

Electrosynthesis Using Microflow Systems

Roberto Horcajada, Masayuki Okajima, Seiji Suga, and Jun-ichi Yoshida

Department of Synthetic Chemistry & Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510

Micro flow reactors have received significant interest in the stream of downsizing of chemistry, and they are expected to make an innovative and revolutionary change for chemical synthesis. In addition to the safety and environmental benefits of dealing with smaller quantities of material, microflow reactors have several advantages over conventional systems stemming from the high surface-to-volume ratio; e.g. precise temperature control and high efficiency of heterogeneous mass transfer. Short residence times in reactors may also be advantageous from a viewpoint of the control of highly reactive intermediates. The advantages of microflow reactors of easy modulation and the possibility of combining reactors in parallel promising a quick means for scale-up also warrant comment.

Recently we have developed “cation flow” method using microflow electrochemical reactors, which involves generation of highly reactive carbocations by low temperature electrolysis.¹ This method enables the manipulation of carbocation intermediates to achieve direct oxidative C-C bond formation.

The advantages of microflow electrochemical reactors² over conventional electrochemical reactors are as follows: (1) high electrode surface to reactor volume ratio, (2) short distance between the anode and the cathode. Based on these inherent advantages of microflow electrochemical reactors, we have been developing organic electrochemical processes using microflow systems and herein we report some preliminary results of this study.

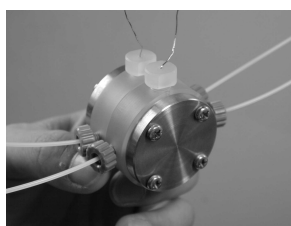
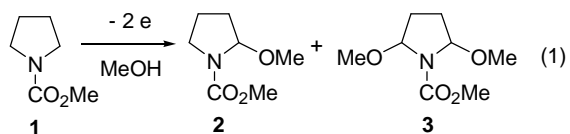


Figure 1. Microflow electrochemical reactor (outside)

At first we focused on anodic methoxylation of methyl pyrrolidinecarboxylate (**1**) (eq 1), because this reaction serves as a useful transformation in organic synthesis of a variety of nitrogen-containing compounds.³



A microflow electrochemical reactor shown in Figure 1, which was composed of diflone and stainless steel bodies by a mechanical manufacturing technique, was used. The two-compartment cell was divided by a diaphragm of PTFE membrane. Each compartment was filled with carbon felt electrode made of carbon fibers ($\phi = 10 \mu\text{m}$).

The reaction proceeded smoothly to give monomethoxylated compound **2** together with dimethoxylated compound **3**. The effects of process parameters (the direction of the flow, the flow rate, the shape and size of the chambers (electrodes) (Figure 2) on the yield and distribution of the product were examined.

The applications of microflow systems to other organic electrochemical synthesis will be also discussed in the presentation.



Figure 2. Some microflow electrochemical reactors (inside)

References

- (a) S. Suga, M. Okajima, K. Fujiwara, and J. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 7941; (b) J. Yoshida and S. Suga, *Chem. Eur. J.* **2002**, *8*, 2650.
- (a) H. Löwe, W. Ehrfeld, *Electrochimica Acta* **1999**, *44*, 3679; (b) M. Küpper, V. Hessel, H. Löwe, W. Stark, J. Kinkel, M. Michel, H. Schmidt-Traub, *Electrochimica Acta* **2003**, *48*, 2889; (c) V. Mengeaud, O. Bagel, R. Ferrigno, H. H. Girault, A. Haider, *Lab Chip* **2002**, *2*, 39; (d) C. A. Paddon, G. J. Pritchard, T. Thiemann, and F. Marken, *Electrochem. Commun.* **2002**, *4*, 825. For macroflow electrochemical reactors, see: C. Karakus and P. Zuman, *J. Electrochem. Soc.* **1995**, *142*, 4018.
- (a) T. Shono, Y. Matsumura, K. Tsubata, *J. Am. Chem. Soc.* **1981**, *103*, 1172; (b) T. Shono, Y. Matsumura, K. Tsubata, S. Yamane, T. Kanazawa, T. Aoki, *J. Am. Chem. Soc.* **1982**, *104*, 6697.