SELECTIVE ELECTROCATALYTIC OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS MEDIATED BY DECAHYDROQUINOLINYL-N-OXYL RADICAL

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Abstract — (±)-cis,cis-4-Benzyloxy-2,2,8a-trimethyldecahydroquinolinyl-N-oxyl reveals a reversible redox peak whose oxidation potential is at +0.67 V vs. Ag/AgCl. The compound catalyzed the selective oxidation reactions of primary and secondary alcohols to aldehydes and ketones, respectively, in high current efficiency (86.4-92.7%) and selectivity (100%).

Oxidation of alcohols using metallic or nonmetallic catalysts is currently under a practical operation. However, use of even a catalytic amount of hazardous metallic reagents is a matter of economic and environmental concern. Oxoammonium ions as nonmetallic oxidizing reagents are available easily from the corresponding nitroxyl radicals by one-electron oxidation on the electrode. Numerous studies have demonstrated the ability of nitroxyl radicals to mediate alcohol oxidation by electrolysis, apparently via the oxoammonium ion. A considerable body of these works have used 2,2,6,6-tetramethylpiperidinyl-N-oxyl (TEMPO) derivatives. We have also reported the electrocatalytic oxidation of benzyl alcohol and 1-phenylethyl alcohol on decahydroquinolinyl-N-oxyl radical. To examine the wide applicability of this type of catalyst to the electrocatalytic oxidation of many different kinds of alcohols, we report here the electrocatalytic behavior of (±)-cis,cis-4-benzyloxy-2,2,8a-trimethyldecahydroquinolinyl-N-oxyl (1) in the electro-oxidation reactions of different types of primary and secondary alcohols.

The cyclic voltammetry of 1 was carried out in an acetonitrile solution containing 0.1 M NaClO₄ as a supporting electrolyte. As shown in Figure 1, 1 shows a symmetrical reversible redox wave in the cyclic voltammogram. This redox wave corresponds to the one-electron oxidation of 1 to oxoammonium ion. This nitroxyl radical was quite stable during the repeated potential scan. The oxidation potential of 1 was found at +0.67 V vs. Ag/AgCl. This value was shifted anodically than that for the (±)-trans,cis-isomer of this nitroxyl radical. This means that the oxidizability of 1 is stronger than the (±)-trans,cis-isomer of 1. The peak splitting between the anodic and cathodic peak
potential of 1 was 65 mV. This value was smaller than that for the (±)-trans,cis-isomer of 1 and 4-hydroxy-TEMPO benzoate, which means a progress of smooth electron transfer on electrode. In addition, the peak current is proportional to the square root of the scan rate, from which the diffusion coefficient of 1 was estimated to be $2.15 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. These observations suggest a possible use of 1 as a catalyst in the electrocatalytic oxidation reactions. Based on the cyclic voltammetric results, a preparative and controlled-potential electrolysis of alcohols at +0.8 V vs. Ag/AgCl was performed. The electrolyte solution (5 mL) contained 1 mmol of alcohol (0.5 mmol of diols), 0.05 mmol of 1, 0.5 mmol of tetralin as a standard for chromatography analysis, 2 mmol of 2,6-lutidine as a deprotonating agent, and 0.25 mmol of supporting electrolyte (NaClO$_4$). A graphite felt electrode, the size of 0.5 x 0.5 x 0.5 cm, was used as working anode electrode. During electrolysis, the substrates and products were occasionally analyzed by gas chromatography (GC) and high performance liquid chromatography (HPLC). A time course of the electrocatalytic oxidation of benzyl alcohol by 1 is shown in Figure 2. One mmol of benzyl alcohol reacted almost completely in about 10 h to yield benzaldehyde. The current efficiency in the electrolysis was ca. 88% during the course of electrolysis, and no by-product was observed (100% selectivity). The turnover number (given by the ratio of mole of product x 2 / mole of 1) was calculated to be 38.5 at 10 h of electrolysis. The results from the oxidation reactions of a variety of alcohols are shown in Table 1. The primary and secondary alcohols were oxidized to the corresponding aldehydes and ketones, respectively, in high current efficiency (86.4-92.7 %), high yield (94.7-96.2 %) and 100 % selectivity. The turnover numbers for the oxidation of primary and secondary alcohols are larger than 37. (R)- and (S)-forms of racemic 1-
Table 1. Electrocatalytic Oxidation of Alcohols by 1

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Charge passed / C</th>
<th>Current efficiency / %</th>
<th>Selectivity %</th>
<th>Yield %</th>
<th>Turnover number</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzyl alcohol</td>
<td>benzaldehyde</td>
<td>204.3</td>
<td>90.5</td>
<td>100</td>
<td>95.8</td>
<td>38.3</td>
</tr>
<tr>
<td>phenethyl alcohol</td>
<td>acetophenone</td>
<td>210.7</td>
<td>88.1</td>
<td>100</td>
<td>96.2</td>
<td>38.5</td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>cyclohexanone</td>
<td>197.1</td>
<td>92.7</td>
<td>100</td>
<td>94.7</td>
<td>37.9</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>ethyl glycolate</td>
<td>212.8</td>
<td>86.4</td>
<td>100</td>
<td>95.3</td>
<td>38.1</td>
</tr>
<tr>
<td>1,2-diols</td>
<td>lactones</td>
<td>202.4</td>
<td>80.2</td>
<td>89.2</td>
<td>84.1</td>
<td>33.6</td>
</tr>
<tr>
<td>1,3-diols</td>
<td>203.0</td>
<td>78.6</td>
<td>87.5</td>
<td>82.7</td>
<td>33.1</td>
<td></td>
</tr>
</tbody>
</table>

phenethyl alcohol were equally oxidized to acetophenone, though 1 contains chiral centers. On the other hand, the oxidation of 1,4- and 1,5-diols led to γ- and δ-lactones, respectively, in adequate current efficiency (78.6-80.2 %) and yield (82.7-84.1 %). A slightly lower selectivity (87.5-89.2%) observed for the terminal diols was assumed to come from the formation of a small amount of intermolecular products.

A possible reaction mechanism is shown in Figure 3, in which an adduct made up of the alcohol and the oxoammonium ion as one-electron oxidized species of 1 is attacked by a Lewis base to form the second intermediate leading to the products.6

\[ \text{Figure 3. Schematic diagram of the oxidation of alcohols with nitroxy radical.} \]

In conclusion, the electrochemical oxidation of alcohols catalyzed by 1 afforded the corresponding aldehydes, ketones and lactones in high yield (82.7-96.2 %), high current efficiency (78.6-92.7 %) and high selectivity (87.5-100 %). It became apparent that decahydroquinolinyl-N-oxyl radical (1) has valuable potentiality as an electron mediator for electrocatalytic oxidation of many different types of alcohols.

ACKNOWLEDGEMENT
This work was supported in part by Grants-in-Aid for Scientific Research on Priority Areas (No.
REFERENCES AND NOTES


9. (±)-cis,cis-4-hydroxy-2,2,8a-trimethyldecahydroquinolinyl-N-oxyl was prepared according to the reported procedure: J. S. Roberts and C. Thomson, J. Chem. Soc., Perkin Trans. 2, 1972, 2129. Compound (1) was obtained by a conventional reaction of (±)-cis,cis-4-hydroxy-2,2,8a-trimethyldecahydroquinolinyl-N-oxyl with benzoyl chloride.

10. A glassy carbon disk electrode (3 mm diameter) and a platinum wire were employed as the working electrode and the counter electrode, respectively. The anode potentials were referred to Ag/AgCl (saturated AgCl and (CH$_3$)$_3$C$_4$H$_2$NCI in acetonitrile). Cyclic potential sweeps were generated by a Hokuto Denko Model HABF-501 potentiostat/galvanostat. Cyclic voltammograms were recorded on a Graphtec Model WX1200 X-Y recorder. All electrochemical measurements were carried out at room temperature (ca. 20°C).


12. The GC analysis was carried out using CP-Cyclodextrin-B-2,3,6-M-19 capillary column (0.25 mm φ x 25 m). The column temperature was increased at 3 °C min$^{-1}$ from 80 to 150 °C. The injection and detector temperatures were 200 °C and 240°C, respectively. The HPLC analysis was carried out using Daiel CHIRALCELL-OD column (46 mm φ x 250 mm). The column temperature was kept constant at 40 °C. The analytes were eluted by a mixture of 2-propanol and n-hexane (2:33 by volume) at 0.7 mL min$^{-1}$ flow rate, and detected by UV absorption at 254 nm.

Received, 19th April, 1999