



Electroreductive hydrogenation of activated olefins using the concept of site isolation



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ARTICLE INFO

Article history:

Received 17 October 2016

Received in revised form 27 October 2016

Accepted 27 October 2016

Available online 29 October 2016

Keywords:

Site isolation

Electroreductive hydrogenation

Activated olefin

Solid-supported acid

Cation exchange

ABSTRACT

Electroreductive hydrogenation of activated olefins was investigated using the concept of site isolation. It was shown by electrochemical measurements as well as preparative electrolyses that the use of silica gel-supported sulfonic acid (Si-SO₃H) promotes the protonation step in electroreductive hydrogenation of activated olefins without electroreductive destruction at the cathode. On the basis of the concept of site isolation, electroreductive hydrogenation of several activated olefins was successfully carried out to provide the corresponding hydrogenation products in high yields.

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1. Introduction

In principle, opposing reagents such as an acid and a base cannot be put in a single reactor without their mutual destruction. On the other hand, immobilization of the opposing reagents onto respective solid materials suppresses their mutual destruction to allow the simultaneous use in a single reactor [1–2]. This is well-known as the concept of site isolation, which is based on the spatial isolation of opposing active sites. On the basis of the concept of site isolation, one-pot multistep reactions have been demonstrated using a variety of solid-supported catalysts [3–8]. However, its application to electrochemistry has been limited to electrochemical measurements of site-isolated electroactive sites [9–10].

Electrodes in electrochemical reactions are inherently site-isolated heterogeneous redox reagents. Therefore, an anode and a cathode can be put in a single reactor without their mutual destruction. On the other hand, we found that solid-supported bases are not oxidized at anodes [11–12]. It can be regarded as site isolation in electrochemical reactions. Solid-supported reagents, which cannot diffuse into electric double layer, are not subject to electrochemical destruction at electrodes.

On the basis of the concept of site isolation in electrochemical reactions, we demonstrated promotion of the deprotonation step in anodic methoxylation of sulfides using solid-supported bases [13]. In the reaction, solid-supported bases acted as electrochemically inactive bases at the anode. On the other hand, solid-supported acids could also play a

role of electrochemically inactive acids at cathodes. This prompted us to apply solid-supported acids to electrochemical reactions for promoting the protonation step without electroreductive destruction at cathodes. We herein demonstrate electroreductive hydrogenation of activated olefins [14] using the concept of site isolation.

2. Materials and methods

2.1. Materials

Silica gel-supported sulfonic acid (Si-SO₃H, size: 40–63 μm, loading: 0.68 mmol g⁻¹) was purchased from SiliCycle. All other reagents were purchased from commercial suppliers and used without further purification.

2.2. Electrochemical measurements

Electrochemical measurements were carried out with a three-electrode system using a glassy carbon (GC) disk working electrode ($\phi = 1$ mm), a Pt wire counter electrode, and an Ag|Ag⁺ electrode as a reference electrode.

2.3. General procedure for electroreductive hydrogenation of an activated olefin using Si-SO₃H

Electroreductive hydrogenation of an activated olefin (1 mmol) was carried out with a Pt plate anode (2 × 2 cm²) and a GC plate cathode (2 × 2 cm²) in 0.1 M Bu₄NBF₄/MeCN (10 ml) in the presence of Si-SO₃H (1 mmol based on the SO₃H group) using an undivided cell.

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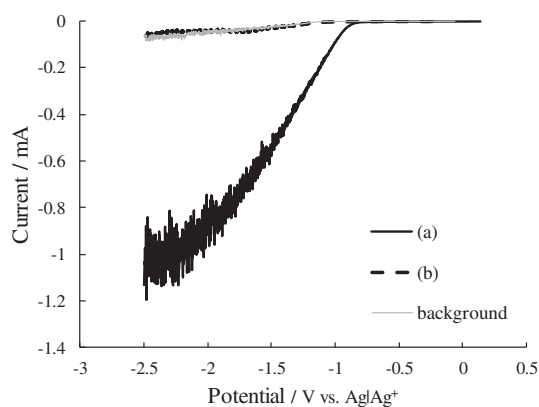


Fig. 1. Linear sweep voltammograms of (a) MeSO₃H (1 mmol) and (b) Si-SO₃H (1 mmol based on the SO₃H group) in 0.1 M Bu₄NBF₄/MeCN under mechanical stirring, recorded at a GC disk electrode ($\phi = 1$ mm). The sweep rate was 10 mV s⁻¹.

Constant current electrolysis (10 mA cm⁻²) was conducted with mechanical stirring at room temperature. After the electrolysis, the electrolytic solution was passed through a glass filter (pore size: 5–10 μ m) to remove Si-SO₃H. The filtrate was concentrated under reduced pressure and the residue was passed through a short column of silica gel eluting with CHCl₃. The eluent was concentrated under reduced pressure and the hydrogenation product in the residue was identified by comparison with an authentic sample using ¹H NMR and mass spectroscopy. The yield of the product was calculated by means of ¹H NMR using a known amount of toluene or nitromethane (1 mmol) as an internal standard.

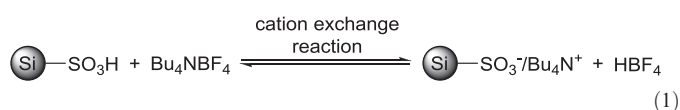
3. Results and discussion

3.1. Linear sweep voltammetry of MeSO₃H and Si-SO₃H

In order to verify site isolation between a solid-supported acid and a cathode, we measured the linear sweep voltammograms of methanesulfonic acid (MeSO₃H) and Si-SO₃H, respectively. A GC disk electrode was employed for the measurements. As shown in Fig. 1(a), the reduction current for H⁺ was clearly observed in the presence of MeSO₃H (the onset potential was ca. -0.9 V vs. Ag|Ag⁺). In contrast, no reduction current was observed in the presence of Si-SO₃H as shown in Fig. 1(b). These results indicate that site isolation between Si-SO₃H and the cathode is achieved.

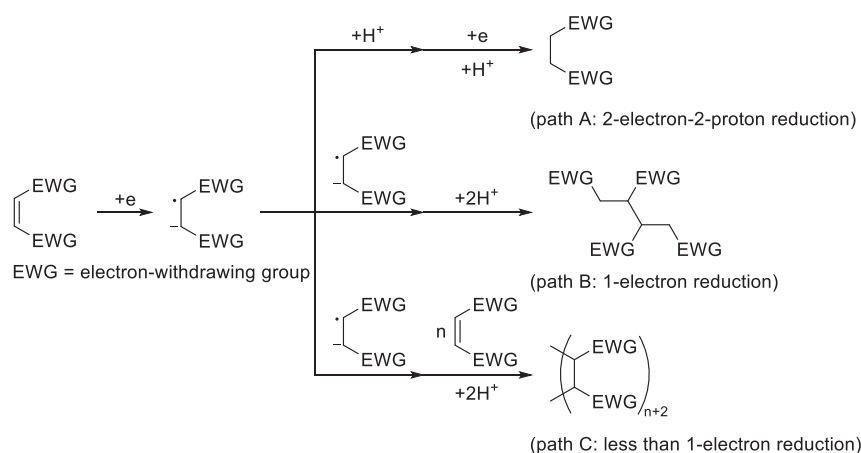
3.2. Cyclic voltammetry of dimethyl maleate in the absence and presence of Si-SO₃H

It has been reported that electroreduction of activated olefins in aprotic organic solvents leads to the corresponding hydrogenation, coupling, and polymeric products depending on the reaction conditions as shown in Scheme 1 [15]. The hydrogenation product is preferentially formed under acidic conditions via 2-electron-2-proton reduction (Scheme 1, path A), while the coupling and/or polymeric products are predominantly formed under neutral and basic conditions via 1-electron reduction or less (Scheme 1, paths B and C). With these facts in mind, we measured the cyclic voltammograms of dimethyl maleate (**1**) in the absence and presence of Si-SO₃H. As shown in Fig. 2(a), the reduction wave for **1** was observed at ca. -2.05 V vs. Ag|Ag⁺ in the absence of Si-SO₃H. On the other hand, the reduction wave became larger in the presence of Si-SO₃H as shown in Fig. 2(b). In addition, the reduction current was slightly observed from ca. -1.25 V vs. Ag|Ag⁺ in the presence of Si-SO₃H, which seems to correspond to the reduction of HBF₄ derived from the cation exchange reaction between Si-SO₃H and Bu₄NBF₄ as a supporting electrolyte (Eq. (1)). These results suggest that the use of Si-SO₃H promotes the protonation of the radical anion intermediate of **1** without electroreductive destruction.



3.3. Electroreductive hydrogenation of dimethyl maleate in the absence and presence of acids

We investigated the electroreductive hydrogenation of **1** in the absence and presence of acids as shown in Table 1. In the absence of acids, the corresponding hydrogenation product **2** was generated in low yield (entry 1). On the other hand, only a small amount of **2** was formed and a certain amount of **1** was recovered in the presence of MeSO₃H (entry 2). In this case, MeSO₃H seems to be mainly reduced at the cathode. In contrast, the yield of **2** increased up to 81% with increasing the amount of Si-SO₃H (entries 3–5). These results indicate that the use of Si-SO₃H promotes the protonation step without electroreductive destruction at the cathode. However, the yield decreased using a larger amount of Si-SO₃H (entry 6). In this case, electroreduction of **1** might compete with that of HBF₄ derived from the cation exchange reaction between Si-SO₃H and Bu₄NBF₄ (Eq. (1)). We next focused on the cathode materials. Pb and Pt, which respectively have high and low hydrogen overvoltages, were selected as cathodes. In spite of their hydrogen overvoltages, the use of Si-SO₃H was effective for electroreductive hydrogenation of **1** (entries



Scheme 1. Reaction mechanism of electroreduction of activated olefins.

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