Reductive Electrochemical Decomposition of Chloroform on Metal Electrodes

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

(Received September 26, 1996)

The electrochemical reductive decomposition of chloroform was carried out using 15 kinds of metal electrodes. The efficiency of the decomposition and the main product of reaction largely depended on the metal electrodes. The hydrogenation of chloroform by Ag, Zn, Pd and Cu electrodes proceeded in about 100% efficiency. These electrodes produced methane mainly. Pb electrode produced dichloromethane selectively.

In 1970s, it was revealed that trihalomethanes formed in the disinfection process of tap water are carcinogens.[1] Recently, trichloroethylene and tetrachloroethylene, wasted from the factories, contaminated groundwater widely and chlorinated hydrocarbons dissolved in water came to be a serious social problem. The studies of the decomposition of these volatile chlorinated hydrocarbons have been carried out mainly by the photo-catalytic method [2] and gene-manipulated bacteria.[3,4] However, these methods are still in experimental stages. The electrochemical method is already used, e.g., for the treatment of cyanide. However, there have been few reports on the decomposition of volatile chlorinated hydrocarbons by the electrochemical method.[5, 6] Horinyi and Torkos investigated electrolysis of chloroform using Pt electrode and found methane gas was produced.[5] Nishimoto *et al.* carried out electrolysis of chloroform using five kinds of metal electrodes.[6] They reported that by using of Cu electrode, a small amount of hydrocarbons (ethane, ethylene and propylene) was produced as well as methane and Pb electrode produced dichloromethane as a main product of electrolysis. In spite of these reports, the number of metal electrodes tested is not enough and the metal electrodes which have good catalytic activity for volatile chlorinated hydrocarbons are still unknown. In this paper, we carried out the reductive electrochemical decomposition of chloroform, the representative volatile chlorinated hydrocarbon, using 15 kinds of metal electrodes and found that the decomposition of chloroform proceeds in about 100% efficiency by using Ag, Zn, Pd and Cu electrodes.

All the metal electrodes were polished electrolytically in conc H_3PO_4 (85%) or with an alumina polishing suspension. The area of working electrodes was 16-18 cm^2. A Pyrex cell was employed; the anode compartment was separated from the cathode by glass filter. The potential of cathode was measured with respect to an Ag/AgCl/saturated KCl reference electrode. A Pt wire was used as an anode. The electrode potential was corrected for the IR drop between the reference and the cathode. The aqueous electrolyte was 0.1 M K_2SO_4 (GR Wako pure Chemical). Purified N_2 gas was bubbled into the solution at least for 20 min to remove dissolved oxygen. 0.1 ml of chloroform (for trihalomethane measurement; Wako) was introduced into solution (200 ml) by using a syringe. The concentration of chloroform was 6.20 m mol/l. Solution was stirred vigorously with a magnetic stirrer until chloroform was dissolved into the solution. The sampled gas from the cell was analyzed by gas chromatography. Galvanostatic electrolysis experiments were carried out at a constant current (1 mA cm^{-2}). The total charge passed during electrolysis was 50C.

The Faradaic efficiencies of main products using each metal electrode were summarized in Table 1. The products of Cu, Ni, Pb and Fe agreed with the result of Nishimoto *et al.*.[6] In Table 1, Ef_r, Ef_c and Ef_d are the efficiency of the decomposition of chloroform, that of the production of hydrocarbons and that of the production of dichloromethane defined by the following equations,

$$Ef_r = \frac{FE_c + FE_d}{FE_c + FE_d + FE_H} \quad (1)$$

$$Ef_c = \frac{FE_c}{FE_c + FE_d + FE_H} \quad (2)$$

$$Ef_d = \frac{FE_d}{FE_c + FE_d + FE_H} \quad (3)$$

where, FE_c, FE_d and FE_H are the faradaic efficiencies of hydrocarbons, dichloromethane and hydrogen, respectively. Ef_c and Ef_d are defined for the detailed comparison of electrodes, because the total faradaic efficiencies for electrodes were not the same.

The efficiencies of reduction of chloroform and the products of electrolysis depended strongly on the electrode metal. Main products of reduction of chloroform were methane and dichloromethane. Ethane, ethylene, propane and propylene were produced on many metal electrodes with low efficiency. This result indicates that reduction of chloroform causes the release of Cl^- ion and following hydrogenation. As a by-product, H_2 gas was produced from the electroreduction of H_2O. As shown in Table 1, Cu, Zn, Pd, Ag and Pb showed good catalytic activity of reduction of chloroform. Ag and Zn indicated especially good catalytic activity near to 100% with little H_2 production. Concerning the selectivity of the products, Ag, Pd, Cu and Zn electrodes produced mainly methane. Pb and Sn electrodes produced dichloromethane preferentially. The main product of the other electrodes was H_2. The Faradaic efficiency of H_2 by Al electrode exceeded 100% significantly. This result would be attributable to the dissolution of Al electrode by HCl which is produced by reduction of chloroform.

A careful inquiry of Table 1 suggests that the decomposition efficiency of chloroform and the selectivity of the products have periodicity to a certain extent. Pd (the group VIII) and groups I B, II B and IV B(Cu, Ag, Zn and Pb) have good activity of the decomposition of chloroform and the other metals have low activity on the whole. The efficiency of the production of hydrocarbon was high in a part of group VIII and groups I B and II B(Pd, Cu, Ag and Zn). For the efficiency of the production of dichloromethane, the group IV B showed high activities; Pb showed very high activity and Sn electrode produced

Table 1. Faradaic efficiency and efficiency defined by eqs. (1)-(3) of electrochemical reduction of chloroform on various electrodes

	E^a	Faradaic efficiency /%					Efficiency defined by eqs. (1)-(3)		
Electrode	/V	CH_4	HC^b	CH_2Cl_2	H_2	Total	Ef_r	Ef_c	Ef_d
Cu	-1.10	42.7	6.0	32.9	3.6	85.2	95.8	57.2	38.6
Ag	-0.96	66.0	9.5	6.2	n	81.7	100	92.4	7.6
Pd	-1.15	48.3	7.7	19.4	5.3	80.7	93.4	69.4	24.0
Zn	-0.65	93.6	0.4	13.5	0.5	108.0	99.5	87.0	12.5
Ni	-1.27	20.5	4.7	23.8	41.4	90.4	54.2	27.9	26.3
Pb	-0.65	3.4	n^c	87.4	8.5	99.3	91.4	3.4	88.0
Sn	-0.85	3.5	0.3	27.4	63.1	94.3	33.1	4.0	29.1
Co	-1.24	3.1	0.7	9.3	89.8	102.9	12.7	3.7	9.0
Nb	-1.09	27.4	2.6	18.1	40.9	89.0	54.0	33.7	20.3
Ta	-1.38	7.0	0.7	9.2	81.4	98.3	17.2	7.8	9.4
Mo	-0.64	5.1	0.6	11.0	84.0	100.7	16.6	5.7	10.9
Ti	-0.64	18.9	0.8	18.2	52.9	90.8	41.7	21.7	20.0
Fe	-0.63	3.1	0.8	16.2	76.6	96.7	20.8	4.0	16.8
Zr	-0.65	4.4	0.4	6.9	80.3	92.0	12.7	5.2	7.5
Al	-0.82	3.1	0.4	7.5	178.0	189.0	5.8	1.9	4.0

[a] E: Electrode potential v.s. Ag/AgCl, [b] Total of other hydro carbons (ethane, ethylene, propane and propylene), [c] n: Not detected.

dichloromethane seven times more than hydrocarbons. In the electrochemical reaction in aqueous medium, reductive reactions on the electrode compete with reduction of water. Therefore, the products of electrolysis seem to depend on the hydrogen overvoltage of the electrodes; the electrode with a low hydrogen overvoltage mainly produces hydrogen and the electrode with a high hydrogen overvoltage is liable to produce other products. Contrary to this expectation, reduction of chloroform does not follow this tendency; e.g., Pd electrode with a low hydrogen overvoltage produced H_2 with only 6.5% efficiency and Sn electrode with a high hydrogen overvoltage produced H_2 with 67% efficiency. This difference in efficiency seems to be attributable to the difference in the adsorption of chloroform on electrode metals.

Concerning the toxicity of chloro-hydrocarbons, Masuda *et al.* reported that the toxicity decreases with the decrease of the number of chlorine.[7] Therefore, the electrochemical method would be effective in detoxifying the chloroform dissolved water.

References and Notes

1 R.H.Harris and E.M.Brechen, "Is the water safe to drink", Part 1,2 and 3, Consumers report (1974).
2 A.L.Pruden and D.F.Ollis, *Environ.Sci.Technol.*, **17**, 628 (1983).
3 R.B.Winter, K.-M.Yen and B.D.Ensley, *Bio/technology*, **7**, 282 (1989).
4 G.J.Zylstra, L.P.Wackett and D.T.Gibson, *Appl. Environ. Microbio.*, **55**, 3162 (1989).
5 G.Horinyi and K.Torkos, *J.Electroanal.Chem.*, **140**, 329 (1982).
6 S.Nishimoto, H.Hatta, H.Fu, T.Atsumi and T.Kagiya, *Jpn. J. Water Pollution Res.*, **11**, 107 (1988).
7 Y.Masuda, I.Yano and T.Murano, *J.Pharm.Dyn.*, **3**, 53 (1980).