Conversion of CFC-13 to Trifluoroacetic Acid by Electrochemical Reaction with Carbon Dioxide

Noriyuki Sonoyama* and Tadayoshi Sakata
Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8502

(Received November 20, 2001; CL-011173)

The electrochemical conversion of CFC-13 ($CClF_3$) and carbon dioxide into trifluoroacetic acid (TFAA) was attempted at a Ag wire electrode under high pressure. TFAA was efficiently produced and the current efficiency was slightly dependent on the potential during electrolysis and pressure of co-existing carbon dioxide.

Chlorofluorocarbons (CFCs) are known to cause depletion of the ozone layer in the stratosphere[1,2] and the production of the specified CFCs has been discontinued since 1995. However, large amounts of CFCs are still in use as the refrigerants in refrigerators and air conditioners. These CFCs in use should be recovered and converted into recyclable compounds. One of the most reasonable CFC treatment methods would be to replace chlorine in CFCs, that gives CFCs the potential for ozone layer depletion, with other atoms without removing fluorine atoms from CFCs. We have carried out the electrochemical conversion of CFCs to hydrofluorocarbons (HFCs) that have no potential for depleting the ozone layer and therefore are considered as the substitute of CFCs.[3,4] Although HFCs are recyclable as the substitute of CFCs, the development of the next generation refrigerants has been attempted.[5] From the long-term point of view, a method of CFC conversion to other valuable products would be needed. The electrochemical formation of tetrafluoroethylene, the monomer of Teflon, from CFC-12 (CCl_2F_2) was reported by several groups.[6,7] This method would be very useful for the recycle of CFC-12, because this method produces a recyclable industrial material from CFC-12. In the case of mono-chloro-CFCs, such as CFC-13 ($CClF_3$), dimer products are not able to be recycled as the monomer of plastics because no double bond is produced by the dimerization of mono-chloro-CFCs with selective dechlorination. On the other hand, it is well known that carbanions attack carbon dioxide and efficiently forms carboxylic acids. If fluoro carbanions can be electrochemically produced from mono-chloro-CFCs by the electrochemical method, mono-chloro-CFCs can be converted to fluorocarboxylic acids via the reaction with carbon dioxide that is also a greenhouse gas. This method will be useful for the recycle of CFCs, because fluorocarboxylic acids are also recyclable as industrial materials. In this letter, we attempted electrochemical conversion of CFC-13 to trifluoroacetic acid using a Ag electrode, that is known to selectively break the C-Cl bond of CFC-13[4], in the presence of carbon dioxide.

All electrolyses were carried out in the stainless steel autoclave. The structure of the autoclave was described elsewhere.[3] As the working and counter electrodes, Ag (length (L) 50 cm, diameter (D) 1 mm) and Al (L 30 cm, D 1 mm) wires were used, respectively. A Ag wire (L 10 cm, D 0.5 mm) was used as a reference electrode. For the measurement of the current-potential curves, a Ag wire (L 3 cm, D 1 mm) and a Pt wire (L 30 cm, diameter 0.3 mm) were used as the working and counter electrodes, respectively. The electrolyte solution was 50 ml of dry acetonitrile (Kanto Chemical Co., Inc.) containing 0.1 M tetra(n-butyl ammonium) bromide (Wako Pure Chemical Industries, Ltd.) that was dried in a vacuum oven at 110 °C for 3 days. Before electrolysis, dissolved oxygen was removed from the electrolyte solution by bubbling purified Ar gas for at least 20 min. 10 atm of CFC-13 was introduced into the autoclave and then further compressed carbon dioxide was introduced. Electrolysis started 1 h after the introduction of the gases for saturation of the electrolyte solution with the gases. Electrolyses were carried out at least twice with an error of at most 10% in current efficiency, where the current efficiency is defined as the ratio of the charge used for the formation of each product to the total charge passed during electrolysis. Analysis of products in the gas and liquid phases was carried out by gas chromatography and ^{19}F-NMR, respectively.

Figure 1 shows the current-voltage (C-V) curves at a Ag electrode under the atmospheric pressure of Ar, carbon dioxide and CFC-13 gas. Under CFC-13, the current began to flow around -1.0 V, whereas the current started flowing from -1.5 V under the carbon dioxide atmosphere. Considering the result that the current was hardly observed even at -2.0 V under the Ar gas, these cathodic current under CFC-13 and carbon dioxide is the reduction current of these gases. This reduction potential hardly affected by the increase in the pressure. These results indicate that CFC-13 can be selectively reduced in the potential range from -1.0 to -1.5 V. Current efficiencies for the product formation in electrolysis at the Ag wire electrode at the various potentials are summarized in Table 1. The condition was that the initial 10 atm of CFC-13 was introduced into the autoclave and then carbon dioxide was introduced until the total pressure reached 20 atm (the initial partial pressure of each gas was 10 atm). Trifluoroacetic acid (TFAA) was obtained with high selectivity (69.6–

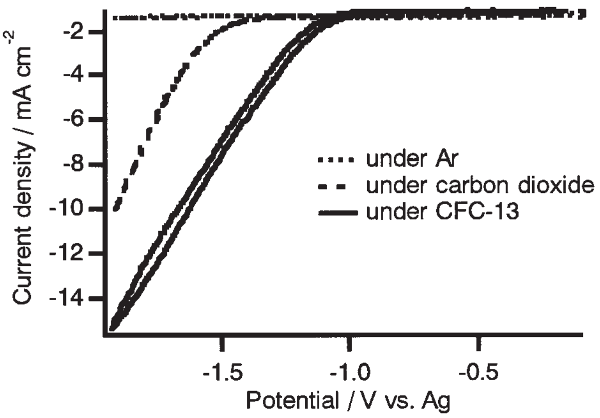

Figure 1. The current-voltage curves at the Ag electrode in acetonitrile. The scan rate was 50 mV s^{-1}.

Table 1. The current efficiency for the product formation at the various potentials in electrolysis of CFC-13 in the presence of carbon dioxide at the Ag electrode

Potential	Current eficiency/%						
	[a]TFAA	CHF_3	CO	CH_4	formic acid	H_2	total
−1.0	69.6	12.3	[b]nd	nd	0.1	12.0	93.7
−1.25	75.3	10.2	nd	nd	0.4	18.0	103.9
−1.5	85.2	5.6	nd	nd	0.2	6.1	97.1
−2.0	72.5	2.0	4.7	nd	0.2	18.9	98.3

The initially introduced partial pressure of CFC-13 and carbon dioxide were 10 atm. [a]Trifluoroacetic acid. [b] Not detected.

85.2% in the current efficiency). Other by-products were hydrogen, trifluoromethane (HFC-23) and the carbon dioxide reduction products (carbon monoxide and formic acid). The current efficiency for the TFAA formation was not significantly dependent on the potential during electrolysis and the carbon dioxide reduction products were the minor ones even at −2.0 V, where a certain reduction current of carbon dioxide was observed in the C-V curve (Figure 1). These results suggest that CFC-13 is selectively reduced at the Ag electrode even in the presence of carbon dioxide. In Figure 2, the dependence of the current efficiency for the product formation on the initial partial pressure of carbon dioxide co-existing with CFC-13 was plotted under the condition that the initial partial pressure of CFC-13 was 10 atm at −1.5 V vs Ag. Although trifluoromethane was produced with a current efficiency of about 10% in the lower pressure region, the selectivity of TFAA hardly depended on the pressure of co-existing carbon dioxide. The dimer products of CFC-13 also could not be detected. These results indicate that the TFAA formation efficiently proceeds even under the condition that the concentration of carbon dioxide in the electrolyte solution is lower. The mechanism of this reaction is presumed as follows. Accepted electron from the Ag electrode localizes in the Cl atom of CFC-13. After the elimination of the Cl^- anion, CF_3^- anion radical is produced on the surface of the Ag electrode by the reduction of $CF_3\bullet$ radical. Aymard et al. also stipulated CF_3^- as the intermediate of the electrochemical reduction of CF_3Br.[8] CF_3^- anion radical nucleophilically attacks carbon dioxide to form TFAA. If sufficient amount of carbon dioxide is not supplied to the surface of the electrode, CF_3^- anion radical would abstract hydrogen from the solvent molecule to form trifluoromethane, or attack CFC-13 and dimer products are formed, because an anion radical is generally very reactive intermediate. Contrary to this consideration, the current efficiency for the TFAA formation was hardly dependent on the partial pressure of co-existing carbon dioxide. This result seems to suggest that CF_3^- anion radical is stabilized on the surface of the Ag electrode and selectively attacks carbon dioxide.

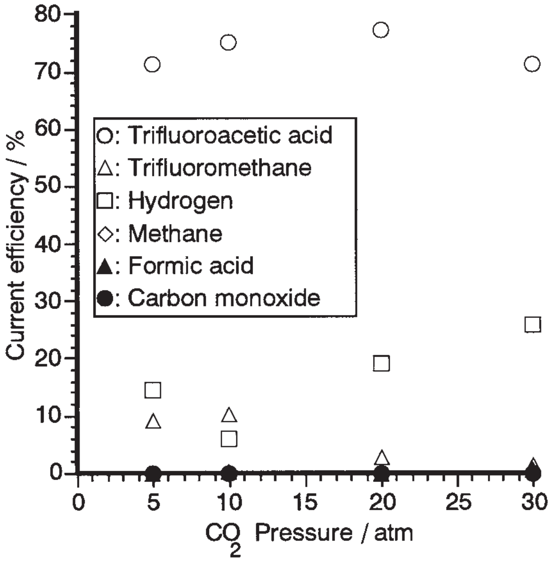

Figure 2. Relationship between the current efficiencies for product formations and the initial partial pressure of co-existing carbon dioxide at the Ag electrode at −1.5 V vs Ag in acetonitrile.

We thank Prof. Toshio Fuchigami and Dr. Hideki Ishii for the NMR measurements and their kind advice. We are thankful for the helpful discussion with Dr. Hidetoshi Tokuyama. This study was partly supported by "Ground Research Announcement for Space Utilization" promoted by NASDA and Japan Space Forum.

References

1 M. J. Molina and F. S. Rowland, *Nature*, **249**, 810 (1974).
2 M. J. Prather and R. T. Watson, *Nature*, **344**, 729 (1990).
3 N. Sonoyama and T. Sakata, *Environ. Sci. Technol.*, **32**, 375 (1998).
4 N. Sonoyama and T. Sakata, *Environ. Sci. Technol.*, **32**, 4005 (1998).
5 A. Sekiya and S. Misaki, *CHEMTECH*, **26**, 44 (1996).
6 N. S. Stepanova, M. M. Gol'din, and L. G. Feoktistov, *Soviet Electrochem.*, **12**, 1070 (1976).
7 A. Schizodimou, G. Kyriacou, and Ch. Lambrou, *J. Electroanal. Chem.*, **471**, 26 (1999).
8 F. Aymard, J.-Y. Nédélec, and J. Périchon, *Tetrahedron Lett.*, **35**, 8623 (1994).