# ELECTROCATALYTIC OXIDATION OF BENZYL ALCOHOL AND 1-PHENETHYL ALCOHOL BY A DECAHYDROQUINOLINYL-*N*-OXYL RADICAL

Futoshi Kurashima, Yoshitomo Kashiwagi,* Chikara Kikuchi, Jun-ichi Anzai, and Tetsuo Osa

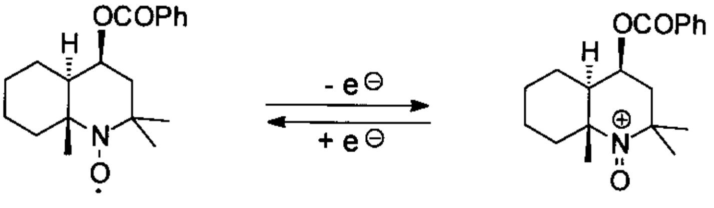
Faculty of Pharmaceutical Sciences, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan

***Abstract*** - (±)-*trans,cis*-4-Benzoyloxy-2,2,8a-trimethyldecahydroquinolinyl-*N*-oxyl reveals a reversible redox peak whose oxidation potential is at + 0.55 V *vs*. Ag/AgCl. The compound catalyzed the oxidation reactions of benzyl alcohol and 1-phenethyl alcohol to benzaldehyde and acetophenone, respectively, in satisfied current efficiency (74.4-80.6%) and selectivity (100%).

*N*-Oxyl radical is a usually stable organic radical, and its oxidized species (*i.e.*, an oxoammonium ion) can be easily prepared electrochemically by one-electron oxidation of *N*-oxyl radical (Scheme).[1] The oxoammonium ion is known to be a specific and useful oxidant for several functional groups, and piperidine and pyrrolidine type *N*-oxyl radicals such as 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO) and 2,2,5,5-tetramethyl-3-pyrrolinyl-*N*-oxyl (PROXYL) have been used extensively as catalyst for the electro-oxidation reaction of alcohols.[2-9] However, no other *N*-oxyl radical has been used as catalyst in electro-oxidation reactions. In order to improve the performance of the electrocatalytic features of *N*-oxyl radicals, the development of other type of *N*-oxyl radicals is still required. In this communication, we report electrocatalytic behavior of decahydroquinoline type *N*-oxyl radical, (±)-*trans,cis*-4-benzoyloxy-2,2,8a-trimethyldecahydroquinolinyl-*N*-oxyl (**1**),[10] in the electro-oxidation reaction of primary and secondary alcohols.

The cyclic voltammetry of **1** was carried out in an acetonitrile solution containing 0.1 M $NaClO_4$ as supporting electrolyte.[11] Figure 1 shows the cyclic voltammograms of **1**, in which a reversible redox

**Scheme**



*N*-oxyl radical (**1**)

oxoammonium ion

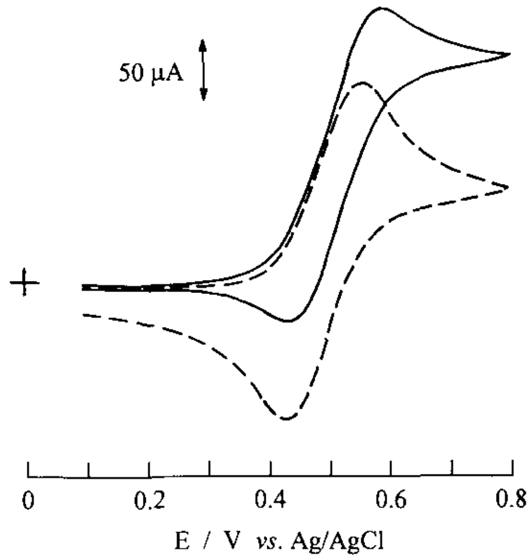


**Figure 1.** Cyclic voltammograms of 0.01 M **1** in the presence (——) and absence (-----) of 0.2 M benzyl alcohol and 0.4 M 2,6-lutidine in 0.1 M $NaClO_4$/acetonitrile. Scan rate: 50 mV $sec^{-1}$.

couple can be observed. This redox couple corresponds to the one-electron oxidation of **1** to the oxoammonium ion. The oxidation potential and the difference between the anodic peak potential and cathodic peak potential of 1 are + 0.55 V *vs.* Ag/AgCl and 75 mV, respectively. These values are comparable to those for TEMPO derivatives.[12] In addition, the diffusion coefficient of **1** was estimated to be 2.4 x $10^{-5}$ $cm^2$ $sec^{-1}$ based on the plot of the peak current vs. (scan rate)$^{1/2}$ in the cyclic voltammetry.[13] These observations suggest a possible use of **1** as catalyst in the electrocatalytic oxidation of substrates. 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 220 μA in the presence of benzyl alcohol, as compared with 170 μA in the absence of benzyl alcohol at + 0.59 V *vs.* Ag/AgCl, suggesting that **1** is electrocatalytically active for the oxidation of benzyl alcohol.

Preparative electrolysis reactions of alcohols were performed at a constant potential (+ 0.8 V *vs.* Ag/

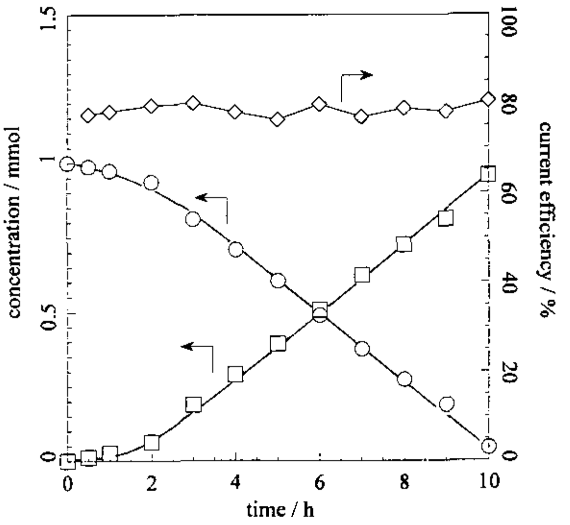


**Figure 2.** Macroelectrolysis of benzyl alcohol by **1** in the presence of 2,6-lutidine. ○ : benzyl alcohol, □ : benzaldehyde and ◇ : current efficiency.

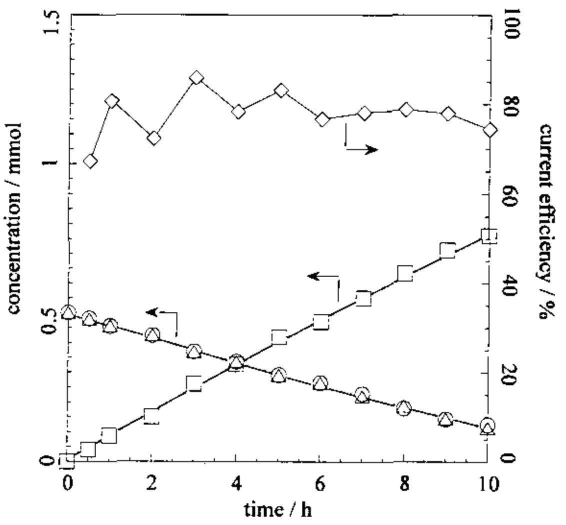


**Figure 3.** Macroelectrolysis of 1-phenethyl alcohol by **1** in the presence of 2,6-lutidine. ○ : (*R*)-1-phenethyl alcohol, △ : (*S*)-1-phenethyl alcohol, □ : acetophenone and ◇ : current efficiency.

AgCl) in an acetonitrile solution. The electrolyte solution (5 mL) contained 1 mmol of benzyl alcohol or 1-phenethyl alcohol, 0.05 mmol of **1**, 0.5 mmol of tetralin as a standard for high performance liquid chromatography (HPLC) 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 5 x 5 x 5 mm, was used as working anode electrode. During electrolysis, the substrates and products were occasionally analyzed by HPLC.[14]

A time course of the electro-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 is *ca.* 80% during the course of electrolysis, and no by-product was observed (100% selectivity). The turnover number based on **1** was calculated to be 38.4 at 10 h of electrolysis.

Figure 3 shows the similar results for the electrolysis of racemic 1-phenethyl alcohol. About 76% of 1-phenethyl alcohol was consumed in 10 h to afford acetophenone and no by-product was produced. The current efficiency and turnover number were 74.4% and 30.4, respectively, at 10-hour electrolysis. The oxoammonium ion of **1** oxidized (*R*)- and (*S*)-form of 1-phenethyl alcohol equally, though **1** contains chiral centers. No oxidation reaction occurred in the absence of **1** for both alcohols under the same reaction conditions, confirming the electrocatalytic oxidation mediated by **1**.

The results of macroelectrolysis of benzyl alcohol and 1-phenethyl alcohol clearly demonstrate that **1** can be used successfully as catalyst which mediates electron relay between electrode and the substrates for the electro-oxidation of both primary and secondary alcohols. It should be emphasized that, in the electrocatalytic oxidation by **1**, the alcohols are converted into the corresponding aldehyde and ketone in 100% selectivity with adequate current efficiency (74.4-80.6%). The turnover number of **1** for the reactions is satisfactorily high, being comparable to those reported for TEMPO derivatives.[15] Thus, it became apparent that **1** has valuable potentiality as an electron mediator for electrocatalytic oxidation of alcohols.

The successful use of **1** in homogeneous system suggests that the electrocatalytic oxidation of alcohols can be performed using **1**-modified electrodes in which **1** is immobilized covalently on the electrode. This system is expected to provide improved current efficiency and turnover number together with enantioselectivity for the reactions. We are now fabricating the **1**-modified electrodes for this purpose.

## ACKNOWLEDGEMENT

This work was supported in part by Grants-in-Aid for Scientific Research on Priority Areas (No. 10132206: "Innovative Synthetic Reactions") and for Encouragement Research (No. 10771266) from the Ministry of Education, Science, Sports and Culture of Japan.

## REFERENCES AND NOTES

1. M. F. Semmelhack, C. R. Schmid, D. A. Cortes, and C. S. Chou, *J. Am. Chem. Soc.*, 1983, **105**, 4492.
2. T. Endo, T. Miyazawa, S. Shiihashi, and M. Okawara, *J. Am. Chem. Soc.*, 1984, **106**, 3877; E. Yoshida, T. Takata, T. Endo, T. Ishizone, A. Hirao, and S. Nakahama, *Chem. Lett.*, **1994**, 1827.

3. (a) V. A. Golubev, R. V. Miklyush, and Z. G. Rozantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1972**, 656 (*Chem. Abstr.*, 1972, **77**, 101344k). (b) V. A. Golubev and R. V. Miklyush, *Zh. Org. Khim.*, 1972, **8**, 1356 (*Chem. Abstr.*, 1972, **77**, 151087z).
4. D. H. Hunter, *Tetrahedron Lett.*, 1984, **25**, 603.
5. M. F. Semmelhack and C. R. Schmid, *J. Am. Chem. Soc.*, 1983, **105**, 6732.
6. J. M. Bobbitt, M. C. F. Guttermuth, Z. Ma, and H. Tang, *Heterocycles*, 1990, **30**, 1131; J. M. Bobbitt and M. C. Flores, *Stud. Org. Chem.*, 1987, **30**, 25.
7. D. H. Hunter, J. S. Rocok, A. W. Ray, and Y. Z. Ponce, *J. Org. Chem.*, 1988, **53**, 1278.
8. T. Osa, Y. Kashiwagi, K. Mukai, A. Ohsawa, and J. M. Bobbitt, *Chem. Lett.*, **1990**, 75; Y. Kashiwagi, A. Ohsawa, T. Osa, Z. Ma, and J. M. Bobbitt, *Chem. Lett.*, **1991**, 581; Y. Kashiwagi, H. Ono, and T. Osa, *Chem. Lett.*, **1993**, 81; Y. Kashiwagi, H. Ono, and T. Osa, *Chem. Lett.*, **1993**, 257.
9. A. Deronzier, D. Limosin, and J. -C. Moutet, *Electrochimica Acta*, 1987, **32**, 1643.
10. (±)-*trans,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 (±)-*trans,cis*-4-hydroxy-2,2,8a-trimethyldecahydroquinolinyl-*N*-oxyl with benzoyl chloride and was used in an isolated form. The electrocatalytic activity of this compound has not been reported.
11. A glassy carbon disk electrode (3 mm ϕ) and a platinum wire were employed as a working electrode and a counter electrode, respectively. The anode potentials were referred to Ag/AgCl (0.1 M $NaClO_4$ 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. J. M. Bobbitt and M. C. L. Flores, *Heterocycles*, 1988, **27**, 509.
13. A. J. Bard and L. R. Faulkner, 'ELECTROCHEMICAL METHODS', John Wiley & Sons, Inc, New York, 1980, p. 215.
14. The HPLC analysis was curried out using Daisel CHIRALCEL®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.
15. Y. Yanagisawa, Y. Kashiwagi, F. Kurashima, J. Anzai, and T. Osa, *Chem. Commun.*, **1996**, 2745.

Received, 6th July, 1998