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

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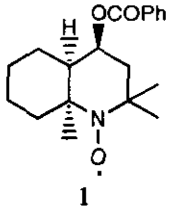
Abstract — (±)-*cis,cis*-4-Benzoyloxy-2,2,8a-trimethyldecahydroquinolinyl-*N*-oxyl reveals a reversible redox peak whose oxidation potential is at + 0.67 V *vs.* Ag/AgCl. The compound catalyzed the selective oxidation reactions of primary and secondry alcohols to aldehydes and ketones, respectively, 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.[1] However, use of even a catalytic amount of hazardous metallic reagents is a matter of economic and environmental concern.[2] Oxoammonium ions as nonmetallic oxidizing reagents are available easily from the corresponding nitroxyl radicals by one-electron oxidation on the electrode.[3] Numerous studies have demonstrated the ability of nitroxyl radicals to mediate alcohol oxidation by electrolysis, apparently *via* the oxoammonium ion.[3-7] 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.[8] 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-benzoyloxy-2,2,8a-trimethyldecahydroquinolinyl-*N*-oxyl (**1**)[9] in the electro-oxidation reactions of different types of primary and secondary alcohols.



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The cyclic voltammetry of **1** was carried out in an acetonitrile solution containing 0.1 M $NaClO_4$ as a supporting electrolyte.[10] 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.[8] 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

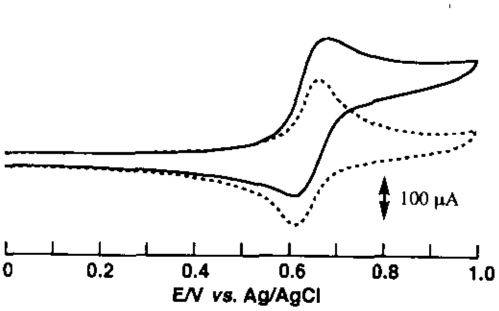


Figure 1. Cyclic voltammograms of 0.01 M **1** in the presence of (———) and absence (- - - - -) of 0.2 M benzyl alcohol and 0.4 M 2,6-lutidine in 0.1 M $NaClO_4$ / CH_3CN at scan rate of 50 mV sec^{-1}. Working electrode: glassy carbon disk electrode (3 mm ϕ).

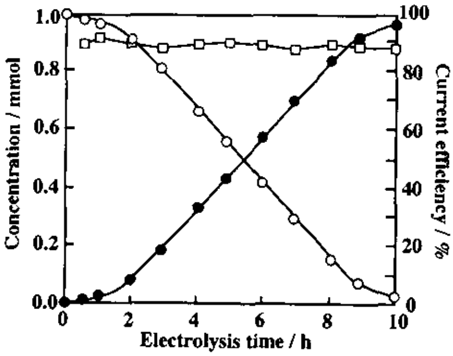


Figure 2. Macroelectrolysis of benzyl alcohol by **1** in the presence of 2,6-lutidine. ○: benzyl alcohol, ● : benzaldehyde and □ : current efficiency.

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 2.15×10^{-5} cm^2 sec^{-1}.[11]

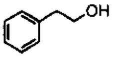
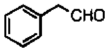
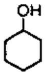
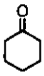
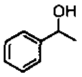
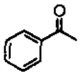
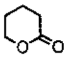
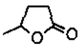
These observations suggest a possible use of **1** as a catalyst in the electrocatalytic oxidation reactions. The cyclic voltammogram of **1** in the presence of benzyl alcohol and 2,6-lutidine is also shown in Figure 1. The oxidation peak current of the cyclic voltammogram was enhanced up to 260 μA at + 0.69 V *vs.* Ag/AgCl in the presence of benzyl alcohol, as compared with 160 μA in the absence of benzyl alcohol, suggesting that **1** mediates an electron relay between the electrode and benzyl alcohol.

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).[12]

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**

Substrate	Product	Charge passed / C	Current efficiency / %	Selectivity %	Yield %	Turnover number
		204.3	90.5	100	95.8	38.3
		210.7	88.1	100	96.2	38.5
		197.1	92.7	100	94.7	37.9
		212.8	86.4	100	95.3	38.1
		202.4	80.2	89.2	84.1	33.6
		203.0	78.6	87.5	82.7	33.1

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 mechanisum 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]

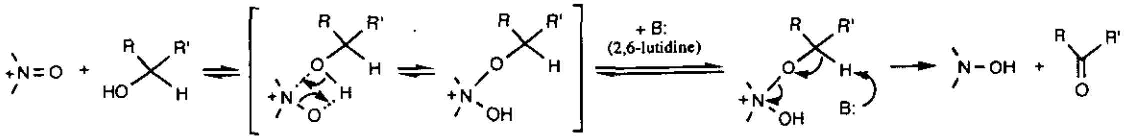


Figure 3. Schematic daiagram of the oxidation of alcohols with nitroxyl radical.

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

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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 $(CH_3)_3C_2H_5NCl$ 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°).
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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 ℃ min^{-1} from 80 to 150 ℃. The injection and detector temperatures were 200 ℃ and 240℃, respectively. The HPLC analysis was curried out using Daisel CHIRALCELL-OD column (46 mm ϕ x 250 mm). The column temperature was kept constant at 40 ℃. 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.

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