, 10 times mole amount of compound ***1E*** or ***1T***) was added to the reaction solution to initiate the reaction. The same amount of NaClO was added a total of five times at constant intervals of 10 min, so that the total amount of NaClO added was 1.5 mmol. The reactions were terminated at a reaction time of 60 min (20 min after the final NaClO addition).

A portion of the reaction solution was withdrawn at prescribed reaction times to quantify the surviving compound ***1E*** or ***1T*** and to measure the pH. The detailed workup procedures for quantification were the same as those described in our previous reports [11–13] except for neutralizing the acidic reaction solution with sodium hydrogen carbonate.

Oxidation in chlorite systems

The reaction was as described above for the NaClO oxidation except that: (1) sodium chlorite ($NaClO_2$) was employed instead of NaClO, maintaining the molar ratio to compound ***1E*** or ***1T***, and (2) the temperature was 70 °C for all reactions.

Oxidation in a manganese dioxide system

Commercially available manganese dioxide (MnO_2, Wako Pure Chemical Industries, Ltd.) was ground into powder on a mortar and iodometrically titrated, revealing that the oxidation power of the MnO_2 powder was 89% of the theoretical value. The MnO_2 powder (26 mg, 0.30 mmol) was aged in 25 mL of sulfate buffer solution (0.50 mol/L, pH 1.0) for 120 min in a round-bottom glass flask (50 mL) at room temperature. Either compound ***1E*** or ***1T*** (6.0 μmol) was dissolved in 5.0 mL of another sulfate buffer solution (0.50 mol/L, pH 1.0), and this buffer solution was added to the buffer solution containing the aged MnO_2 powder to initiate the reaction. The reaction was conducted at room temperature for 350 min. The initial concentration of compound ***1E*** or ***1T*** was 0.20 mmol/L, giving a molar ratio to the MnO_2 powder of 1/50.

A portion of the reaction solution was withdrawn to quantify the surviving compound ***1E*** or ***1T*** at prescribed reaction times. The withdrawn solution was immediately extracted with ethyl acetate (EtOAc) containing an internal standard compound, 3,4,5-trimethoxybenzaldehyde. The water layer was further immediately extracted twice with EtOAc. The combined EtOAc layer was washed with a saturated sodium hydrogen carbonate solution followed by brine, and concentrated under reduced pressure. An aqueous 50% methanol (CH_3OH) solution (v/v) was added to the residue and filtrated with a membrane filter. The obtained mixture was analyzed by a high-performance liquid chromatograph (HPLC, LC-10A, Shimadzu Co., Kyoto, Japan) equipped with an SPD-M10A detector (Shimadzu Co.), using the absorbance at 280 nm.

Conditions of HPLC were as follows. Column: Luna 5u C18 (2) 100A (150 mm × 4.6 mm, Phenomenex Inc., Torrance, CA, USA); oven temperature: 40 °C; flow rate: 0.2 mL/min; solvent system: gradient CH_3OH/H_2O (v/v) from 30/70 to 40/60 for 30 min and maintained for 15 min, total time 45 min.

Oxidation in permanganate systems

As an acidic reaction, either compound ***1E*** or ***1T*** was dissolved in 24.6 mL of sulfate buffer solution (0.50 mol/L, pH 2.0). To this buffer solution was added 0.40 mL of 20 mmol/L potassium permanganate ($KMnO_4$) solution to initiate the reaction. The reaction was conducted at room temperature. The initial concentrations of compound ***1E*** (or ***1T***) and $KMnO_4$ were 0.20 and 0.32 mmol/L, respectively.

As a neutral reaction, either compound ***1E*** or ***1T*** was dissolved in 23 mL of water (pH 6.3). To this solution was added 2.0 mL of 20 mmol/L $KMnO_4$ solution to initiate the reaction. The reaction was conducted at room temperature. The initial concentrations of compound ***1E*** (or ***1T***) and $KMnO_4$ were 0.20 and 1.6 mmol/L, respectively.

A portion of the reaction solution was withdrawn to quantify the surviving compound ***1E*** or ***1T*** at prescribed reaction times. The detailed workup procedures for quantification and conditions for the HPLC analysis were the same as described above for the MnO_2 system.

Results and discussion

Oxidation in hypochlorite systems

Figure 2a shows the degradation of compound ***1E*** or ***1T*** when either compound was individually (twice each) or both compounds were together (once) reacted at an alkaline pH of 13.3 and 70 °C. Any observed degradation was always less than 5% at the end of the reaction (60 min). No clear difference was observed in the degradations between compounds ***1E*** and ***1T***. An iodometric titration confirmed almost no consumption of the oxidation power at the end of the reaction. Because hypochlorite anion (ClO^-) rather than hypochlorous acid (HClO) existed as the major species due to the pK_a value of HClO (7.58 at 20 °C [14]), the result indicates that ClO^- is rather stable under the conditions and compounds ***1E*** and ***1T*** do not have any good reaction sites with ClO^-.

Figure 2b shows the degradation of compound ***1E*** or ***1T*** when either compound was individually (once each) or both compounds were together (once) reacted at a neutral pH of 6.3 and 70 °C. Any observed degradation was rapid, with complete disappearance at a reaction time of about 40 min. No clear difference was observed in the degradations between compounds ***1E*** and ***1T***. HClO rather than ClO^- existed as the major species due to the pK_a value. A possible reaction mechanism is nucleophilic attack of a nucleophile on the Cl atom of HClO, which is essentially the reaction of chlorine cation (Cl^+) with the nucleophile. The aromatic ring of compound ***1E*** or ***1T*** is a more plausible candidate for the nucleophile than the side chain portion. This would explain why no clear stereo-preference was observed in the reaction with compound ***1E*** or ***1T***, each of which has a stereo-structurally different side chain. Both compounds ***1E*** and ***1T*** were stable without the addition of NaClO under these conditions.

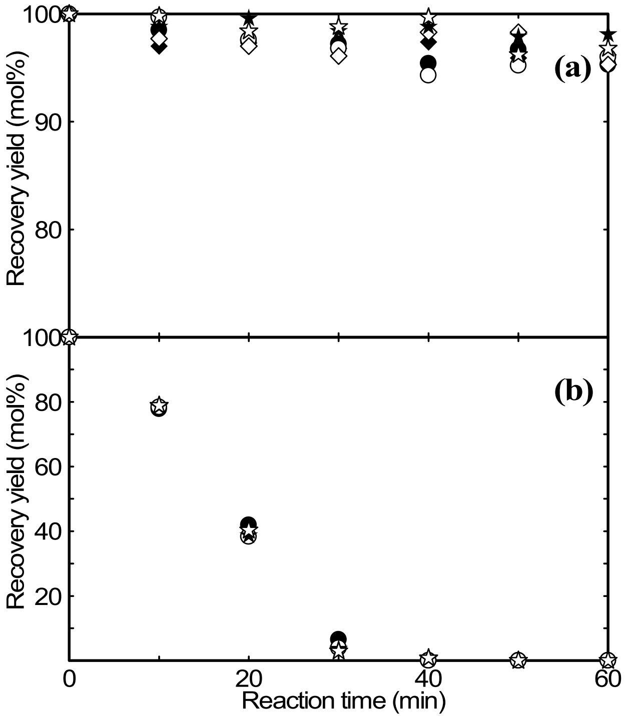

Fig. 2 Time courses of the changes in the recovery yields of compounds ***1E*** and ***1T***, when either compound was individually or both compounds were together treated in the hypochlorite system at a pH of: **a** 13.3 and 70 °C or **b** 6.3 and 70 °C. Compound ***1E***: filled circle, filled diamond, filled star; compound ***1T***: open circle, open diamond, open star; in the individual reaction of compound ***1E*** or ***1T***: filled circle, filled diamond, open circle, open diamond; in the reaction of both compounds ***1E*** and ***1T*** together: filled star, open star

Both compounds ***1E*** and ***1T*** were together reacted at an acidic pH of 1.0 and room temperature (twice). Because the degradation was quite rapid in a preliminary experiment, room temperature was employed (data not shown). The degradation was still fast, and the recovery yields were 6 and 3%, respectively, at the first sampling time (10 min). This result indicates that compounds ***1E*** and ***1T*** were efficiently oxidized. However, the difference was not large enough to safely state that compound ***1T*** was stereo-preferentially degraded rather than compound ***1E***. Generally, molecular chlorine (Cl_2) is generated when HClO reacts with hydrogen chloride (HCl) at a low pH. Because H_2SO_4 was used for the pH adjustment, little generation of Cl_2 took place. A nucleophilic attack of the aromatic ring to the Cl atom of HClO would be a possible major reaction, similar to the above-described reaction at the neutral pH. However, this attack would be more rapid than that at the neutral pH due to the protonation of HClO at the acidic pH (H_2O^+Cl) and consequent increase of the electrophilicity of the Cl atom. This would result in the efficient oxidation of compounds ***1E*** and ***1T*** and a lack of stereo-preferential degradation. Both compounds ***1E*** and ***1T*** were rather stable without the addition of NaClO under these conditions.

Oxidation in chlorite systems

Figure 3a shows the degradation of compound ***1E*** or ***1T*** when either compound was individually (once each) or both compounds were together (once) reacted at an alkaline pH of 13.3 and 70 °C. Any observed degradation was less than 5% at the end of the reaction. No clear difference was observed in the degradations between compounds ***1E*** and ***1T***. An iodometric titration confirmed almost no consumption of the oxidation power at the end of the reaction. Because chlorite anion (ClO_2^-) rather than chlorous acid ($HClO_2$) existed as the major species due to the pK_a value (1.94 at 25 °C [15]), the result indicates that ClO_2^- is rather stable under these conditions and compounds ***1E*** and ***1T*** do not have any good reaction sites with ClO_2^-.

Figure 3b shows the degradation of compound ***1E*** or ***1T*** when either compound was individually reacted at a neutral pH of 6.3 and 70 °C (thrice each). The degradation was relatively rapid until a reaction time of about 40 min and accelerated during this period. (This period is hereafter described as ‘the period of rapid degradation’.) After the final addition of $NaClO_2$ at a reaction time of 40 min, slower but continuous degradation was observed until the reaction was terminated at a reaction time of 60 min (‘the period of slower degradation’). No clear difference was observed in the degradations between compounds ***1E*** and ***1T*** in the period of rapid degradation, while a difference gradually appeared with slight stereo-preferential degradation of compound ***1T*** in the period of slower degradation. It is generally considered that chlorine dioxide (ClO_2) is generated by the disproportionation of ClO_2^- or other similar reactions as the most active species, although other chlorine-related oxidants are also produced. On the basis of the obtained results, we suggest that ClO_2 as well as other chlorine-related oxidants attacks compound ***1E*** or ***1T*** without any clear stereo-preference in the period of rapid degradation and the formation of ClO_2 as well as other chlorine-related oxidants from ClO_2^- (rather than from $HClO_2$ due to the pK_a value) accelerates with the progress of the reaction. Because the major oxidant ClO_2 is a radical and preferably adds to aromatic nucleus of an aromatic substrate including lignin model compounds as an electrophile accompanied by the liberation of ClO_2^- or $HClO_2$ (depending on pH) and generation of an aromatic radical cation [16–19], it is natural that no clear stereo-preference was observed in the period of rapid degradation. It is unclear, on the other hand, why the slight ***T*** stereo-preference was observed in the period of slower degradation. Some oxidants generated from ClO_2^-, ClO_2, and others would still exist in the period of slower degradation, and show the slight ***T*** stereo-preference. Both compounds ***1E*** and ***1T*** were stable without the addition of $NaClO_2$ under these conditions.

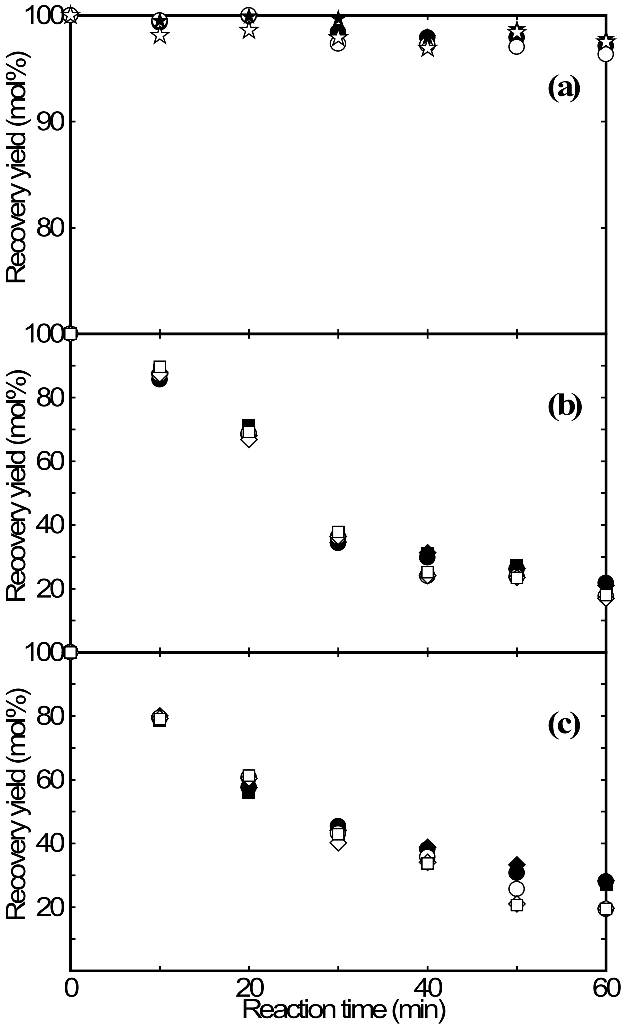

Fig. 3 Time courses of the changes in the recovery yields of compounds ***1E*** and ***1T***, when either compound was individually or both compounds were together treated in the chlorite system at a pH of: **a** 13.3 and 70 °C, **b** 6.3 and 70 °C, or **c** 1.0 and 70 °C. Compound ***1E***: filled circle, filled diamond, filled square, filled star; compound ***1T***: open circle, open diamond, open square, open star; in the individual reaction of compound ***1E*** or ***1T***: filled circle, filled diamond, filled square, open circle, open diamond, open square; in the reaction of both compounds ***1E*** and ***1T*** together: filled star, open star

Figure 3c shows the degradation of compound ***1E*** or ***1T*** when either compound was individually reacted at an acidic pH of 1.0 and 70 °C (thrice each). Although the degradation of each compound was similar to that observed at the neutral pH, the following observations were different from those at the neutral pH. (1) The degradation was slightly slower than that at the neutral pH, and acceleration of the degradation was not observed in the period of rapid degradation. (2) The degradation of compound ***1T*** was slightly greater than that at the neutral pH in the period of slower degradation, and the difference in the degradations between compounds ***1E*** and ***1T*** was larger than that at the neutral pH. Observation (1) may indicate that the generation of ClO_2 does not exactly follow the same mechanism as that at the neutral pH. $HClO_2$ was the main species rather than ClO_2^- at the acidic pH due to the pK_a value, which might result in different formation mechanisms of ClO_2 from that at the neutral pH. Observation (2) suggests that the profile of oxidants responsible for the degradation of compound ***1E*** or ***1T*** was not exactly the same as that at the neutral pH. In accordance with the expectation on the basis of the description in the previous paragraph, no clear stereo-preference was observed in the period of rapid degradation. Both compounds ***1E*** and ***1T*** were rather stable without the addition of $NaClO_2$ under these conditions.

Oxidation in a manganese dioxide system

Figure 4 shows the degradation of compound ***1E*** or ***1T*** when either compound was individually reacted at a pH of 1.0 and room temperature (thrice each). The degradation of compound ***1T*** was clearly more rapid than that of compound ***1E***, which indicates that the stereo-preference of MnO_2 is the ***T*** isomer. Because MnO_2 oxidized compound ***1E*** or ***1T*** as large precipitating aggregates, it can be understood that the stereo-structure of the side chain affects the reaction rate. It is presumed that MnO_2 aggregates are able to approach compound ***1T*** more easily than compound ***1E*** due to the stereo-structure of the side chain. The obtained results, however, are not sufficient to rule out the possibility that the stereo-preference of MnO_2 observed here is dependent on a particular structure of the aggregates and that other MnO_2 aggregates prepared by other methods show the reverse or almost no stereo-preference.

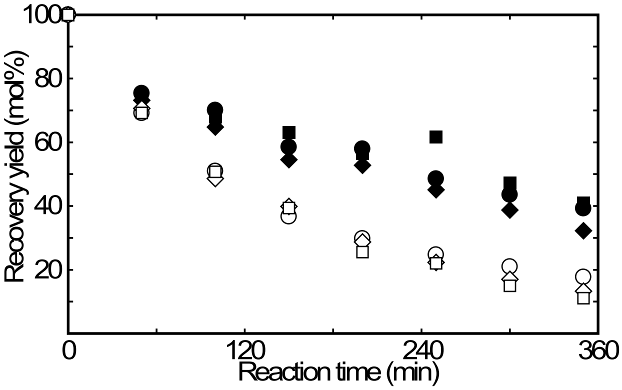

Fig. 4 Time course of the change in the recovery yield of compound ***1E*** or ***1T***, when either compound was individually treated in the manganese dioxide system at a pH of 1.0 and room temperature. Compound ***1E***: filled circle, filled diamond, filled square; compound ***1T***: open circle, open diamond, open square

Oxidation in permanganate systems

Figure 5a, b shows the degradation of compound ***1E*** or ***1T*** when either compound was individually reacted at a pH of 2.0 or 6.3, respectively, and room temperature. Because the degradation was too rapid to follow at a pH of 1.0 using a large excess of $KMnO_4$ in a preliminary experiment, the applied pH was 2.0 and the molar ratio of $KMnO_4$ to compound ***1E*** or ***1T*** was 1.6 in the acidic system. The molar ratio of $KMnO_4$ to compound ***1E*** or ***1T*** was 8.0 at a pH of 6.3.

The degradation of compound ***1T*** was clearly greater than that of compound ***1E*** at a pH of 2.0. It is possible to assume that MnO_2 was generated as an intermediate at this pH and

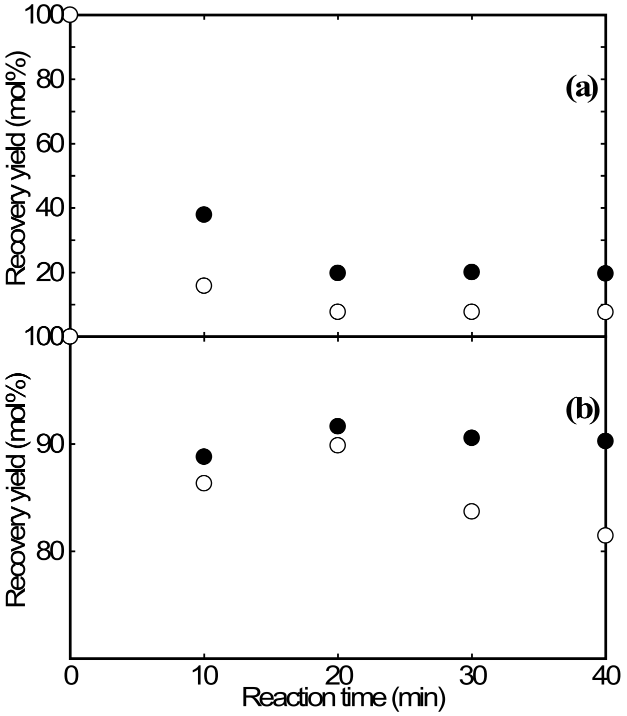

Fig. 5 Time course of the change in the recovery yield of compound ***1E*** or ***1T***, when either compound was individually treated in the permanganate system at a pH of: **a** 2.0 and room temperature or **b** 6.3 and room temperature. Compound ***1E***: filled circle; compound ***1T***: open square

co-oxidized compound ***1E*** or ***1T***, although the half-reaction of permanganate (MnO_4^-) in an acidic medium is described as: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. Because the MnO_2 oxidation of compound ***1E*** or ***1T*** was confirmed to be much slower than the observed oxidation rate at the pH, the observed ***T*** stereo-preference is concluded to be due to the reaction of MnO_4^- at the pH without the effect of MnO_2. Because the oxidation system was homogeneous differently from that of MnO_2 and it is commonly believed that the oxidation mechanism of MnO_4^- is the attack on an electron rich double bond, aromatic nucleus, etc., the effect of the stereo-structure of the side chain on the MnO_4^- oxidation cannot easily be explained. The large size of MnO_4^- may possibly relate to the ***T*** stereo-preference, resulting in the side chain of compound ***1T*** being more ready than that of compound ***1E*** to interact with MnO_4^-.

The degradation of compound ***1T*** was also greater than that of compound ***1E*** at a pH of 6.3, although the degradation was not great. The half-reaction of MnO_4^- in a neutral medium is described as: $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$, which explains the observed slow oxidation at this pH due to the requirement for H^+. Because the degradation of compound ***1E*** or ***1T*** was not great and was observed only at an early stage of the reaction in spite of the application of 8 times mole amount of $KMnO_4$, some degradation products might have been oxidized by MnO_4^- more easily than compound ***1E*** or ***1T***. The ***T*** stereo-preference is not easily explainable, either.

Conclusions

The *erythro* (***E***) or *threo* (***T***) isomer of the most common non-phenolic *β*-*O*-4-type lignin model compound was individually or both isomers together oxidized in hypochlorite, chlorite, manganese dioxide, or permanganate systems to examine which isomer was stereo-preferentially oxidized. No stereo-preference was observed in any hypochlorite or chlorite system at any applied pH except in the later stage of the chlorite system at neutral or acidic pH, where the stereo-preferential degradation of the ***T*** isomer was observed in this later stage. Stereo-preferential degradation of the ***T*** isomer was also observed in the manganese dioxide and permanganate systems. These stereo-preferences cannot easily be explained, although some of them may possibly result from the ease of approach of the oxidant to the ***T*** isomer rather than to the ***E*** isomer.

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