Asian Journal of Chemistry; Vol. 27, No. 9 (2015), 3197-3200

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18373

Electrochemical Oxidation of Benzyl Alcohol on Platinum Electrode with TEMPO in CH_3CN/H_2O

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Received: 25 June 2014; *Accepted*: 10 September 2014; *Published online*: 26 May 2015; AJC-17222

In situ FT-IR and cyclic voltammetry were employed to study the oxidation reaction of benzyl alcohol on platinum electrode with 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) in CH_3CN/H_2O solution containing $NaClO_4$. Cyclic voltammograms were characterized by a well-defined one electron reversible redox couple. The possible catalytic oxidation mechanism of benzyl alcohol with TEMPO was studied using *in situ* FT-IR spectroscopy. It suggested that oxoammonium ion was generated by one-electron oxidation of TEMPO at low oxidation potential and benzyl alcohol was mainly oxidized to benzaldehyde instead of benzoic acid.

Keywords: TEMPO, Benzyl alcohol, Platinum electrode.

INTRODUCTION

The organocatalyst 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) has been recognized for its high activity and selectivity[1,2]. Its corresponding oxoammonium ion $TEMPO^+$ can be formed by electrochemical[3,4] or catalyst promoter (H_2O_2, O_2, metal halide)[5,6] oxidation of 2,2,6,6-tetramethylpiperidin-1-yloxy and applied to the selective oxidation of alcohols to form the corresponding aldehydes or ketones in the presence of the Lewis base. Generally, HPLC[7], GC[8] and chromatography-mass spectrum[9] are adopted to analyze the intermediates and products during the oxidation of alcohols with TEMPO. However, these methods always need tedious pretreatment and long time to analysis by instruments. In addition, there is also large sample matrix interference and limitation in the application.

in situ FT-IR spectroscopy technique as a real-time analysis method has been widely employed to investigate the mechanism of some electrochemical reactions, which can obtain the change information of reactants and products during the electrochemical reaction without any pretreatment[10,11]. According to the literatures, study of electrocatalytic oxidation mechanism of alcohol with TEMPO using *in situ* FT-IR spectroscopy technique has seldom been reported[12]. In this paper, benzyl alcohol was chosen as the model molecule and TEMPO in solution as the catalyst. The electrocatalytic oxidation mechanism of benzyl alcohol with TEMPO on platinum electrode was investigated by cyclic voltammetry and *in situ* FT-IR.

EXPERIMENTAL

The following chemicals were all of analytical reagent grade: TEMPO, acetonitrile, benzyl alcohol, 2,6-lutidine, sodium perchlorate. All solutions were prepared using deionized water. The experiments were carried out at room temperature.

Cyclic voltammetry: CHI620B electrochemical workstation (CH Instrument Inc., USA) was used for voltammetric study. A platinum sheet (0.4 cm × 0.5 cm) was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum sheet (1.5 cm × 2 cm) as the counter electrode. Experiments were carried out in CH_3CN/H_2O solution containing 0.1 M $NaClO_4$ and 0.01M TEMPO.

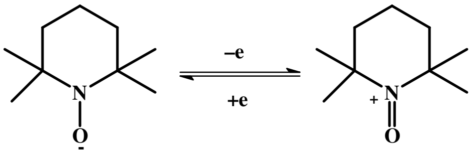
***in situ* FT-IR experiments:** *in situ* FT-IR spectroscopic experiments were carried out on Nicolet 670 FTIR spectrometer equipped with a MCT-A detector cooled with liquid nitrogen. The resulting spectrum recorded was defined as the potential-difference spectra and was calculated by the following formula[11]:

$$\frac{\Delta R}{R} = \frac{\left[R(E_S) - R(E_R)\right]}{R(E_R)} \tag{1}$$

where $R(E_S)$ and $R(E_R)$ were single-beam spectra collected respectively at the sample potential (E_S) and the reference potential (E_R). Accordingly, the negative-going bands in the resulting spectra represented the formation of intermediates and products, while the positive-going bands denoted the consumption of reactants. Two hundreds interferograms were collected and co-added into a single beam spectrum. The spectral resolution was set at 8 cm^{-1}. The disk electrode of platinum (d = 6 mm) was used as the working electrode, which was polished by 0.03-0.05 µm α-Al_2O_3. A saturated calomel electrode was used as the reference electrode and a platinum sheet as the counter electrode.

RESULTS AND DISCUSSION

Cyclic voltammetry studies: Fig. 1 showed cyclic voltammograms of benzyl alcohol electrochemical oxidation with TEMPO on platinum electrode in CH_3CN/H_2O solution. As could be seen from Fig. 1a, there was a pair of well-defined reversible redox waves at about 0.50 to 0.55V in the CH_3CN/H_2O solution with TEMPO, which was related to the redox reaction of TEMPO on the surface of platinum electrode. It was represented as the following equation:



(2)

With the addition of benzyl alcohol in the above-mentioned solution, there were no obvious changes could be observed in Fig. 1b, suggesting that the electrochemical oxidation of benzyl alcohol was quite weak on the surface of platinum electrode. The reversible redox waves were also little affected by the addition of 2,6-lutidine as the base (Fig. 1c). Therefore, it was difficult to analyze the electrochemical oxidation of benzyl alcohol on platinum electrode with TEMPO. To further investigation, *in situ* FT-IR spectroscopy technique was applied to study the electrochemical oxidation mechanism of benzyl alcohol with TEMPO in CH_3CN/H_2O solution.

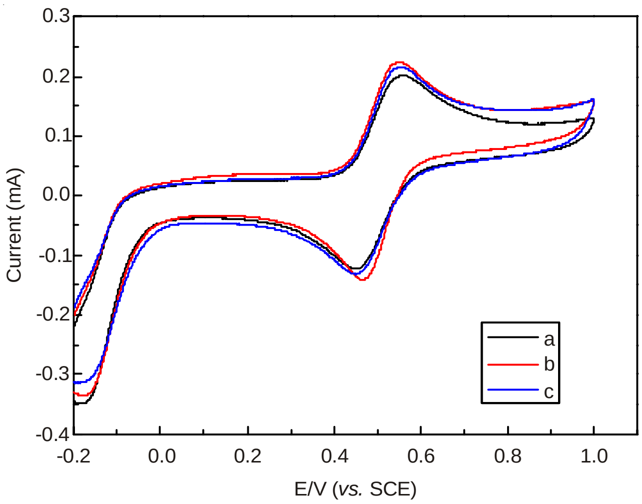


Fig. 1. Cyclic voltammograms of electrooxidation of benzyl alcohol on platinum electrode in CH_3CN/H_2O solution containing TEMPO and $NaClO_4$; (a) blank solution; (b) in the presence of benzyl alcohol (10 mM); (c) in the presence of benzyl alcohol (10 mM) and 2,6-lutidine (20 mM)

***in situ* FT-IR spectroscopic analysis:** Fig. 2 showed *in situ* FT-IR spectra obtained during electrochemical oxidation of TEMPO on platinum electrode. When the potentials were more negative than 400 mV, obvious changes could hardly be observed from the FT-IR spectra in Fig. 2. It indicated that the electrochemical oxidation was quite weak. When it stepped to more positive potentials, the corresponding infrared spectra signals became obvious gradually. Four characteristic positive-going bands at 1363, 1386, 1346, 1241 cm^{-1} were observed, which were assigned to N-O· stretching vibration[13] and heterocyclic framework vibration of TEMPO[14], respectively. In addition, there was a characteristic negative-going band 1620 cm^{-1}, which was related to N^+=O stretching vibration of oxoammonium ion[13]. It suggested that oxoammonium ion of TEMPO was generated by one-electron oxidation of TEMPO on platinum electrode with the consumption of TEMPO.

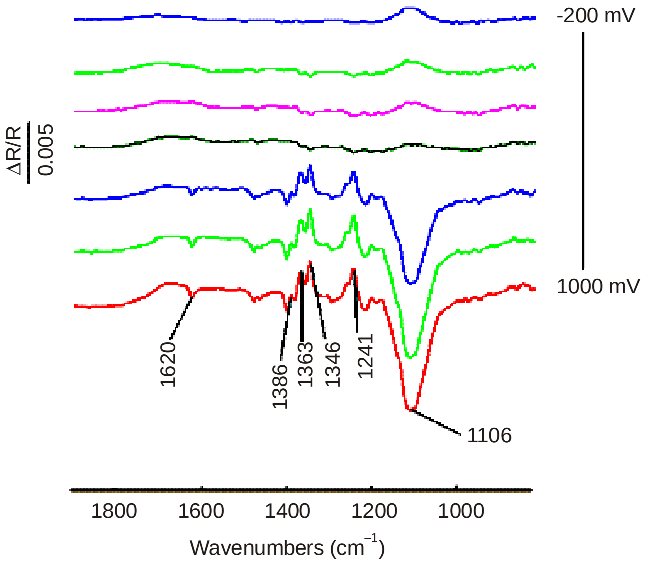


Fig. 2. *in situ* FT-IR spectra collected during electrochemical oxidation of TEMPO on platinum electrode in CH_3CN/H_2O solution containing TEMPO and $NaClO_4$

Fig. 3 showed the *in situ* FT-IR spectra collected during electrooxidation of 10 mM benzyl alcohol in the absence (a) and presence (b) of 2,6-lutidine in CH_3CN/H_2O solution with TEMPO. As shown in Fig. 3a, when the potentials stepped to more positive than 400 mV, the corresponding infrared spectra signals could be obviously observed. It indicated that the oxidation of benzyl alcohol occurred on the surface of platinum electrode. Three negative-going bands at 1700, 1620, 1206 cm^{-1} and three positive-going bands at 1386, 1363, 1346 cm^{-1} could be observed. Bands at 1700 and 1206 cm^{-1} were attributed respectively to C=O stretching vibration and C-C stretching vibration of benzaldehyde[15,16]. In addition, another three important bands at 1620, 1363 and 1346 cm^{-1} were related respectively to N^+=O stretching vibration[13], N-O• stretching vibration[13] and heterocyclic framework vibration[14]. It suggested that with the consumption of TEMPO and the generation of oxoammonium ion, benzyl alcohol was oxidized to benzaldehyde. Fig. 3b showed *in situ* FT-IR spectra collected in the above solution with the addition of 2,6-lutidine. Five obvious negative-going bands at 1700, 1659, 1620, 1206, 1171 cm^{-1} and two positive-going bands at 1363 and 1346 cm^{-1} were observed. Bands at 1659 and 1171 cm^{-1} were ascribed respectively to ring stretching vibration and C-H in-plane bending of 2,6-lutidinium cation[17,18]. It suggested that 2,6-lutidine received a hydrogen

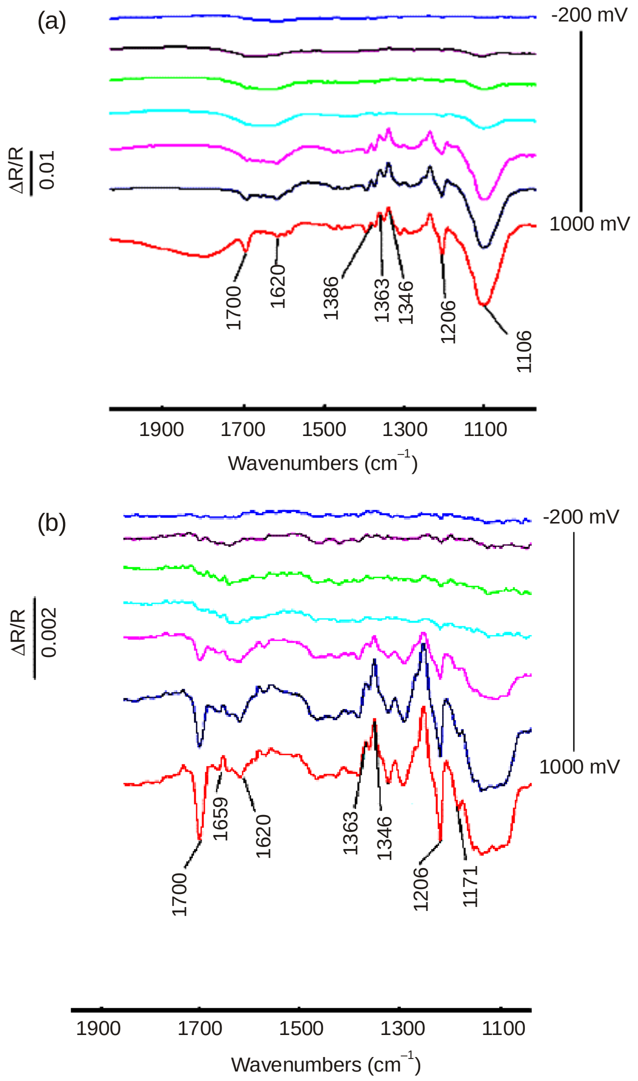


Fig. 3. *in situ* FT-IR spectra collected during electrooxidation of 10 mM benzyl alcohol with TEMPO in the absence (a) and presence (b) of 2,6-lutidine

proton to generate 2,6-lutidinium cation. Meanwhile, characteristic absorption peaks at 1700, 1620, 1363, 1346 and 1206 cm^{-1} enhanced significantly. The above results indicated that 2,6-lutidine could promote the catalytic oxidation of benzyl alcohol in CH_3CN/H_2O solution with TEMPO. Thus, it was inferred that oxoammonium ion selectively oxidizing benzyl alcohol to benzaldehyde in the presence of 2,6-lutidine.

In order to better exemplify the final product in the oxidation of benzyl alcohol in CH_3CN/H_2O solution with TEMPO, Na_2CO_3 was added to the same solution as Fig. 3 and *in situ* FT-IR spectra were collected, as shown in Fig. 4. In Fig. 4a, negative-going bands at 1700 and 1206 cm^{-1} which were related to benzaldehyde almost disappeared, while a negative-going band at 1616 cm^{-1} assigned to $\nu_{as}(COO^-)$ of sodium benzoate emerges[19] could be observed. It indicated that the main product for the electrooxidation of benzyl alcohol in the blank solution was benzoic acid. However, in Fig. 4b, the characteristic negative-going bands at 1700, 1311, 1206 cm^{-1} still existed and the band at 1616 cm^{-1} which was related to sodium benzoate could not be observed. It suggested that benzaldehyde was not been over-oxidized to benzoic acid with the effect of TEMPO.

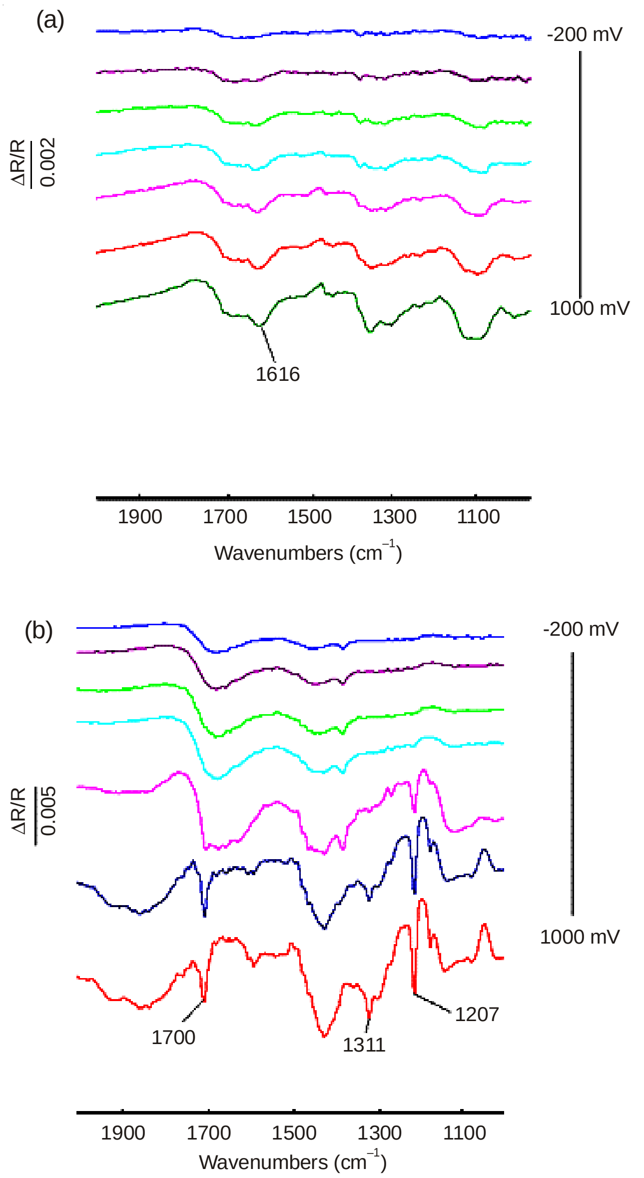


Fig. 4. *in situ* FT-IR spectra collected during oxidation of benzyl alcohol in CH_3CN/H_2O solution with benzyl alcohol, 2,6-lutidine and Na_2CO_3 in the absence (a) and presence (b) of TEMPO

Conclusion

The electrocatalytic oxidation mechanism of benzyl alcohol with TEMPO in CH_3CN/H_2O solution was investigated by cyclic voltammetry and *in situ* FT-IR. Cyclic voltammetry results showed that TEMPO was oxidized to oxoammonium ion on the surface of platinum electrode with the peak potential at about 0.5/0.55 V. In the presence of 2,6-lutidine as the base in CH_3CN/H_2O solution, benzyl alcohol was oxidized by oxoammonium ion. 2,6-Lutidine achieved an electron from benzyl alcohol, and benzyl alcohol was selective oxidized to benzaldehyde. TEMPO in CH_3CN/H_2O could prevent the overoxidation of benzyl alcohol to benzoic acid.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support from the National Natural Science Foundations of China (Grant No. 21206147, 21376224) for this work.

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