

Development in New Electrolytic Systems. Anodic Substitution Reactions Using Solid-Supported Bases

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The study of the electrochemistry of organic compounds has more than 150 years of history and well-known Kolbe reaction seems to be the first finding which suggests that the electrochemical reaction is one of the most useful methods in organic synthesis. The electrohydrodimerization of acrylonitrile to adiponitrile, an intermediate to nylon, developed by Monsanto in early 1960's is operating at several sites worldwide now.¹ In electroorganic synthesis the formation of an active species from a substrate is achieved by the electron transfer between the substrate and an electrode. Therefore, an attractive feature of electroorganic synthesis is that it has the possibility of controlling not only electron transfer but also reactions because oxidation and reduction processes depend mainly on the potential of the electrode at which they take place. In addition, electroorganic synthesis is an environmentally friendly process because electrons are inherently environmentally friendly reagents compared with conventional oxidizing and reducing reagents. In spite of these characteristics, only a few processes of electroorganic synthesis have been commercialized. There are some reasons for the slow development in electroorganic synthetic processes. One of the biggest reasons is the use of supporting electrolytes. Supporting electrolytes are required in order to provide ionic conductivity to electrolytic organic solvents. However, it is necessary to remove or recycle supporting electrolytes from the solvents after the electrolysis, and the removed supporting electrolytes become industrial wastes. From these facts in mind, it is very important to develop the supporting electrolyte free system for electroorganic synthesis, and it will contribute the industrialization of electroorganic synthetic processes.

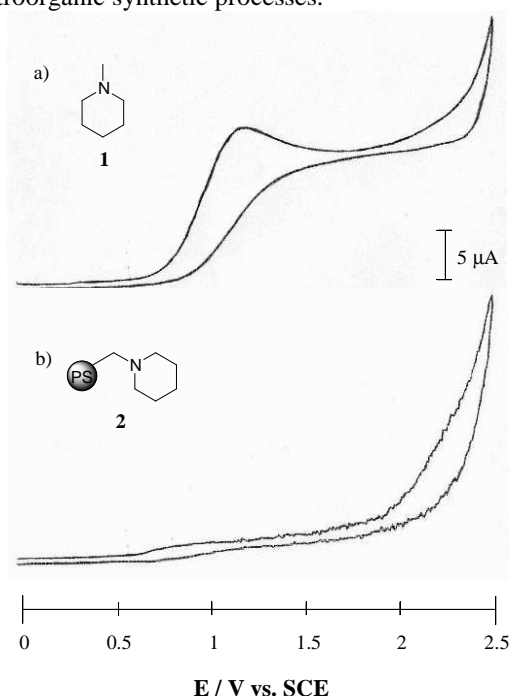


Fig. 1 Cyclic Voltammograms of **1** and **2**.

Substrate: 0.1 mmol, 0.1 M Bu₄N-BF₄ / MeCN,
W.E.: Pt Disc, C.E.: Pt Wire, Scan Rate: 100 mV/sec.

It is well known that electron transfer between solid and solid is very difficult. Therefore, it was expected that solid-supported bases play roles of not only bases in bulk solutions but also electrochemically inactive reagents at the electrode surface. On the other hand, a lot of solid-supported bases are now commercially available owing to development in combinatorial chemistry in the last decade. Then, at first, the cyclic voltammograms of *N*-methylpiperidine **1** and piperidinomethyl polystyrene **2** were measured in 0.1 M *n*-Bu₄N-BF₄/anhydrous acetonitrile. As shown in Fig. 1, **1** was easily oxidized (Fig. 1a), but **2** was not oxidized even with stirring (Fig. 1b).

Next, **2** was added into methanol (0.1 M), and the cyclic voltammogram of this solution was measured. As shown in Fig. 2, the oxidation wave of methoxide anions was observed, and it seems that methanol was dissociated into a methoxide anion and a proton. Therefore, in this system, when methanol and **2** are mixed, methoxide anions and protons are generated and the resulting protons become main carrier of an electronic charge. Then, we investigated anodic α -methoxylation in this system.

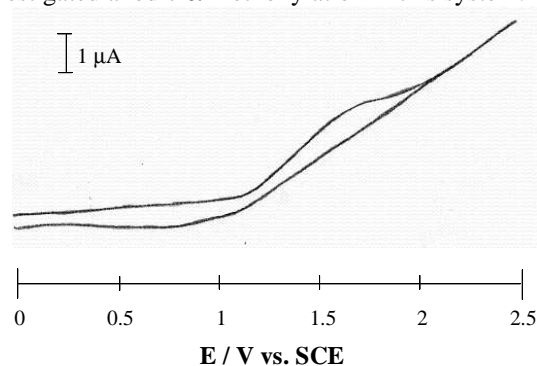


Fig. 2 Cyclic Voltammograms of **2** in Methanol.

W.E.: Pt Disc, C.E.: Pt Wire, Scan Rate: 100 mV/sec.

Anodic methoxylation of sulfide **3** was attempted using various silica gel supported bases. As shown in Table 1, anodic methoxylation of **3** took place efficiently to provide the methoxylated product **4** in moderate to high yields. Further investigation is now in progress.

Table 1. Anodic Methoxylation of **3** Using Silica Gel Supported Bases

$\text{PhS-CH}_2\text{-CF}_3 \xrightarrow[\text{3 F/mol, 10 mA/cm}^2 \text{ (Pt)-(Pt)}]{\text{0.1 M (S)}_3\text{Base / Methanol}} \text{PhS-CH(OMe)-CF}_3$					
Entry	Base	Yield (%) ^a	Entry	Base	Yield (%) ^a
1		52	5		76
2		51	6		89
3	-NMe ₂	36	7		70
4		54			

^a Determined by ¹⁹F NMR Spectroscopy.

Acknowledgements

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Reference

- 1) H. Lund, O. Hammerich, *Organic Electrochemistry*, 4th ed., Marcel Dekker, New York, 2001.