An Electrolytic System Based on the Acid-Base Reaction between Solid-Supported Acids and Water

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ABSTRACT

We have developed an electrolytic system based on the acid-base reaction between Amberlite IR-120 as a solid-supported acid and water. On the basis of the electrolytic system, electroreduction of activated olefins was carried out to provide the corresponding hydrogenation products in moderate to good yields. Furthermore, the spent Amberlite IR-120 was recyclable for many times by regeneration.

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Keywords : Acid-Base Reaction, Electrolytic System, Electroreduction, Solid-Supported Acids

1. Introduction

Organic electrosynthesis has big potential to contribute to green chemistry, because it can achieve oxidative and/or reductive transformations of organic compounds without the use of any harmful redox reagents.¹ However, the use of supporting electrolytes causes their separation and waste problems after the electrolysis. Although several electrolytic systems have been developed to minimize or eliminate the use of supporting electrolytes, they require special equipment and/or conditions.^{2–6}

We have recently developed an electrolytic system using solid-supported bases.^{7–9} The system is based on the acid-base reactions between protic solvents and solid-supported bases, and the conjugate acid-base pairs seem to act as supporting electrolytes. Therefore, it is possible to conduct organic electrosynthesis without any additional supporting electrolytes. On the other hand, solid-supported acids should also be applied to the electrolytic system based on the acid-base reactions. This would enable us to apply the electrolytic system based on the acid-base reactions to a wide range of organic electrosynthesis. With these facts in mind, we herein report an electrolytic system based on the acid-base reaction between solid-supported acids and water [Eq. (1)].

2. Experimental

2.1 General

¹H NMR spectra were recorded on a 400 MHz spectrometer (JEOL JNM-ECS400) in CDCl₃. EI mass spectra were recorded on a gas chromatograph-mass spectrometer (Shimadzu PARVUM2). Cyclic voltammetry was performed by using a bi-potentiostat (ALS Model 2323). Mili-Q water (typically 18.2 MΩ·cm at 25°C) was used in all experiments.

2.2 General procedure for electroreduction of activated olefins

Electroreduction of an activated olefin (1 mmol) was carried out with a platinum plate anode (2 × 2 cm²) and a glassy carbon (GC) plate cathode (2 × 2 cm²) in 0.2 M Amberlite IR-120 (ca. 0.84 g)/water (10 mL, the concentration was based on the SO₃H group) using an undivided cell. Constant current electrolysis (10 mA cm^{−2})

was conducted with magnetic stirring. After the electricity was passed until the complete consumption of the starting material, the electrolytic solution was passed through a glass filter to remove Amberlite IR-120. The filtrate was extracted repeatedly with CHCl₃. The combined extracts were dried over anhydrous Na₂SO₄. After removal of the drying agent, the organic layer was concentrated under vacuum and the yield of the corresponding hydrogenation product was calculated in the residue by means of ¹H NMR spectroscopy using a known amount of toluene (1 mmol) as an internal standard. In addition, the product was identified by the comparison with the authentic sample (**2**, **5**, and **7**) using ¹H NMR and mass spectroscopy.

2.3 Regeneration of the spent Amberlite IR-120

After the spent Amberlite IR-120 was washed with water (10 mL) and acetone (10 mL), it was regenerated by treating with 1 M aq. HCl (10 mL). The regenerated Amberlite IR-120 was washed with water (50 mL), and then used in the recycling experiments.

3. Results and Discussion

First, in order to evaluate the acid-base reaction between solid-supported acids and water, we measured the cyclic voltammograms of water in the absence and presence of Amberlite IR-120 (terminal group: SO₃H) as a solid-supported strong acid using a platinum disk electrode. As shown in Fig. 1(a), ionic conductivity was hardly obtained in the absence of Amberlite IR-120. In contrast, both the oxidation current for water and the reduction current for H⁺ were clearly observed in the presence of Amberlite IR-120 as shown in Fig. 1(b). These results indicate that the acid-base reaction between Amberlite IR-120 and water takes place, and the conjugate acid-base pair seems to act as a supporting electrolyte. On the other hand, the cathodic potential window was extended to the negative direction up to ca. −2.0 V vs. Ag|AgCl by using a GC disk electrode as shown in Fig. 1(c). The wide reduction potential window would be available for electroreduction of organic compounds.

We then investigated electroreduction of dimethyl maleate (**1**)¹⁰ as a model reaction using solid-supported acids in water. As shown in Table 1, electroreduction of **1** took place to provide the corresponding hydrogenation product **2** in moderate yield using Amberlite IRC86 (terminal group: CO₂H) as a solid-supported weak acid (entry 1). When Amberlite IR-120 was used (entry 3), the yield

Figure 1. Cyclic voltammograms of (a) water using a Pt disk electrode ($\phi = 1$ mm), (b) 0.2 M Amberlite IR-120/water using a Pt disk electrode ($\phi = 1$ mm), and (c) 0.2 M Amberlite IR-120/water using a GC disk electrode ($\phi = 1$ mm). The scan rate was 100 mV s^{-1} .

Figure 2. Yield of **2** in the recycling of Amberlite IR-120.

Table 1. Electroreduction of **1** using solid-supported acids.

$ \begin{array}{ccc} \text{CO}_2\text{Me} & \xrightarrow[\text{Pt - GC undivided cell}]{\text{solid-supported acid, H}_2\text{O, 10 mA cm}^{-2}} & \text{CO}_2\text{Me} \\ \diagdown & & \diagup \\ \text{C} & & \text{C} \\ \diagup & & \diagdown \\ \text{CO}_2\text{Me} & & \text{CO}_2\text{Me} \\ \mathbf{1} & & \mathbf{2} \end{array} $			
Entry	Solid-supported acid	Electricity / F mol^{-1}	Yield ^a / %
1	0.2 M Amberlite IRC86	6	48
2	0.1 M Amberlite IR-120	5	67
3	0.2 M Amberlite IR-120	5	76
4	0.5 M Amberlite IR-120	5	53
5	0.2 M Silicycle SCX-2	10	7 (76) ^b

^aDetermined by ^1H NMR spectroscopy using toluene as an internal standard.

^bRecovery of **1** in parentheses.

was higher than that in entry 1. The yield of **2** seems to be affected by the acidity of solid-supported acids. However, the yield did not increase simply with increasing the concentration of Amberlite IR-120 (entries 2–4). On the other hand, a large amount of **1** was recovered using Silicycle SCX-2 (terminal group: SO_3H) as a solid-supported strong acid (entry 5). In this case, hydrogen evolution mainly occurred at the cathode. The pH value of the solution was ca. 3 in the presence of Silicycle SCX-2 (solid matrix: silica gel, entry 5), while it was ca. 7 in the presence of Amberlite IR-120 (solid matrix: polystyrene, entries 2–4). The difference of the pH values might be caused by the difference of the water compatibility of the solid matrices. From these results, we selected entry 3 as the best reaction conditions for electroreduction of activated olefins.

Next, we examined the recyclability of Amberlite IR-120 in electroreduction of **1** under the conditions of entry 3 in Table 1. In the recycling experiments, the spent Amberlite IR-120 was regenerated by treating with 1 M aq. HCl. As shown in Fig. 2, the yield of **2** was always more than 65% and did not decrease at all in the recycling of Amberlite IR-120. This clearly suggests that Amberlite IR-120 is recyclable for many times by regeneration. On the other hand, we also examined the reusability of Amberlite IR-120. As a result, Amberlite IR-120 was reusable three times without regeneration. However, the yield of **2** fluctuated after the three times of reuse. The details are now under investigation.

Table 2. Electroreduction of activated olefins using Amberlite IR-120.

$ \begin{array}{ccc} \text{substrate} & \xrightarrow[\text{Pt - GC undivided cell}]{\text{0.2 M Amberlite IR-120, H}_2\text{O, 10 mA cm}^{-2}} & \text{product} \end{array} $				
Entry	Substrate	Electricity / F mol^{-1}	Product	Yield ^a / %
1	$ \begin{array}{c} \text{MeO}_2\text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CO}_2\text{Me} \\ \mathbf{3} \end{array} $	10	$ \begin{array}{c} \text{CO}_2\text{Me} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CO}_2\text{Me} \\ \mathbf{2} \end{array} $	51 (12) ^b
2	$ \begin{array}{c} \text{CO}_2\text{Et} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CO}_2\text{Et} \\ \mathbf{4} \end{array} $	10	$ \begin{array}{c} \text{CO}_2\text{Et} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CO}_2\text{Et} \\ \mathbf{5} \end{array} $	40 [8] ^c
3 ^d	4	4	5	50 [25]
4	$ \begin{array}{c} \text{CO}_2\text{Bu} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CO}_2\text{Bu} \\ \mathbf{6} \end{array} $	10	$ \begin{array}{c} \text{CO}_2\text{Bu} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CO}_2\text{Bu} \\ \mathbf{7} \end{array} $	5 (86)
5 ^d	6	10	7	4 (79)

^aDetermined by ^1H NMR spectroscopy using toluene as an internal standard.

^bRecovery of the substrate in parentheses.

^cCurrent efficiency in brackets.

^dMeCN/H₂O = 1/9 v/v% was used as a solvent.

Finally, as shown in Table 2, we investigated electroreduction of some activated olefins on the basis of the acid-base reaction between Amberlite IR-120 and water. Although **1** had enough solubility, **3** had low solubility to be suspended in water owing to the low polarity (entry 1). Therefore, a large amount of electricity (10 F mol^{-1}) was required until the rough consumption of **3** to provide the corresponding hydrogenation product **2** in moderate yield. The low solubility of **4** in water also caused the low current efficiency (entry 2). In order to solve the solubility problem, we used MeCN as a co-solvent (entry 3). The yield of **5** slightly increased, while the current efficiency increased about three times

compared to that in entry 2. On the other hand, regardless of the use of MeCN as a co-solvent, a large amount of **6** was recovered due to the extremely low solubility in water (entries 4 and 5). This limitation might be overcome by optimizing the co-solvent. From these results, this electrolytic system using solid-supported acids can be available for electroreduction of activated olefins, which have enough solubility in water.

4. Conclusion

We have successfully developed an electrolytic system using solid-supported acids. The system is based on the acid-base reaction between solid-supported acids and water, and the conjugate acid-base pair seems to act as a supporting electrolyte. This system enabled us to conduct electroreduction of some activated olefins without any additional supporting electrolytes. The scope, limitation, and the further application of the electrolytic system are now under investigation.

Acknowledgment

This work was supported by The Iwatani Naoji Foundation.

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