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RAPID COMMUNICATION

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Reaction selectivity of active oxygen species produced by oxygen-alkali oxidation of a phenolic compound

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In an oxygen bleaching process, the degradation of carbohydrate is not directly caused by molecular oxygen but by active oxygen species that are secondary reaction products of lignin and molecular oxygen.[1,2] In addition to the degradation of carbohydrate, active oxygen species are thought to play a role in delignification during oxygen bleaching. Ek and her coworkers concluded that hydroxyl radical (HO·) degrades nonphenolic lignin model compounds five to six times faster than carbohydrate model compounds.[3] Their results seem to have been widely accepted as the reaction selectivity of active oxygen species between lignin and carbohydrate during oxygen bleaching. However, it is inappropriate to generalize their results because active oxygen species produced during an oxygen bleaching process cannot be restricted to the hydroxyl radical, and the structural variety of the model compounds examined in their report is not enough to draw a general conclusion.

In the present report, active oxygen species were generated by the reaction of 2,4,6-trimethylphenol (TMPh) with molecular oxygen in the presence of ferric ion.[1,2] By this reaction, substrates can be subjected to the reaction with a variety of active oxygen species generated in a manner similar to that of an oxygen bleaching process. This reaction system contained TMPh 9 mmol/l, $FeCl_3$ 0.36 mmol/l, and NaOH 0.5 mol/l in 300 ml ultra-pure water. The reaction temperature and oxygen pressure were 95°C and 1.1 MPa, respectively. By subjecting a nonphenolic lignin model compound and a carbohydrate model compound together to this reaction mixture, the reaction selectivity between these two model compounds with active oxygen species can be obtained.

When veratryl alcohol (VA), a nonphenolic lignin model compound at 4 mmol/l, and methyl β-D-glucopyranoside (MGP), a carbohydrate model compound at 4 mmol/l, were subjected to this reaction system, MGP disappeared faster than VA (Fig. 1). Apparently, the conclusion obtained by Ek et al. is not applicable to these compounds. They used veratrylglycol as one of the nonphenolic lignin model compounds and MGP as one of the carbohydrate model compounds. The discrepancy in the results suggested that not only the aromatic part but also the side-chain structure, especially the number and nature of hydroxyl groups, affect the reactivity of lignin.

The effect of hydroxyl groups was demonstrated by conducting the reaction of various alditols in this reaction system. The alditols chosen here had different numbers and different proportions of hydroxyl methyl and hydroxyl methylene groups as hydroxyl groups. A reaction of an equimolar mixture (4 mmol/l each) of different alditols indicated that the alditols with more hydroxyl methylene groups reacted faster (Table 1). This result does not necessarily mean that hydroxyl methylene groups reacted faster than hydroxyl methyl groups because a large molecule with more hydroxyl groups would be more easily attacked than a small one. To obtain more direct information about the relative reactivity of hydroxyl methyl and hydroxyl methylene groups, a reaction was studied by adjusting the amount of alditol so that each alditol has an equal number of hydroxyl groups in the reaction mixture. The degradation rate of each alditol in this system could be converted to the reaction rate of hydroxyl groups of the alditol by dividing the initial degradation rate by the number of hydroxyl groups in the alditol. This protocol was based on the assumption that the initial degradation of alditols was caused by a reaction of one hydroxyl group. As shown in Table 2,

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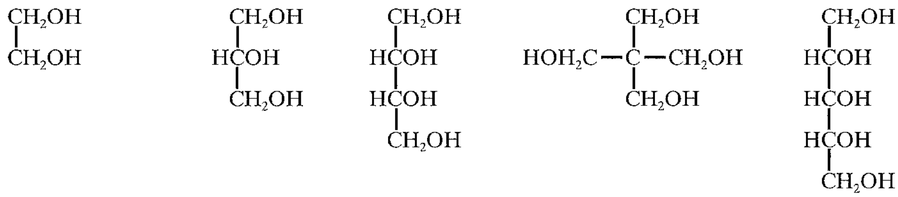
Table 1. Effects of the position and number of hydroxyl groups on the recovery of model compounds

Model compound	Recovery (%)
Ethylene glycol	100
Glycerol	75
Erythritol	40
Pentaerythritol	90
Ribitol	15

Ethylene glycol Glycerol Erythritol Pentaerythritol Ribitol



Recoveries were determined when all of the 2,4,6-trimethylphenol (TMPh) was degraded. Initial concentrations of all sugar model compounds and TMPh are 4 and 9 mmol/l, respectively

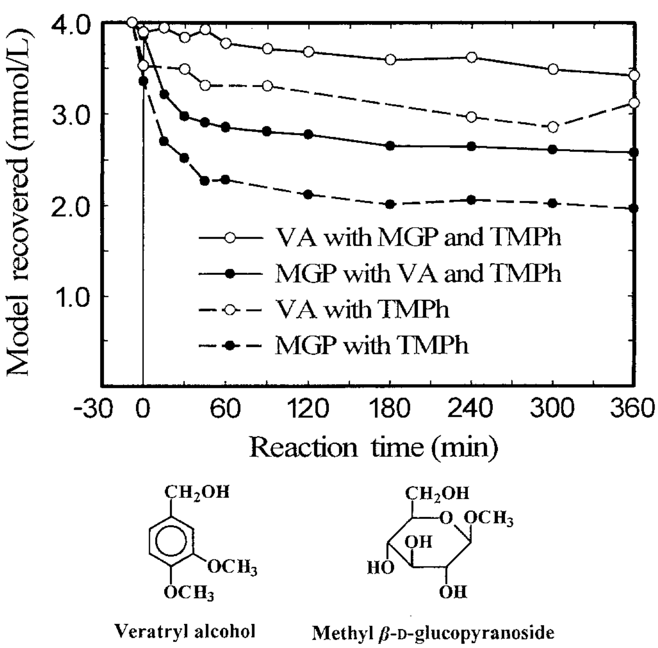


Fig. 1. Degradation of veratryl alcohol (*VA*) and methyl-β-D-glucopyranoside (*MGP*) by active oxygen species. Active oxygen species were produced by the reaction of 2,4,6-trimethylphenol (TMPh) and oxygen in the presence of $FeCl_3$. Initial concentration of TMPh is 9 mmol/l

the presence of hydroxyl methylene groups greatly affects the reactivity of the molecule.

The results obtained in this experiment clearly indicate that the hydroxyl methylene group is much more reactive than the hydroxyl methyl group in an oxidation reaction under an oxygen bleaching condition. Therefore, the nature and number of hydroxyl groups in a molecule are important factors that govern the reactivity of the molecule during oxygen bleaching.

Table 2. Reaction rate of hydroxyl groups of each alditol in the early stage of reaction

Model compound[a]	Reaction rate ($\mu eq \cdot l^{-1} \cdot min^{-1}$)
Ethylene glycol	0
Glycerol	35
Erythritol	70
Pentaerythritol	10
Ribitol	100

[a]Initial concentrations of ethylene glycol, glycerol, erythritol, pentaerythritol, ribitol, and TMPh are 8, 5.33, 4, 4, 3.2 and 9 mmol/l, respectively

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