



Electrocatalytic synthesis of nitriles from aldehydes with ammonium acetate as the nitrogen source



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ABSTRACT

A simple synthesis method of nitriles from corresponding aldehydes by electrochemical oxidation was developed with ammonium acetate as the nitrogen source and 4-acetamido-2,2,6,6-tetramethylpiperidinyl-1-oxy (4-AcNH-TEMPO) as the catalyst. Cyclic voltammetry was performed to investigate the electrocatalytic activity of 4-AcNH-TEMPO for the conversion of benzaldehyde to benzonitrile. On the basis of in situ FTIR data and cyclic voltammetry experiments, a reaction mechanism, involving the redox of 4-AcNH-TEMPO and the generation of intermediate imine during the reaction, was proposed. This electrocatalytic reaction system provided an efficient protocol for synthesis of aromatic nitriles at room temperature with moderate to high yields.

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1. Introduction

Nitriles are known to be an important key intermediate and are widely used in synthesis of various organic compounds including amines [1], amides [2–4], ketones [5,6], carboxylic acids [7,8] and heterocyclic compounds [9]. The traditional methods to synthesize nitriles, such as halides/CN exchange [10–12], Sandmeyer reaction [13], dehydration of amides [14,15] and direct functionalizations of C–H bonds [16], usually suffer from severe reaction conditions, limited substrate scope, or use of hazardous reagents and expensive catalysts. Because aldehydes are readily accessed and easy to handle, synthesis of nitriles from corresponding aldehydes is one of the most recognized strategies in organic chemistry. Over the years, different nitrogen sources and oxidants have been applied in this transformation [17–23]. However, some drawbacks could not be avoided in these reported methods: (i) stoichiometric oxidants, like *tert*-butyl hydroperoxide and NaCl₂, should be used; (ii) substrate scope was limited. Thus, from both economic and environmental viewpoints, there is an urgent need for more efficient and greener methods.

2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO) and its derivatives have been widely utilized in organic functional group

transformation. It was successfully employed as the catalyst in our previous studies of aerobic oxidation [24,25] and electro-oxidation [26–30] of alcohol. In recent years, TEMPO and its derivatives were introduced into the oxidative conversion of amines or aldehydes into nitriles. Muldoon et al. reported that copper/TEMPO catalysts could be used to prepare nitriles from aldehydes using aqueous ammonia as the nitrogen source and 2,2-bipyridine as the ligand with air as the oxidant [31]. Bailey et al. reported metal-free oxidation protocols to convert amines into nitriles using a stoichiometric quantity of 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate (AcNH-TEMPO⁺BF₄⁻) [32] or a catalytic quantity of 4-acetamido-2,2,6,6-tetramethylpiperidinyl-1-oxy (4-AcNH-TEMPO) [33]. Nitriles could also be prepared from aldehydes mediated by 2.5 equiv. of AcNH-TEMPO⁺BF₄⁻ with hexamethyldisilazane (HMDS) as the nitrogen source in the presence of 1.1 equiv. of pyridine [34]. Then we developed an efficient methodology for the oxidative conversion of aldehydes into nitriles with HMDS as the nitrogen source and oxygen as the terminal oxidant using TEMPO as the catalyst, NaNO₂ or *tert*-butyl nitrite as the co-catalyst [35]. Almost at the same time, Kim et al. reported a similar methodology with ammonium acetate (NH₄OAc) as the nitrogen source using 4-AcNH-TEMPO as the catalyst, NaNO₂ and HNO₃ as the co-catalyst [36].

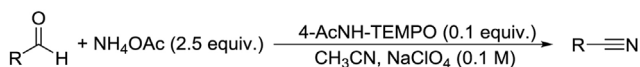
It is well-known that electrochemical syntheses possess significant advantages such as high atom economy and less pollution [37,38]. Chiba et al. reported that aldehydes could be electrooxidated indirectly into nitriles using KI as the redox catalyst and ammonia as the nitrogen source [39]. Unfortunately,

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no desired products could be obtained when nitrobenzaldehyde and furan-2-carbaldehyde were used as substrates. Very recently, our group reported a TEMPO-catalyzed method for electrochemical oxidation of aldehydes to nitriles with HMDS as the nitrogen source [40]. In continuation of our work on the development of electrochemical synthetic methodologies under different reaction conditions, herein we developed another method for electro-oxidative conversion of aldehydes into nitriles using 4-AcNH-TEMPO as the catalyst and employing NH_4OAc as the nitrogen source, which is cheaper, safer and more stable than HMDS. The redox properties of the reaction were studied by cyclic voltammetry and further mechanistic insight was investigated by *in situ* FTIR.



2. Experimental

2.1. Reagents

Benzofuran-2-carbaldehyde was prepared in our laboratory and was fully characterized. Other reagents and solvents were purchased from commercial suppliers and used without further purification.

2.2. Cyclic voltammetry of aldehyde oxidation

Cyclic voltammetry experiments were carried out in an undivided cell in 15 mL MeCN solution containing 0.1 M NaClO_4 as the supporting electrolyte and 0.1 mmol 4-AcNH-TEMPO as the catalyst. The reactions were performed using Vertex Potentiostat/Galvanostat with an “L” type Pt electrode as the working electrode at the scan rate of 50 mV/s. The reference electrode and counter electrode referred in this paper were Ag/Ag^+ (0.1 M AgNO_3 in acetonitrile) and Pt sheet (2.25 cm^2), respectively.

2.3. *In situ* FTIR experiments of aldehyde oxidation

In situ FTIR spectra were obtained on a Nicolet 670 FTIR spectrometer equipped with a liquid nitrogen cooled MCT-A detector. A three-electrode spectro-electrochemical cell which was fitted at the bottom with CaF_2 window was used. The working electrode was a Pt disk (5 mm in diameter).

2.4. Preparative electrolysis experiments

The electrolysis experiments were performed in 15 mL 0.1 M $\text{NaClO}_4/\text{MeCN}$ solution containing 1.0 mmol aldehyde (66.7 mM), 0.1 mmol 4-AcNH-TEMPO and 2.5 mmol NH_4OAc using Pt sheet (2.25 cm^2) as the working electrode in an undivided cell on Vertex Potentiostat/Galvanostat at the potential about 1.5 V. The products were confirmed by ^1H NMR and MS. NMR was performed on a Bruker Avance III spectrometer. GC-MS was performed on Thermo Trace ISQ instrument with TG 5MS capillary column.

3. Results and Discussion

3.1. Cyclic voltammetric study of benzaldehyde oxidation

Cyclic voltammograms were recorded for benzaldehyde in 15 mL MeCN containing 0.1 M NaClO_4 and 0.1 mmol 4-AcNH-TEMPO. As shown in Fig. 1A, a pair of redox potentials at 0.41 V and 0.29 V vs Ag/Ag^+ (0.1 M AgNO_3 in acetonitrile) were displayed,

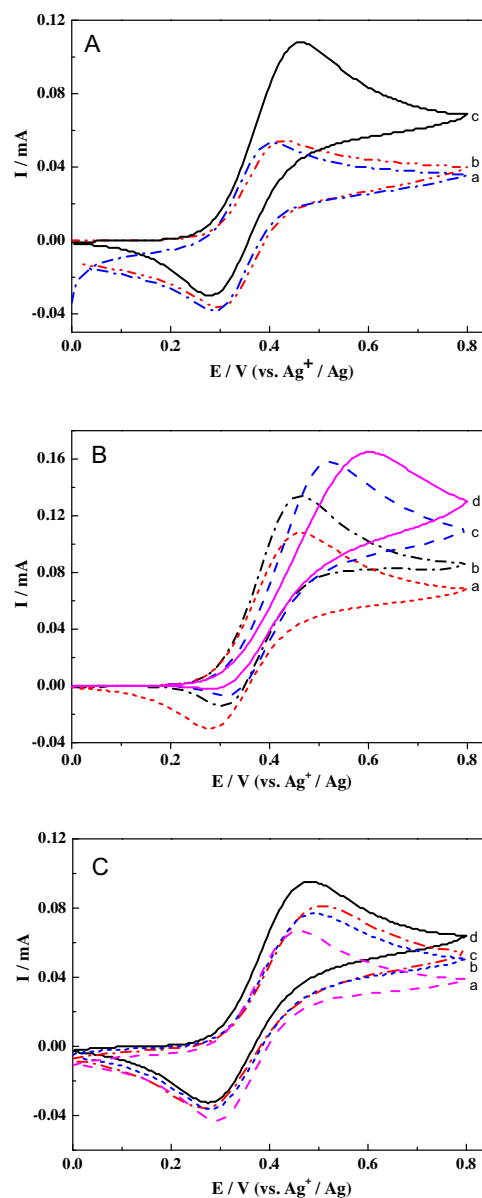


Fig. 1. A. Cyclic voltammograms recorded in 0.1 M $\text{NaClO}_4/\text{MeCN}$ with (a) 4-AcNH-TEMPO (0.1 mmol); (b) 4-AcNH-TEMPO (0.1 mmol) and benzaldehyde (1 mmol); (c) 4-AcNH-TEMPO (0.1 mmol), benzaldehyde (1 mmol) and NH_4OAc (2.5 mmol). **Fig. 1B.** Cyclic voltammograms of 4-AcNH-TEMPO (0.1 mmol) and NH_4OAc (2.5 mmol) in 0.1 M $\text{NaClO}_4/\text{MeCN}$ solution with benzaldehyde of (a) 1.0 mmol; (b) 1.5 mmol; (c) 2.0 mmol; (d) 5.0 mmol. **Fig. 1C.** Cyclic voltammograms of 4-AcNH-TEMPO (0.1 mmol), NH_4OAc (2.5 mmol) and benzaldehyde (1 mmol) in 0.1 M $\text{NaClO}_4/\text{MeCN}$ solution at pH of (a) 4.6; (b) 5.6; (c) 6.6; (d) 7.6.

which corresponded to one electron transfer between nitroxyl radical and oxoammonium ion of 4-AcNH-TEMPO (4-AcNH-TEMPO $^+$) (curve a) [41]. In order to investigate the electrocatalytic ability of 4-AcNH-TEMPO for oxidation of benzaldehyde, 1.0 mmol benzaldehyde was added into the solution (curve b). As compared with curve a, it could be found that the peak current at curve b didn't change obviously, which implied that almost no voltammetric response of benzaldehyde was detected at the electrode. Then with the addition of the nitrogen source NH_4OAc , the oxidation peak of 4-AcNH-TEMPO increased dramatically (curve c). It could be ascribed to the reaction between 4-AcNH-TEMPO $^+$ and benzaldehyde/ NH_4OAc , which greatly promoted the electrochemical oxidation of 4-AcNH-TEMPO to 4-AcNH-TEMPO $^+$.

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