Kinetics of Mono- and Dimethoxy-substituted Benzyl Alcohol Oxidation by Phthalamido-N-oxyl Radical

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Kinetics of mono and dimethoxy-substituted benzyl alcohols oxidation by electrogogenerated phthalamido-N-oxyl radical were investigated using rotating disk electrode voltammetry. The kinetic data arranged in a Hammett correlation indicated the validity of the peculiar reactivity of veratryl alcohol.

Key Words: N-hydroxyphthalimide, Benzyl Alcohol, Nitroxy Radical, Hammett Rule

1 Introduction

Methoxy-substituted benzyl alcohols (MSBs) are known to secondary metabolites of hydrophobic lignin polymer which has three-dimensional irregular structure, and such secondary metabolites work as efficient natural electron mediators during oxidative decomposition by the enzyme. From the viewpoint of the production of renewable resource, it has been noted that the electrochemical activation of MSB combined with mediators and/or enzymes will be an important technology as a model reaction. Especially, veratryl alcohol (VA, 3,4-dimethoxybenzyl alcohol) is a typical representative compound of the non-phenolic lignin monomer, and is also the standard substrate for the enzyme, lignin peroxidase. On the other hand, the nitroxide compounds are well known as an electron-transfer mediator to the catalytic oxidation of aromatic alcohols.

Recently we have shown that electrogogenerated phthalamido-N-oxyl radical (PINO-) works as an effective mediator to aromatic alcohols oxidation, and rotating disk electrode voltammetry under steady-state condition is useful technique to obtain kinetic data of the oxidation process. In this study, we will report the kinetics of mono- and dimethoxy-substituted benzyl alcohols oxidation by PINO radical, and attempt to elucidate of the peculiar reactivity of VA compare to other MSBs from the standpoint of the substituent effect using a Hammett correlation.

2 Experimental

N-Hydroxyphthalimide (NHP, Wako Pure Chemical), 2-methoxybenzyl alcohol (2MB, Aldrich Chemical), 3-methoxybenzyl alcohol (3MB, Aldrich), p-anisyl alcohol (4-methoxybenzyl alcohol, AA, Aldrich), veratryl alcohol (3,4-dimethoxybenzyl alcohol, VA, Aldrich), 2,3-dimethoxybenzyl alcohol (23DMB, Aldrich), 2,4-dimethoxybenzyl alcohol (24DMB, Tokyo Kasei Kogyo), 3,5-dimethoxybenzyl alcohol (35DMB, Aldrich), benzyl alcohol (BA, Wako) and lutidine (Wako) as a base were reagent grade and used without further purification. Acetonitrile (α-pure grade, 0.004% H₂O, Wako) and tetraethylammonium perchlorate (TEAP, Wako) were used as the solvent and the supporting electrolyte.

Electrochemical apparatus and the experimental procedures are the same as those described previously. The measurements were performed using the conventional three-electrode cell configuration. A glassy carbon (GC, Grade GC-20SS, Tokai Carbon Co. Ltd., Japan) disk electrode (1 mm diameter), a Pt wire and an Ag⁺/Ag (0.01 mol dm⁻³ (M) AgNO₃ in acetonitrile) electrode were the working, auxiliary and reference electrodes. The electrode potential was controlled by a potentiostat (HA-151, Hokuto Denko Co., Ltd., Japan) and a function generator (HB-111, Hokuto Denko), and the current-potential curves were recorded on an X-Y recorder (D72BP, Riken Denshi Co., Ltd., Japan). For steady-state voltammetry, the working electrode was rotating using a controller (HR-101A, Hokuto Denko). All experiments were carried out at room temperature (25 ± 1°C).

3 Results and Discussion

The electrooxidation of NHP in the presence of a base was confirmed as a one-electron transfer process to PINO-, which was substantiated by the ESR measurement, and electrogogenerated PINO- can oxidize MSBs into corresponding aldehydes. Figure 1 shows the typical steady-state current-potential curves for the oxidation of MSB by NHP at a GC rotating disk electrode (RDE). We can observe the kinetic limiting current. Under steady-state condition using an RDE, if the condi-
Fig. 1 Typical steady-state current-potential curves for the oxidation of 30 mM VA by 5 mM NHPI in 0.1 M TEAP/CH₂CN solution containing 10 mM lutidine at GC electrodes. The rotation rates were (1) 200 and (2) 1800 rpm.

![Graph](image1)

Fig. 2 Relationship between $I_{\text{cat}}/I_{\text{ Lev}}$ vs. (rotation rate, $\omega$)$^{-1/2}$ for the oxidation of 30 mM VA by 5 mM NHPI in 0.1 M TEAP/CH₂CN solution containing 10 mM lutidine at GC electrodes.

![Graph](image2)

Fig. 3 Relationship between $\log(k/k_0)$ vs. $\sigma$ for the oxidation of MBAs by NHPI.

![Graph](image3)

Table 1 Kinetic data for the catalytic oxidation of dimethoxy benzylalcohols by NHPI.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^{-1}k_0$/M$^{-1}$s$^{-1}$</th>
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<tbody>
<tr>
<td>VA (34 DMB)</td>
<td>35.0 ± 2.1</td>
</tr>
<tr>
<td>24 DMB</td>
<td>22.0 ± 2.0</td>
</tr>
<tr>
<td>35 DMB</td>
<td>14.5 ± 2.0</td>
</tr>
<tr>
<td>23 DMB</td>
<td>9.0 ± 2.0</td>
</tr>
</tbody>
</table>

Table 2 Kinetic data for the catalytic oxidation of monomethoxy benzylalcohols by NHPI.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^{-1}k_0$/M$^{-1}$s$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>AA (4 MB)</td>
<td>18.0 ± 2.0</td>
</tr>
<tr>
<td>2 MB</td>
<td>15.0 ± 2.0</td>
</tr>
<tr>
<td>3 MB</td>
<td>10.0 ± 2.0</td>
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</table>

The reactivity in order to correlate the reactivity with the structure of the MSBs, we attempted to resort to the determination of the Hammett correlation, where the electronic effects of the substituents on the kinetic data become apparent. Figure 3 shows $\log(k/k_0)$ vs. $\sigma$ plot, where $k$ and $k_0$ in $\log(k/k_0)$ are rate constants of 3- or/and 4-methoxy substituted and unsubstituted benzyl alcohols ($k_i = 70$ M$^{-1}$ s$^{-1}$), respectively. Rate constants except for those of 24DMB and 23DMB are normalized using the above $k_i$ value. The slopes which have negative values in Fig. 3 correspond to Hammett $p$ parameter, confirming that the reaction is promoted in the presence of the electron-donating substituent, $-OCH_3$. The $\log(k/k_0)$ values for 24DMB and 23DMB, which were derived by dividing the $k_i$ values for 2MB ($k_i = 150$ M$^{-1}$ s$^{-1}$), suggests that the presence of methoxy group in 2-position of dimethoxy benzylalcohols lowers the reactivity.

We can conclude that the peculiar reactivity of VA is due to the presence of two-methoxy moieties as electron-donating groups and further one of them is located on 4-position of the aromatic ring.

References
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