Detailed Examination of the Degradation of Phenol Derivatives under Oxygen Delignification Conditions

Tomoya Yokoyama,* Yuji Matsumoto, and Gyosuke Meshitsuka[†]

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

Several phenolic compounds were subjected to oxygen-alkali oxidations under oxygen delignification conditions, and their degradations were examined in detail by applying a novel formula. The formula was established on the basis of the two following considerations. The degradation of the phenolic compounds should be expressed by the sum of two types, each of which is caused by molecular oxygen and by highly reactive active oxygen species (HAOS). The degradation should be described by a mathematical equation to which a rate function, $k(t)$, dependent on reaction time t, is applied instead of a rate constant. By rearrangements, the following formula was obtained: $k(t) = A/(t + B)$ (A, B are constants). This is hyperbola, and the illustration of $k(t)$ visualized the contribution of HAOS to the degradation of the phenolic compounds. HAOS did not contribute so much to the degradation, especially at 70 °C, which suggests the low energy supply for the HAOS generation at 70 °C. The extrapolation of $k(t)$ to the beginning of the reaction gives its initial value, k(initial), which is the rate constant of the reaction between the phenolic compounds and molecular oxygen. As expected, k(initial) was dependent on the electronic property of their substituents. Quantification of the phenolic compounds degraded by HAOS showed that the contribution of HAOS to the degradation is not great. The maximum contribution was observed in the oxidation of 2,6-dimethylphenol at 85 °C. In this case, 5 and 95% of the compound were degraded by HAOS and molecular oxygen, respectively.

KEYWORDS: Active oxygen species; bleaching; lignin; oxygen delignification; phenol

INTRODUCTION

It is now a global interest that there will be a shortage of paper supply in the near future due to the huge expansion of paper demands in China, India, and other countries. The pulp and paper industry is now undertaking many projects to overcome this serious problem. These projects include, for example, the intensive management of fast-growing plantation forests, the development of non-wood-based materials for papermaking, and the improvement of present mill equipment to produce pulp and paper more efficiently. We are now focusing our attention on the improvement of the pulp production efficiency.

Chemical pulp for papermaking is produced by multiple steps to remove lignin from wood chip. Kraft pulping is the first step, which removes >90% of lignin, followed by oxygen delignification. The latter degrades and dissolves about half of the residual lignin in unbleached kraft pulp. Finally, oxygen-delignified kraft pulp is bleached in multiple stages, which are currently in accordance with an elemental chlorine free (ECF) bleaching sequence generally consisting of chlorine dioxide, alkaline extraction, and hydrogen peroxide stages. Among these steps, the oxygen delignification process should be the most probable candidate for improved efficiency.

The lignin macromolecule consists of C_6-C_3 phenylpropane units. Some of the units have phenolic hydroxyl groups, which are the main reaction sites of molecular oxygen among pulp constituents in the oxygen delignification process. The reactions between these units and molecular oxygen produce active oxygen species (AOS). The thermal and/or transition metal catalyzed decomposition of peroxides, a kind of AOS, generates highly reactive AOS such as the hydroxyl radical (HO•), although these AOS may be produced through other routes (*1*–*5*). The highly reactive AOS attack carbohydrates and cause their depolymerization, which is a serious problem in the oxygen delignification process (*1*, *2*). The AOS initiate chain-type reactions in carbohydrates, so that intermediates of these reactions are also AOS (*6*). The AOS attack nonphenolic lignin units, which are resistant to molecular oxygen and, hence, also contribute to delignification (*6*–*8*). Carbohydrates, except their reducing end groups, are stable under oxygen delignification conditions when AOS are not produced in the system (*2*). Therefore, it is how AOS are generated and react under the conditions that should be focused on. Because phenolic lignin units are origins of AOS and also degraded by AOS, it is very

* Author to whom correspondence should be addressed (telephone +81-3-5841-5264; fax +81-3-5802-8862; e-mail yokoyama@woodchem.fp.a.u-tokyo.ac.jp).
† Present address: Department of Clothing Science and Fine Arts, Faculty of Home Economics, Tokyo-Kasei University, 1-18-1 Kaga, Itabashi-ku, Tokyo 173-8602, Japan.
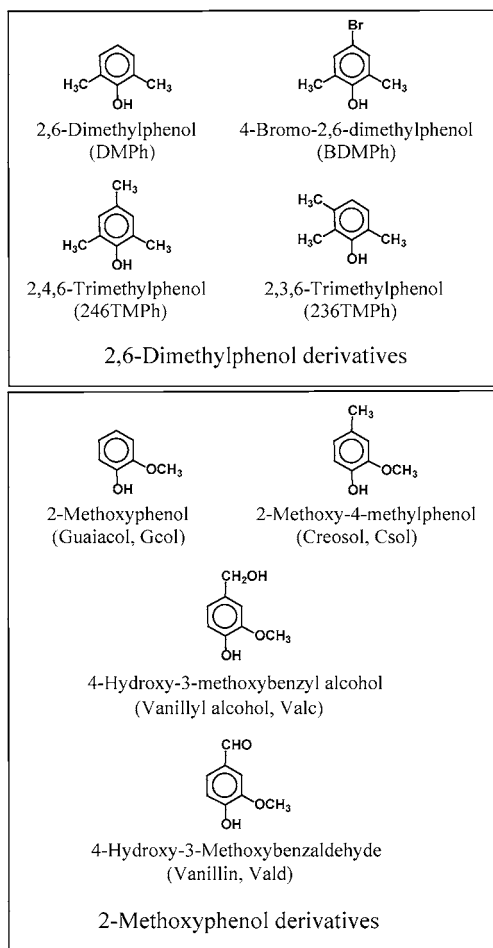
Figure 1. Chemical structures of the phenolic compounds used in this study.

important to examine the degradation of the units in detail under the conditions concerned.

The degradation of phenol derivatives in oxygen oxidation has been examined well in the field of wet air oxidation, which is an effective method for the destruction of hazardous organic wastes (*9−14*). However, the reaction conditions employed are very different from those in oxygen delignification. The temperature and pressure are much higher, and the solution pH is near neutral, whereas it is >12 in the initial stage of oxygen delignification.

In this paper, the degradation of several phenol derivatives was examined in detail under oxygen delignification conditions. Because phenol derivatives should be degraded both by molecular oxygen and by AOS as mentioned above, the effort was devoted to differentiating the degradation caused by each species.

MATERIALS AND METHODS

Materials. The chemical structures of the phenolic compounds used in this study are illustrated in **Figure 1**. These compounds are categorized into two series, 2,6-dimethylphenol and 2-methoxyphenol derivatives. Although the compounds in the former category are not appropriate as representatives of lignin, various types of phenolic compounds should be examined to deepen the knowledge, and the information obtained from the analyses of their degradations should be very helpful to further our understanding of the reactions of lignin under oxygen delignification conditions.

All of the phenolic compounds were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and recrystallized from ethanol or

an ethanol/hexane mixture before use except Gcol and Csol. These compounds were vacuum distilled before use. Semiconductor grade sodium hydroxide and iron(III) chloride anhydrous were purchased from Sigma-Aldrich Co. (St. Louis, MO) and used without further purification. Ultrahigh-purity water produced by a reverse osmosis filtration (Puric-Z, Organo Co., Tokyo, Japan) was used in all of the experiments.

Oxygen-Alkali Treatment of Phenols. A typical reaction solution contained NaOH (0.5 mol/L), $FeCl_3$ (0.36 mmol/L), and one of the phenolic compounds (9 mmol/L). The total volume of the solution was 300 mL. The solution was transferred into a Teflon-coated stainless steal autoclave, and oxygen was pressurized to 1.1 MPa. The vessel was electrically heated to 70, 85, or 95 °C in 8 min, and then the temperature was maintained for 360 min with stirring. Reaction time 0 was defined just as temperature reached the target degree. $FeCl_3$ was added in all of the runs to overshadow the effects of other metals possibly present in trace amounts.

Determination of Residual Phenols. A small portion of the solution (1 mL) was periodically withdrawn for the determination of the residual compound. The solution withdrawn was acidified with acetic acid after the addition of an internal standard (2,4,6-tri-*tert*-butylphenol) methanol solution and extracted with diethyl ether three times. The ether layers were collected, dried over sodium sulfate anhydrous, and directly injected to a gas chromatography (GC).

GC analyses were performed on a GC-17A instrument (Shimadzu Co., Kyoto, Japan) equipped with a flame ionization detector using helium as a carrier gas. The temperatures of the injector and detector were 200 and 220 °C, respectively. Separations were achieved on a capillary column of NB-1 (30 m × 0.25 mm, film thickness = 0.25 μm, GL Sciences Inc., Tokyo, Japan). The temperature program was from 100 to 200 °C at a rate of 4.0 °C/min with the initial time delay of 5 min.

RESULTS AND DISCUSSION

Characteristics of the Phenol Degradation under Oxygen Delignification Conditions. As mentioned in the Introduction, oxygen oxidation of phenols has been studied well in the field of wet air oxidation. In this process, the temperature and pressure are generally much higher than those in oxygen delignification and the pH is around neutral. The degradation of phenolic compounds shows an induction period in the initial phase followed by a rapid degradation (*9−14*). The addition of hydrogen peroxide to the system thoroughly shortens the induction period (*12*). These phenomena suggest that a sufficient amount of AOS is accumulated in the induction period to cause the subsequent rapid degradation. The presence of the induction period should be attributed to a relative resistance of phenolic compounds to oxygen oxidation under pH conditions at which phenolic hydroxyl groups are not dissociated (generally pH <10).

Contrarily, the induction period is not observed and the degradation of phenolic compounds is very fast from the beginning under oxygen delignification conditions (see Materials and Methods for detailed conditions) (*12*, *14*). This is because phenolate anions react with molecular oxygen much more rapidly than undissociated phenols. The degradation of phenolic compounds has been reported to follow the pseudo-first-order rate law under oxygen delignification conditions (*15−19*). However, because AOS should actually be produced and degrade phenolic compounds even under these conditions and this fact has been proved in the previous papers (*2*, *4−6*, *8*), the effort was devoted to visualize the action of AOS in this paper.

Fitting of the Phenol Degradation to an Empirical Rate Equation. To mathematically express the degradation of the phenolic compounds under oxygen delignification conditions, the experimental data points observed for each phenolic

Examination of Phenol Degradation in Oxygen Delignification

J. Agric. Food Chem., Vol. 55, No. 4, 2007 **1303**
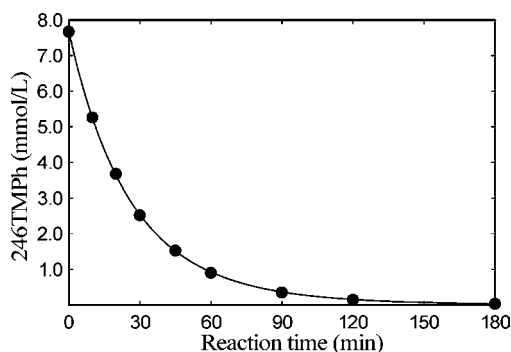
Figure 2. Representative comparison between the experimental data points (●) and the line obtained by the simulation (—) in the degradation of 246TMPh at 70 °C.

Table 1. Constants *k*, *n*, *A*, and *B* Obtained

temp (°C)	compound	*k*	*n*	*A*	*B*
70	246TMPh	0.0325	1.086	11.6	300
	236TMPh	0.0634	0.947	−18.9	−332
	DMPh	0.0210	0.846	−6.5	−419
	BDMPh	0.0118	0.965	−28.6	−2604
	Csol	0.0548	0.929	−14.1	−294
	Gcol	0.0087	1.035	28.6	3044
	Valc	0.0145	0.907	−10.6	−898
85	246TMPh	0.1010	0.972	−35.7	−373
	236TMPh	0.2280	0.763	−4.2	−28
	DMPh	0.0980	0.776	−4.5	−72
	BDMPh	0.0383	0.920	−12.5	−389
	Csol	0.1930	0.664	−3.0	−28
	Gcol	0.0290	1.025	40.0	1308
	Valc	0.0582	0.896	−9.6	−206
95	246TMPh	0.1680	0.939	−16.4	−109
	236TMPh	0.3310	0.889	−9.0	−32
	DMPh	0.1820	0.726	−3.7	−34
	BDMPh	0.0969	0.868	−7.6	−104
	Csol	0.2590	0.876	−8.1	−38
	Gcol	0.0651	0.943	−17.5	−302
	Valc	0.1290	0.868	−7.6	−79

compound were fitted to an empirical rate eq I without any other considerations in the same manner as reported in the previous paper (*2*).

$$-d[\text{phenol}]/dt = k[\text{phenol}]^n \quad \text{(I)}$$

k is a rate constant, *n* is the reaction order, and [phenol] is the concentration of a phenolic compound.

In **Figure 2**, the experimental data points of the 246TMPh degradation at 70 °C are compared with the line described by the simulation using the corresponding constants *k* and *n* obtained from the curve fitting of the 246TMPh degradation at 70 °C. As can be seen, the line is well in accordance with the experimental data points in the whole range of the reaction. The good relationship between these two factors is valid not only for 246TMPh at 70 °C but also for all of the others at any temperature employed. **Table 1** lists the constants *k* and *n* obtained. Most of the *n* values observed are smaller than 1, although some are very close to or larger than 1, especially at 70 °C.

Reaction Order *n* Observed in Equation I. In this section, we discuss which chemical species degrade the phenolic compounds in this system and how such species influence the reaction order *n* observed. Molecular oxygen is most responsible

for the degradation of the phenolic compounds. As mentioned in the Introduction, some AOS have high reactivities and can directly attack and degrade the compounds. These highly reactive AOS are now abbreviated as HAOS. There seem to be several other possible routes for the degradation of the compounds. The condensation between the quinonemethide-type structure produced from Valc and Valc itself is an instance. Reactions between peroxides produced in the system and the quinonemethide from Valc as well as Vald are other instances. The other phenolic compounds except Valc and Vald must be free from these reactions. However, the reaction conditions in this system, relatively lower temperature and concentration of the compounds and alkali, must significantly reduce the occurrence of these possible reactions. Furthermore, this reduction is reinforced by the fact that the amount of stable peroxides in a similar system is small (*4*). Only these stable peroxides can exist for long periods to react with the quininemethide from Valc and Vald. Concerning Vald, it is very stable under the conditions employed, so that almost no reaction occurs and nothing has to be taken into consideration. Consequently, it should be reasonable to conclude that the phenolic compounds are degraded by molecular oxygen and HAOS in this reaction system.

On the basis of this conclusion, a general kinetic equation (eq II) can be described for the degradation of the phenolic compounds. There are possibly many kinds of HAOS, each of which is named $HAOS_1$, $HAOS_2$, ..., $HAOS_n$, ...

$$-d[\text{phenol}]/dt = k_1[\text{phenol}][O_2] + k_2[\text{phenol}][HAOS_1] + k_3[\text{phenol}][HAOS_2] + ... + k_{n+1}[\text{phenol}][HAOS_n] + ... \quad \text{(II)}$$

$$= (k_1[O_2] + k_2[HAOS_1] + ... + k_{n+1}[HAOS_n] + ...)[\text{phenol}] \quad \text{(III)}$$

k_1, k_2, ..., k_n, ... are rate constants and $[HAOS_n]$ is the concentration of $HAOS_n$ at reaction time *t*.

In eq II, the degradation rate is shown by the sum of each rate caused by molecular oxygen and each HAOS. Formula II is rearranged to formula III, and the following formula (eq IV) is obtained when formula III is compared with eq I.

$$k[\text{phenol}]^{n-1} = k_1[O_2] + k_2[HAOS_1] + ... + k_{n+1}[HAOS_n] + ... \quad \text{(IV)}$$

As mentioned in the previous section, most of the *n* values observed are smaller than 1. In this case, the left term of formula IV increases with the progress of the reaction, so that the right term must also become greater. Because the concentration of molecular oxygen can be considered to be constant during the reaction, the concentration of HAOS has to be higher with the progress of the reaction. Therefore, a reaction order *n* observed that is smaller than unity expresses the phenomenon that the concentration of HAOS becomes higher with the progress of the reaction. Because it does not seem that the concentration of HAOS is constant during the reaction, the reaction order 1 observed suggests that almost no HAOS are produced in these cases. This clarifies that the contribution of HAOS becomes greater with the progress of the reaction when the reaction order *n* observed is smaller than 1 and that the smaller the reaction order *n* observed, the more HAOS contribute to the degradation of the phenolic compounds.

On the basis of this consideration, HAOS seem not to contribute to the degradation of the phenolic compounds at 70 °C, because most of the *n* values obtained are close to or larger

1304 *J. Agric. Food Chem.,* Vol. 55, No. 4, 2007

Yokoyama et al.

than 1. It is anticipated that the amount of HAOS generated is small because the energy supply is not large enough for the generation of HAOS at 70 °C. The contribution of HAOS to the degradation of the compounds also seems to depend on the number and/or kind of functional group located at the aromatic ring. However, there can be no reasonable explanation for this observation.

Although only molecular oxygen and HAOS must contribute to the degradation of the phenolic compounds in this study, the method of this analysis can be applied to any reaction system, such as those in which the condensation of the quinonemethide-type structure from Valc and Valc itself and reactions between peroxides and the quinonemethide from Valc take the major contribution. These systems are attained when the initial concentration of the phenolic compounds is very high and the reaction conditions are more severe. The reaction order *n* observed would be larger than 1 in these systems, because formula IV is now described as formula V.

$$k[\text{phenol}]^{n-1} = k_1[\text{O}_2] + k_2[\text{HAOS}_1] + \dots + \\ k_{n+1}[\text{HAOS}_n] + \dots + k_m[\text{QValc}] + \\ k_{m+1}([\text{QValc}]/[\text{phenol}])[\text{peroxide}_1] + \dots + \\ k_{m+i}([\text{QValc}]/[\text{phenol}])[\text{peroxide}_i] + \dots \quad (\text{V})$$

k_m, k_{m+1}, ..., k_{m+i}, ... are rate constants, [QValc] is the concentration of the quinonemethide-type structure from Valc at reaction time *t*, and [peroxide$_i$] is the concentration of peroxide$_i$ at reaction time *t*. In this formula, [phenol] can be substituted for [Valc].

The right-hand term becomes smaller with the progress of the reaction, because [QValc] and [peroxde$_i$] should vary to the lower and the contribution of HAOS to the degradation of the compounds is now of minor importance. The term [QValc]/[phenol] is constant when the equilibrium is attained during the reaction.

In this study, the empirical formula I was used to analyze the degradation of the phenolic compounds, although the eq II type should be applied to a general kinetic analysis. This is because it has not been proven yet what kind of and how much HAOS participate in the degradation of the phenolic compounds under oxygen delignification conditions.

Visualization of the HAOS Contribution to the Phenol Degradation. As already mentioned, HAOS can directly attack and degrade the phenolic compounds due to their high reactivity. Another rate equation, formula VI, can be established to express the degradation of the phenolic compounds on the basis of the fact that the compounds are degraded both by molecular oxygen and by HAOS. The concentration of molecular oxygen can be constant during the reaction.

$$-\text{d}[\text{phenol}]/\text{d}t = k'[\text{phenol}] + k'(t)[\text{phenol}]\Sigma[\text{HAOS}_n] = \\ (k' + k'(t)\Sigma[\text{HAOS}_n])[\text{phenol}] \quad (\text{VI})$$

$k' = k_1[\text{O}_2]$ is a constant, $k'(t)$ is a rate function, and $\Sigma[\text{HAOS}_n]$ is the total concentration of all the HAOS at reaction time *t*. The former term, $k'[\text{phenol}]$, expresses the rate of the degradation caused by molecular oxygen, whereas the latter, $k'(t)$-[phenol]$\Sigma[\text{HAOS}_n]$, represents that brought about by HAOS. Because the number and kind of HAOS operating in the system vary with reaction time *t*, not a rate constant but a rate function, $k'(t)$, has to be applied to this term. By the application of $k'(t)$, this term expresses the rate of the degradation caused by all of the HAOS at reaction time *t*.
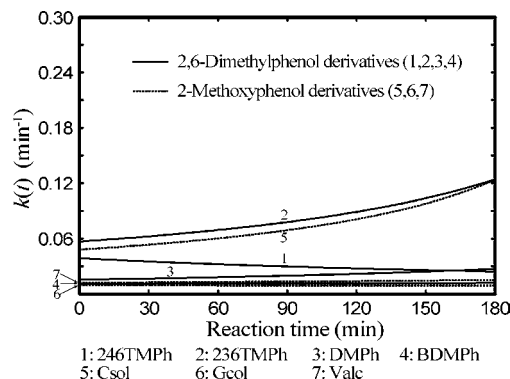
Figure 3. Dependence of the rate function, $k(t)$, on reaction time at 70 °C.

The term $k_1 + k'(t)\Sigma[\text{HAOS}_n]$ in eq VI can be substituted for another rate function, $k(t)$, and described by eq VII as shown below

$$-\text{d}[\text{phenol}]/\text{d}t = (k_1 + k'(t)\Sigma[\text{HAOS}_n])[\text{phenol}] = \\ k(t)[\text{phenol}] \quad (\text{VII})$$

where $k(t) = k_1 + k'(t)\Sigma[\text{HAOS}_n]$. Gersman and Bickel confirmed that the pseudo-first-order rate constant of some phenolic compounds in an autoxidation process becomes larger with the progress of the reaction (*20*). This phenomenon means that the rate constants they applied should actually be substituted for rate functions, which are dependent on reaction time. This observation reinforces the validity of establishing eq VII to which a rate function, $k(t)$, is applied instead of a rate constant.

In this reaction system, only molecular oxygen and HAOS directly attack and degrade the phenolic compounds. However, formula VII is valid not only for this system but also for any system such as those in which the major contributions are taken by the condensation between the quinonemethide-type structure from Valc and Valc and by reactions between peroxides and the quinonemethide from Valc. In these systems, the consideration applied to the establishment of formula V can be utilized.

Now, the degradation rate of the phenolic compounds is expressed by two equations, I and VII. By solving the differential eq I and substituting the answer for eq VII, $k(t)$ can be described by two constants, *k* and *n*, and the variable, *t*, which is shown below.

$$k(t) = k/\{(1 - n)(-kt + C)\} \quad (\text{VIII})$$

C is an integral constant. Formula VIII is represented by formula IX using the constants *A* and *B*

$$k(t) = A/(t + B) \quad (\text{IX})$$

where $A = 1/(n - 1)$ and $B = -C/k$. The rate function, $k(t)$, is plotted against reaction time *t* in **Figures 3−5**. The values of *A* and *B* obtained are listed in **Table 1**. The contribution of HAOS to the degradation of the phenolic compounds is visualized in **Figures 3−5**. Most of the lines drawn in **Figures 3−5** are hyperbolas, and the time, $t = -B$, for each compound is its asymptote. At time $t = -B$, the corresponding phenolic compound disappears from the reaction solution. This time can be calculated, because the reaction order *n* obtained by the curve fitting is smaller than 1. A compound for which degradation follows the pseudo-first-order rate law does not theoretically disappear from the system even at a prolonged reaction time. The positive values of the constant *B* obtained in some cases
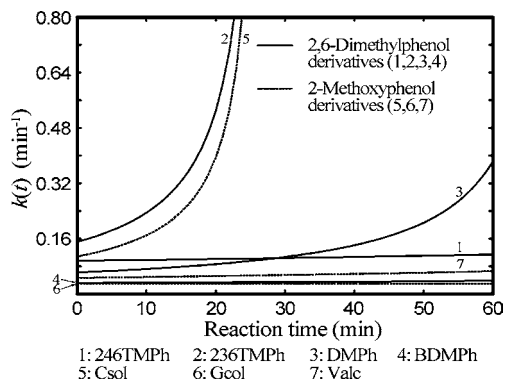
Examination of Phenol Degradation in Oxygen Delignification

J. Agric. Food Chem., Vol. 55, No. 4, 2007   **1305**

Figure 4. Dependence of the rate function, $k(t)$, on reaction time at 85 °C.
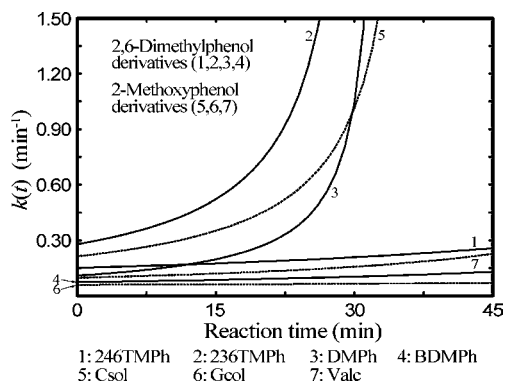
Figure 5. Dependence of the rate function, $k(t)$, on reaction time at 95 °C.

Table 2. k(initial)[a] Obtained

compound	70 °C	85 °C	95 °C
246TMPh	0.0393	0.0950	0.147
236TMPh	0.0564	0.135	0.259
DMPh	0.0150	0.0599	0.0997
BDMPh	0.0109	0.0321	0.0725
Csol	0.0469	0.0922	0.197
Gcol	0.00938	0.0306	0.0574
Valc	0.0118	0.0463	0.0965
Vald	ND[b]	ND	>0

[a] Unit: min^{-1}. [b] ND, not determined.

Table 3. Arrhenius Frequency Factor and Activation Energy for the Reaction between Phenolic Compounds and Molecular Oxygen

compound	frequency factor (min^{-1})	activation energy ($kJ\ mol^{-1}$)
246TMPh	1.28×10^7	55.9
236TMPh	2.67×10^8	63.6
DMPh	3.35×10^{10}	81.0
BDMPh	1.15×10^{10}	79.0
Csol	4.19×10^7	59.0
Gcol	4.25×10^9	76.5
Valc	3.88×10^{11}	88.7

result from the fact that the corresponding reaction order n is larger than 1, which is not rational as the value of n in this reaction system. However, these values are just a little bit larger than 1, which must be within experimental errors. Therefore, in these cases, the n can be regarded as 1, and the extent of the experimental error can be estimated from the positive values.

The order of the magnitude of the reaction order n in the series of the 2-methoxyphenol derivatives is Csol ≤ Valc < Gcol, which indicates that the contribution of HAOS to their degradations is most significant in the Csol system. This result seems to have a correlation with their degradation rates and is understandable because large amounts of HAOS resources are formed within a short period. The order in the series of the 2,6-dimethylphenol derivatives is DMPh ≤ 236TMPh < BDMPh < 246TMPh. No clear explanation can be given for this result. The absence of a functional group at the para position of the phenolic hydroxyl group might be a key factor for the efficient production of HAOS.

Examination of the Reaction between Phenols and Molecular Oxygen. Another important parameter obtained from formula IX is k(initial), which is the value of $k(t)$ at the beginning of the reaction. The value of k(initial) shows the rate constant of the reaction between the phenolic compounds and molecular oxygen, because no HAOS are present at the beginning of the reaction. By the analysis of k(initial), the effect of the functional groups of the compounds on their reactions with molecular oxygen can be examined without any influence of HAOS.

In this study, reaction time 0 was defined just as the temperature reached the targeted degree. Therefore, the reaction time $t = 0$ is not the actual initial point of the reaction. The initial time can be estimated by extrapolating the simulated degradation curve, such as those shown in **Figure 2**, to the time

when the concentration of the corresponding phenolic compound is 9 mmol/L.

Table 2 lists k(initial) values obtained by the extrapolation and subsequent calculation of formula IX. When a methyl group, an electron-donating functional group, is substituted, k(initial) is large, whereas the presence of bromide, an electron-withdrawing substituent, makes it small. This result confirms that the rate of the reaction between the phenolic compounds and molecular oxygen is dependent on the electronic property of the functional groups. When the k(initial) of DMPh is compared with that of Gcol, the former is much larger than the latter. On the other hand, the k(initial) of 246TMPh, the *p*-methyl-substituted derivative of DMPh, is smaller than that of Csol, the *p*-methyl-substituted derivative of Gcol. These phenomena suggest that the electronic effect of the methoxyl group located at the ortho position of phenolic hydroxyl group on the aromatic π-electron system is synergistic with other substituents. The methoxyl group in Csol may increase the electron density more effectively than that in Gcol due to the presence of the methyl group in Csol. At all of the temperatures employed, the k(initial) of 236TMPh is larger than that of 246TMPh. This result indicates that the methyl group located at the meta position of the phenolic hydroxyl group raises the electron density of the aromatic π-electron system more effectively than that located at the para position. This is reasonably explained by the fact that the orientation of the electronic effect of the methyl substituent at the meta position of the phenolic hydroxyl group is consistent with that of the phenolic hydroxyl group, and, in this case, both groups increase the electron density of the same carbons in the aromatic ring.

Table 3 lists the Arrhenius frequency factors and activation energies in the reaction between the phenolic compounds and molecular oxygen. There is no clear explanation for the effect of functional group on the constants.

Quantification of Phenols Degraded by HAOS. At time $t = -B$, the phenolic compounds are predicted to disappear from the solution because the lines $t = -B$ are the asymptotes. Therefore, if it is possible to calculate the amount of the phenolic

1306 *J. Agric. Food Chem.*, Vol. 55, No. 4, 2007

Yokoyama et al.

Table 4. Amount (Percent) of Phenolic Compounds Degraded by HAOS

compound	70 °C	85 °C	95 °C
246TMPh	0	~0	~0
236TMPh	~0[a]	1.5	>0
DMPh	0.2	1.2	2.6
BDMPh	~0	~0	>0
Csol	~0	5.1	>0
Gcol	0	0	~0
Valc	~0	>0[b]	>0

[a] Less than 0.001%. [b] Less than 0.1% as well as equal to or more than 0.001%.

compounds that has been degraded by molecular oxygen since the beginning until time $t = -B$, the compounds degraded by HAOS can be quantified. Because the solution of the differential equation $-d[\text{phenol}]/dt = k(\text{initial})[\text{phenol}]$ shows the degradation behavior of the corresponding phenolic compound when the compound is degraded only by molecular oxygen, the residual concentration at the reaction time $t = -B$ calculated from this equation indicates the amount of the compound degraded by HAOS. **Table 4** lists the percentage of each phenolic compound that has been degraded by HAOS since the beginning until reaction time $t = -B$.

When Csol was treated at 85 °C, 5 and 95% of the compound were degraded by HAOS and molecular oxygen, respectively, at the corresponding reaction time, $t = -B$. This contribution of HAOS to the degradation of Csol is greatest among all of the cases examined. It can be concluded that HAOS do not significantly contribute to the degradation of the phenolic compounds under the conditions employed. This result suggests that the amount of HAOS generated is small. However, this suggestion does not necessarily mean that the amount of AOS generated is small. The following phenomenon can be speculated as an example. Some AOS, which can become HAOS under conditions other than those in this system, cannot attack the phenolic compounds due to their negative charges, causing the electronic repulsions between the AOS and the compounds even though the AOS potentially have the ability to act like HAOS. The superoxide anion radical would be a representative of the AOS. The oxyl anion radical ($O^{\bullet-}$) might be applied to the AOS. It is confirmed by the results obtained here and in the previous paper (6) that the contribution of HAOS to the degradation of 246TMPh shown in **Table 4** is much smaller than that to the degradation of a carbohydrate model compound, methyl β-D-glucopyranoside (MGP), when MGP and 246TMPh were subjected to the identical oxygen-alkali treatment. The amount of MGP degraded was about 10% of the initial amount of 246TMPh at the corresponding reaction time, $t = -B$, even though the initial concentration of MGP was lower (4 mmol/L). Because almost no HAOS contribution to the degradation of 246TMPh was observed in this study (**Table 4**), it is suggested that considerable amounts of AOS, which potentially have abilities to directly attack and degrade a neutral compound, MGP, were produced in this reaction system. The AOS would be quenched from the solution by reacting not with the phenolic compounds but with other AOS. In practical oxygen delignification processes, unbleached kraft pulp consists of residual lignin and carbohydrates. Therefore, the contribution of HAOS to the degradation of the pulp constituents in the process would be more significant than that estimated from the results shown in **Table 4**.

ABBREVIATIONS USED

AOS, active oxygen species; HAOS, highly reactive active oxygen species; DMPh, 2,6-dimethylphenol; BDMPh, 4-bromo-2,6-dimethylphenol; 246TMPh, 2,4,6-trimethylphenol; 236TMPh, 2,3,6-trimethylphenol; Gcol, guaiacol (2-methoxyphenol); Csol, creosol (2-methoxy-4-methylphenol); Valc, vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol); Vald, vanillin (4-hydroxy-3-methoxybenzaldehyde).

LITERATURE CITED

(1) Ericsson, B.; Lindgren, B. O.; Theander, O. Factors influencing the carbohydrate degradation under oxygen-alkali bleaching. *Svensk Papperstidn.* **1971**, *74*, 757−765.

(2) Yokoyama, T.; Matsumoto, Y.; Yasumoto, M.; Meshitsuka, G. The role of peroxide species in carbohydrate degradation during oxygen bleaching II: effect of oxygen pressure on the degradation of lignin and carbohydrate model compounds and on the reaction selectivity. *J. Pulp Pap. Sci.* **1996**, *22*, J151−J154.

(3) Gierer, J.; Imsgard, F.; Theander, O. The reaction of lignins with oxygen and hydrogen peroxide in alkaline media. *Svensk Papperstidn.* **1977**, *80*, 510−518.

(4) Yokoyama, T.; Matsumoto, Y.; Meshitsuka, G. The role of peroxide species in carbohydrate degradation during oxygen bleaching III: effect of metal ions on the reaction selectivity between lignin and carbohydrate model compounds. *J. Pulp Pap. Sci.* **1999**, *25*, 42−46.

(5) Yokoyama, T.; Matsumoto, Y.; Meshitsuka, G. Enhancement of the reaction between pulp components and hydroxyl radical produced by the decomposition of hydrogen peroxide under alkaline conditions. *J. Wood Sci.* **2002**, *48*, 191−196.

(6) Yokoyama, T.; Matsumoto, Y.; Meshitsuka, G. Characterization of active oxygen species under oxygen-alkali bleaching conditions. *Holzforschung* **2005**, *59*, 269−275.

(7) Gierer, J.; Jansbo, K.; Reitberger, T. Formation of hydroxyl radicals from hydrogen peroxide and their effect on bleaching of mechanical pulps. *J. Wood Chem. Technol.* **1993**, *13*, 561−581.

(8) Yokoyama, T.; Matsumoto, Y.; Meshitsuka, G. Reaction selectivity of active oxygen species in oxygen-alkali bleaching. *J. Wood Chem. Technol.* **1999**, *19*, 187−203.

(9) Yang, H. H.; Eckert, C. A. Homogeneous catalysis in the oxidation of *p*-chlorophenol in supercritical water. *Ind. Eng. Chem. Res.* **1988**, *27*, 2009−2014.

(10) Pintar, A.; Levec, J. Catalytic liquid-phase oxidation of refractory organics in waster water. *Chem. Eng. Sci.* **1992**, *47*, 2395−2400.

(11) Portela Miguelez, J. R.; Lopez Bernal, J.; Nobot Sanz, E.; Martinez de la Ossa, E. Kinetics of wet air oxidation of phenol. *Chem. Eng. J.* **1997**, *67*, 115−121.

(12) Rivas, F. J.; Kolaczkowski, S. T.; Beltran, F. J.; McLurgh, D. B. Development of a model for the wet air oxidation of phenol based on a free radical mechanism. *Chem. Eng. Sci.* **1998**, *53*, 2575−2586.

(13) Vicente, J.; Rosal, R.; Diaz, M. Noncatalytic oxidation of phenol in aqueous solutions. *Ind. Eng. Chem. Res.* **2002**, *41*, 46−51.

(14) Alvarez, P. M.; McLurgh, D.; Plucinski, P. Copper oxide mounted on activated carbon as catalyst for wet air oxidation of aqueous phenol part 1: kinetic and mechanistic approaches. *Ind. Eng. Chem. Res.* **2002**, *41*, 2147−2152.

(15) Ljunggren, S. Kinetic aspects in some lignin reactions in oxygen bleaching. *J. Pulp Pap. Sci.* **1986**, *12*, J54−J57.

(16) Ljunggren, S. The kinetic of lignin reactions during oxygen bleaching part 1: the reactivity of *p,p'*-dihydroxystilbene. *Nord. Pulp Pap. Res. J.* **1990**, *5*, 38−43.

(17) Ljunggren, S.; Johansson, E. The kinetic of lignin reactions during oxygen bleaching part 2: the reactivity of 4,4'-dihydroxy-3,3'-dimethoxystilbene. *Nord. Pulp Pap. Res. J.* **1990**, *5*, 148−154.

(18) Ljunggren, S.; Johansson, E. The kinetic of lignin reactions during oxygen bleaching part 3: the reactivity of 4-_n_-propylguaiacol and 4,4′-di-_n_-propyl-6,6′-biguaiacol. _Holzforschung_ **1990**, _44_, 291−296.

(19) Johansson, E.; Ljunggren, S. The kinetic of lignin reactions during oxygen bleaching part 4: the reactivities of different lignin model compounds and the influence of metal ions on the rate of degradation. _J. Wood Chem. Technol._ **1994**, _14_, 507−525.

(20) Gersmann, H. R.; Bickel, A. F. Autoxidation of hindered phenols in alkaline media part 2. _J. Chem. Soc._ **1962**, _1962_, 2356−2360.