An Environmentally Friendly Electrolytic System Based on the Acid–Base Reaction between Water and Solid-supported Bases

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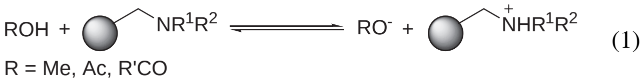
We have developed an environmentally friendly electrolytic system based on the acid–base reaction between water and solid-supported bases. Furthermore, we have successfully applied the electrolytic system to a flow cell.

Since its beginning in the early 1990s, green chemistry has grown into a significant internationally engaged area within chemistry.[1] Over the past two decades, the design of environmentally benign solvents has been one of the leading research areas of green chemistry. Water, ionic liquids, fluorous solvents, and supercritical fluids have emerged as alternative reaction media for organic synthesis. In particular, organic synthesis in water without the use of any harmful organic solvents has long been a major object in green chemistry,[2] because water is a safe, cheap, easily available, and environmentally benign solvent. Therefore, it is of much importance to develop radical new methods for using water as a reaction medium in organic synthesis.

Organic electrosynthesis has recently attracted much attention as one of the most promising green processes in organic synthesis, because it is possible to oxidize and reduce organic compounds without the use of any conventional redox reagents. However, it generally requires large amounts of supporting electrolytes and organic solvents to provide sufficient ionic conductivity and solubilizing ability to the electrolytic media. In order to remove the need for supporting electrolytes, we have recently developed a novel electrolytic system using solid-supported bases.[3,4] The system is based on the acid–base reactions between protic solvents[3] or carboxylic acid substrates[4] and solid-supported bases, and the conjugate acid–base pairs act as supporting electrolytes (eq 1). With the use of solid-supported bases, it is possible to carry out organic electrosynthesis without any additional supporting electrolytes. On the other hand, solid-supported bases may also be applied to the electrolytic system based on the acid–base reaction between water and solid-supported bases. It would enable us to achieve organic electrosynthesis without the use of any additional supporting electrolytes and organic solvents. Thus, we herein report an environmentally friendly electrolytic system based on the acid–base reaction between water and solid-supported bases.



(1)

First of all, in order to confirm the acid–base reaction between water and solid-supported bases, we measured the cyclic voltammograms of water in the absence and presence of silica gel-supported amine (Si–NH_2) using a platinum disk electrode. As shown in Figure 1a, ionic conductivity was hardly observed in the absence of Si–NH_2. In sharp contrast, both the oxidation current for OH^- and the reduction current for H^+ were clearly observed in the presence of Si–NH_2 as shown in Figure 1b. In addition, the solution had a pH of 9.7. These results indicate that the acid–base reaction between water and Si–NH_2 occurs (eq 1; R, R^1, and R^2 = H), and the conjugate acid–base pair seems to play the role of supporting electrolytes. On the other hand, the cathodic potential window was extended to the negative direction up to ca. −2.0 V vs. SCE by using a glassy carbon (GC) disk electrode as shown in Figure 1c. This finding suggests that the electrolytic system based on the acid–base reaction between water and Si–NH_2 is available for electroreduction of organic compounds.

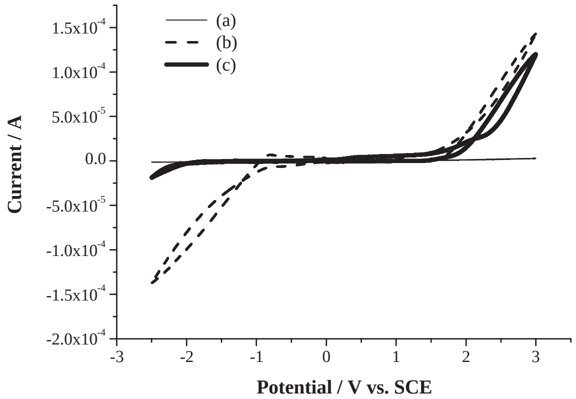


Figure 1. Cyclic voltammograms of (a) water using a Pt disk electrode ($\phi = 1$ mm), (b) 0.1 M Si–NH_2/water using a Pt disk electrode ($\phi = 1$ mm), and (c) 0.1 M Si–NH_2/water using a GC disk electrode ($\phi = 1$ mm). The scan rate was $100\,mV\,s^{-1}$.

We then investigated electroreduction of dimethyl maleate (**1**)[5] as a model reaction using solid-supported bases in water. The typical experimental procedure is illustrated in Figure 2.[6] As shown in Table 1, electroreduction of **1** proceeded smoothly to provide the corresponding hydrogenation product **2** in high to quantitative yields with the use of relatively weak bases (Entries 1–3). While silica gel-supported pyridine, amine (Si–NH_2), and

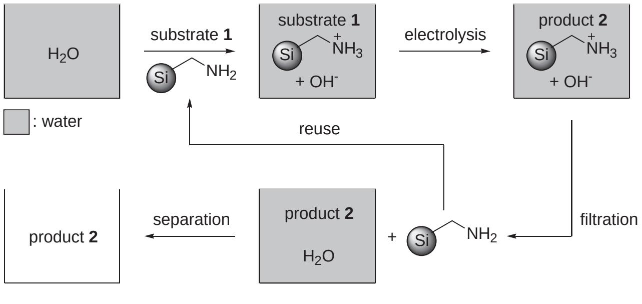
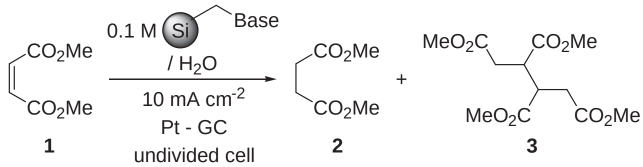
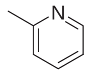
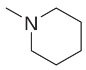
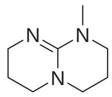


Figure 2. Experimental procedure.

Table 1. Electroreduction of **1** using silica gel-supported bases in water



Entry	Base	pK_a[a]	Electricity /F mol^{-1}	Yield/%[b]	
				2	**3**
1		5.2	7	96	trace
2	—NH_2	9.2	5	quant.	0
3	—NMe_2	10.8	4	88	trace
4[c]		11.2	—	—	—
5		14.5	4	61	15

[a]pK_a value of the conjugate acid. [b]Isolated yield. [c]Silica gel-supported piperidine did not disperse at all in water.

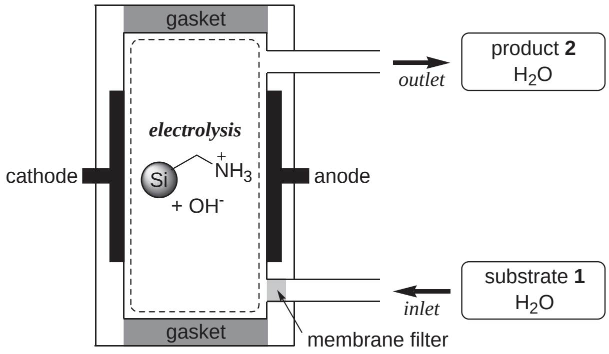
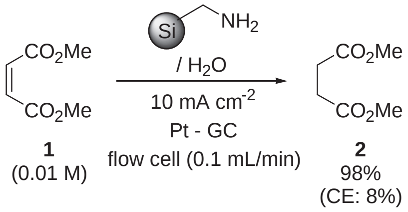


Figure 3. Schematic representation of a flow cell using Si–NH_2.



Scheme 1. Electroreduction of **1** using a flow cell.

dimethylamine uniformly dispersed in water (Entries 1–3), silica gel-supported piperidine did not disperse at all in water even under stirring (Entry 4).[6] This seems to be due to the low hydrophilicity of the piperidine group. When silica gel-supported 1,3,5-triazabicyclo[4.4.0]dec-5-ene was used as a strong base, both the corresponding hydrogenation and coupling products were obtained in 61 and 15%, respectively (Entry 5).[5] From the viewpoints of the dispersibility of solid-supported bases in water and the product selectivity, Si–NH_2 seems to be suitable for hydrogenation of organic compounds.

We next examined the reusability of Si–NH_2 in electroreduction of **1** (Figure 2). Si–NH_2 was reusable for five times [97% (1st), quantitative (2nd), 98% (3rd), 94% (4th), and 95% (5th)] under the conditions of Entry 2 ($6\,F\,mol^{-1}$) in Table 1. However, Si–NH_2 was gradually broken into pieces by mechanical stirring, and hence it swelled in water and clogged the filter in its filtration. In order to overcome the problem, we applied the electrolytic system to a flow cell. The schematic representation of a flow cell using Si–NH_2 is illustrated in Figure 3.[6] Although the current efficiency (CE) was relatively low owing to the limited diffusibility of **1** in the flow cell, electroreduction of **1** was successfully achieved in excellent yield by a single pass of the substrate solution through the flow cell as shown in Scheme 1. Furthermore, Si–NH_2 packed in the flow cell was durable and worked at least for a week. The flow cell enabled us to eliminate a step for the separation of Si–NH_2.

In summary, we have developed an environmentally friendly electrolytic system based on the acid–base reaction between water and solid-supported bases. This system enables us to carry out organic electrosynthesis without any additional supporting electrolytes and organic solvents. Furthermore, we have successfully applied the electrolytic system to a flow cell. It is expected that many useful electroorganic reactions will be achieved by using the flow cell based on the acid–base reactions between various protic solvents or carboxylic acid substrates and solid-supported bases.

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6 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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