

N-Oxyl-Mediated Electrooxidation of Alcohols in Water

Tanaka Hideo,* Kuroboshi Manabu, Shimizu Yusuke, Yoshida Tomonori, and Kubota Jun

Department of Applied Chemistry, Faculty of Engineering, OKAYAMA University

Tsushima-Naka 3-1-1, Okayama 700-8530, Japan

Tanaka95@cc.okayama-u.ac.jp

Water is a cheap, safe, and environmentally benign solvent; indeed, considerable efforts have been devoted to develop many organic transformations in water. However, organic substrates and/or reagents are usually insoluble and/or unstable in water, thus we need some special care and/or designs to carry out the reaction in water. Recently, we have developed *N*-oxyl-mediated electrooxidation of alcohols in silica gel and/or polymer particles/water disperse systems, in which substrates and reagents (catalysts) are adsorbed or immobilized on the particles. In 1999, Schäfer and his co-workers reported electrooxidation of water-soluble sugar derivatives in water containing *N*-oxyl compound (2,2,6,6-tetramethylpiperidine-1-oxyl: TEMPO). In this report are described our further investigations on the *N*-oxyl-mediated electrooxidation of alcohols in water, and the unique behavior of the TEMPO in water will be discussed.

Electrooxidation of methyl α -D-glucopyranoside **1** in a carbonate buffer solution was examined in the presence of a catalytic amount of TEMPO. The electrolysis was carried out in an undivided cell fitted with two Pt electrodes. Constant current (30 mA, 5.5 F/mol) was supplied to afford the corresponding carboxylic acid which was isolated as methyl ester **2** after treatment with Me₂C(OMe)₂ (91% yield, Table 1, Entry 1). Addition of MeCN in the buffer solution retarded the oxidation and the yields of **2** decreased to 69 – 16% (recovery of **1**: 21 – 71%) (Entries 2-4).

Table 1. Oxidation of Methyl α -D-Glucopyranoside **1**

Entry	Buffer ^a /CH ₃ CN mL/mL	Yield 2 /% ^b	Recov. 1 /% ^b
1 ^c	10/0	91	-
2 ^c	7.5/2.5	65	27
3 ^d	5/5	69	21
4 ^c	1.5/8.5	16	71

^a 0.40 M Na₂CO₃/0.30 M NaHCO₃. ^b Isolated yield.

^c Homogeneous solution. ^d Heterogeneous solution.

With water-soluble WS-TEMPO in buffer system, only

67% yield of **2** was obtained, while *N*-Oxyl-immobilized particles/water disperse system did not work at all resulting in the recovery of most of the starting material **1** (Table 2).

Table 2. Electrooxidation of **1**

N-Oxyl	Yield / %
TEMPO	91
WS-TEMPO	67
PE-co-AA-N-Oxyl	-
SiO ₂ -N-Oxyl	-

PE-co-AA: poly(ethylene-co-acrylic acid) (5 w%)
SiO₂: silica gel for column chromatography

Electrooxidation of water-insoluble alcohols were also examined (Table 3). Electrooxidation of benzylic alcohol with TEMPO or WS-TEMPO in buffer afforded the corresponding ketone in only 48-69% yields, which was less effective than that in *N*-oxyl-immobilized PE-co-AA or SiO₂/water disperse system. Oxidation of aliphatic alcohol did not proceed at all in TEMPO and WS-TEMPO/water systems, whereas the oxidation was completed in *N*-oxyl-immobilized PE-co-AA or SiO₂/water disperse system.

Table 3. Oxidation of Alcohols in Water Systems

N-Oxyl	4-ClC ₆ H ₄ -CH ₂ -CH ₂ -OH	Ph-CH ₂ -CH ₂ -CH ₂ -OH
TEMPO ^a	48	-
WS-TEMPO ^a	69	3
PE-co-AA ^b	87	94
SiO ₂ ^b	94	86

^a 0.40 M Na₂CO₃, 0.30 M NaHCO₃.

^b 20w%NaBr-sat. NaHCO₃.

Above all, the *N*-oxyl-mediated electrooxidation of water-soluble sugar derivative **1** in water containing TEMPO proceeded most smoothly. It is not clear at present but lipophilic interaction between TEMPO and the sugar **1** is so strong that they would make an inclusion complex in the buffer solution (Fig. 1), and microscopically heterogeneous reaction field would be constructed.

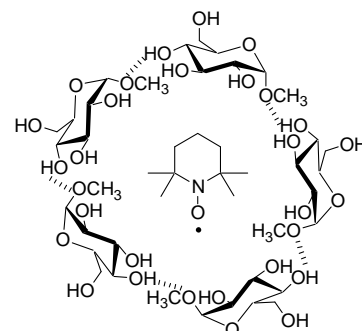


Fig. 1. TEMPO framed by sugar

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