Electrochemical Dechlorination of Chlorinated Hydrocarbons – Electrochemical Reduction of Chloroform in Acetonitrile/Water Mixtures at High Current Density

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Electrochemical reduction of chloroform was studied in 0.1 M (1 M = 1 mol dm^{-3}) tetraethyl ammonium perchlorate solutions of acetonitrile–water mixture using various metal electrodes. High water concentration (1 M) promoted the electrolysis with the products mainly CH_4 and CH_2Cl_2. The partial current density of CH_4 formation amounted to 0.3 A cm^{-2} at an Ag electrode.

Electrochemical reduction of chlorinated hydrocarbons may contribute to a new detoxification process operated safely with a compact device at ambient temperature and pressure. However, the low solubility of chlorinated hydrocarbons limits the electrolysis current less than 1 mA cm^{-2} in aqueous solutions.[1–6] Application of nonaqueous solutions enhances the current density as reported for reduction of 2,4-dichlorophenoxyacetic acid (2,4-D)[7] and CFC-113[8] in methanol based electrolytes with current density of 100 mA cm^{-2} or more. However, the electrodes are deteriorated by formation of thick film[9] or metal organic products[10] on the electrode surface during the electrolysis in nonaqueous solutions, suppressing the current density. This paper demonstrates electrochemical reduction of chloroform at high current density in 0.1 M tetraethylammonium perchlorate (TEAP) solutions of acetonitrile(AN) – water mixture. We also attempt to reveal the catalytic activity of metal electrodes for electrochemical dechlorination of chlorinated hydrocarbons.

The main features of the experimental procedures were described in an article published from our laboratory.[11] The electrodes were wires or foils of 99.99% purity with apparent surface area ca. 0.6 cm^2, etched in 1:1 mixture of nitric acid and water. Electrolysis cell was a one compartment type with the anolyte and catholyte not separated. The potential is given with respect to the ferrocene redox potential, whereas the reference electrode was Ag/Ag$^+$ (0.01 M $AgNO_3$ in AN). The liqid junction potential was corrected. The ohmic drop between the Luggin capillary tip and the electrode was also corrected.

The gaseous products were analyzed with gas chromatographs. The gaseous products were taken from the gas phase, after the gaseous products in the electrolyte were purged out to the gas phase by supersonic irradiation. The products dissolved in the liquid phase were analyzed by a gas chromatograph or a gas chromatograph-mass spectrometer (Shimadzu QP5050).

Cyclic voltammograms were measured with various metal electrodes with water concentration of 10 mM under argon atmosphere. The cathodic current obtained with the electrolyte solution containing 5 mM $CHCl_3$ starts at much more positive potential at all the electrodes than those without chloroform. Thus the reduction of chloroform apparently proceeds more favorably than hydrogen evolution at all the electrodes.

Figure 1 shows a time course of the current density in a controlled potential electrolysis of chloroform at an Ag electrode at −2.58 V with H_2O concentration of 8 mM. The current density steeply dropped in 5 min. Yellowish brown film was found to cover the electrode surface after the electrolysis. The film was insulative, although the substance was not identified. The rapid drop of the current density in Figure 1 may be attributed to the film formation. The current decay and the film formation were observed for all the metal electrodes in the present study. Such film formations were previously reported by others.[9]

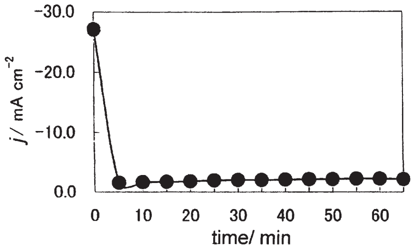

Figure 1. A time course of the current density during the electrochemical reduction of $CHCl_3$ at an Ag electrode at −2.58 V vs Fc/Fc$^+$. Electrolyte: 0.1 M TEAP in acetonitrile. H_2O: 8 mM. $CHCl_3$: 20 mM.

CH_4 and CH_2Cl_2 were the main products in the present measurements with small fraction of C_2H_4 less than 2% in the current efficiency. An electrochemical reaction applied to calculation of the current efficiency is exemplified for CH_4 formation as below. Similar equations are used for other products.

$$CHCl_3 + 3H_2O + 6e^- = CH_4 + 3Cl^- + 3OH^-$$

Table 1 presents the current efficiencies of the products obtained in the controlled potential reduction of chloroform. The

Table 1. Electrochemical reduction of $CHCl_3$

Electrode Metal	H_2O/ mM	Current efficiency/%			Av. C. D.[a] / mA cm^{-2}
		CH_4	CH_2Cl_2	H_2	
Ag	8.2	60.3	3.7	0.2	2.13
Zn	4.5	53.6	7.4	1.9	2.11
Pb	14.9	37.9	23.9	0.7	2.43
Cd	4.9	20.1	28.1	0.5	3.03
Cu	16.2	3.7	52.1	0.7	1.05
Fe	2.7	1.6	43.2	1.6	0.64
Au	3.7	0.7	43.2	0.8	1.42
Ni	7.4	0.2	51.0	1.5	0.64
Pt	7.5	0.2	48.7	3.8	0.58
Sn	3.9	0.2	45.5	0.4	1.13

Electrolyte: 0.1 M TEAP/ AN, $CHCl_3$: 10 mM (20 mM for Ag). Electrode potential: −2.88 V vs Fc/Fc$^+$ for Zn and −2.58 V for other electrodes. Total electricity in the electrolyses: 3 to 16 C. [a]Av. C. D.: Average current density.

electrode potential was −2.88 V for Zn, and −2.58 V for other electrodes. The concentration of chloroform was 20 mM for the Ag electrode, and 10 mM for the other electrodes. The current density changed during the electrolysis as mentioned above, and the average current density are given in Table 1. The total value of the current efficiencies are less than 100%. The rest of the current efficiencies may be attributed to the brown film formation on the electrode, other products not given in Table 1, and gaseous products dissolved in the electrolyte solution not successfully recovered by the present experimental procedures.

We studied the effect of H_2O on the reduction of chloroform at the Ag electrode. Electrolyses in the electrolytes with H_2O concentration exceeding 970 mM did not cause film formation on the electrode; the current density remained stably high during the electrolyses. Table 2 shows that higher H_2O concentration as well as chloroform concentration significantly enhances the current density. The average current density amounted to 358 mA cm^{-2} with the partial current of CH_4 formation exceeding 300 mA cm^{-2}. Such a high current density, equivalent to that of the industrial electrolytic process, encourages further intensive studies aiming at industrial applications of electrochemical detoxification of chlorinated hydrocarbons.

Table 2. Electrochemical reduction of $CHCl_3$ at an Ag electrode

Conc.[a]/mM		Current efficiency/%				Av. C. D.[b]
H_2O	$CHCl_3$	CH_4	CH_2Cl_2	CH_3Cl	H_2	/mM cm^{-2}
244	10	65.5	n. a.[c]	n. a.	0.1	21
973	10	55.4	n. a.	n. a.	2.8	31
1008	50	58.5	6.7	2.6	0.8	121
1036	100	79.8	9.2	2.6	0.4	279
1993	100	78.5	10.4	2.7	0.5	358

Electrolyte: 0.1 M TEAP/ AN. Electrode potential: −2.58 V vs Fc/Fc^+. [a]Conc.: Concentration. [b]Av. C. D.: Average current density. [c]n. a.: not analyzed.

We studied the electrochemical reduction of chloroform at other metal electrodes in 0.1 M TEAP/AN with 1000 mM H_2O. No film formation was observed on the electrodes; the current density was nearly constant during the electrolyses. Table 3 presents the results of controlled potential electrolyses at various metal electrodes at −2.58 V with 1000 mM H_2O and 50 mM $CHCl_3$. Higher water concentration evidently promotes the reduction of chloroform at all the metal electrodes.

A control electrolysis experiment was conducted at −2.58 V with the Ag electrode in 0.1 M TEAP/AN with 1 M H_2O without chloroform. The average current density was as low as −1.3 mA cm^{-2}, and the gaseous product was H_2 with trace amounts of CH_4 and C_2H_4 probably produced from decomposition of AN or TEAP. Therefore the products in the present study were obtained from the reduction of chloroform. Another control measurement was tested; no electrolysis current was given with the Ag electrode and using identical procedures. Neither CH_4 nor CH_2Cl_2 formation was observed at all.

Table 3 demonstrates that the Ag electrode gives the highest electrocatalytic activity among the metal electrodes tested. This result agrees with Sonoyama et al. s' one obtained with aqueous media.[1] Rondinini et al. also reported high activity of Ag for reduction of organic halides in comparison with glassy carbon and Hg electrodes.[9]

Table 3. Electrochemical reduction of $CHCl_3$ in the electrolytes with high H_2O concentration

Electrode	Current efficiency/%				Av. C. D.[a]/
Metal	CH_4	CH_2Cl_2	CH_3Cl	H_2	mA cm^{-2}
Ag	58.5	6.7	2.6	0.8	121.0
Cd	53.4	20.7	2.5	0.1	73.5
Cu	43.6	20.2	1.4	10.5	90.3
In	38.7	19.5	7.3	0.2	74.6
Pd	41.7	33.5	7.7	2.1	56.3
Zn	49.4	45.1	1.3	0.4	68.7
Pt	29.2	31.4	7.8	18.8	190.2
Au	26.0	44.6	2.3	6.9	68.5
Ni	8.7	82.7	2.4	9.1	35.1
Fe	2.0	80.2	0.9	17.0	36.3
Sn	0.3	98.2	3.9	0.6	3.6
Ti	0.7	39.0	0.2	37.5	1.8

Electrolyte: 0.1 M TEAP/ AN, H_2O: 1 M, $CHCl_3$: 50 mM. Electrode potential: −2.58 V vs Fc/Fc^+. [a]Av. C. D.: Average current density.

The metal electrodes may be classified into 3 groups in accordance with the product selectivity. Ag electrode reduces chloroform to CH_4 at high current density, i.e. to the highest degree of reduction. Ni, Fe, Sn and Ti reduce chloroform to CH_2Cl_2 as the major product; the degree of reduction is lower, and the current densities are lower than the other electrodes. Cd, Cu, Pb, In, Zn, Pt and Au belong to the intermediate group; these electrodes yield both CH_4 and CH_2Cl_2 with comparable yields. The current densities are also intermediate between the two groups with the exception of Pt. The trend of the product selectivity of metal electrodes agrees roughly with Sonoyama et al. s' obtained in aqueous media.[1] The product selectivity CH_4/CH_2Cl_2 in the present study is in parallel with the current density. The electrocatalytic activity for dechlorination of chloroform may be evaluated by the selectivity and the current density.

Mr. K. Sasaki carried out part of the experimental work.

References

1 N. Sonoyama, K. Hara, and T. Sakata, *Chem. Lett.*, **1997**, 131.
2 I. F. Cheng, Q. Fernando, and N. Korte, *Environ. Sci. Technol.*, **31**, 1074 (1997).
3 N. C. Ross, R. A. Spackman, M. L. Hitchman, and P. C. White, *J. Appl. Electrochem.*, **27**, 51 (1997).
4 S. G. Merica, W. Jedral, S. Lait, P. Keech, and N. J. Bunce, *Can. J. Chem.*, **77**, 1281 (1999).
5 K. Gebauer and A. Zimmer, *Chem.-Ing.-Techn.*, **72**, 528 (2000).
6 T. Li and J. Farrell, *Environ. Sci. Technol.*, **35**, 3560 (2001).
7 A. I. Tsyganok and K. Otsuka, *Electrochim. Acta*, **43**, 2589 (1998).
8 P. L. Cabot, M. Centelles, L. Segarra, and J. Casado, *J. Electrochem. Soc.*, **144**, 3749 (1997).
9 S. Rondinini, P. R. Mussini, P. Muttini, and G. Sello, *Electrochim. Acta*, **46**, 3245 (2001).
10 S. M. Kulikov, V. P. Plekhanov, A. I. Tsyganok, C. Schlimm, and E. Heitz, *Electrochim. Acta*, **41**, 527 (1996).
11 Y. Tomita, S. Teruya, O. Koga, and Y. Hori, *J. Electrochem. Soc.*, **147**, 4164 (2000).