

Electrocatalytic Dehalogenation of Chloroaromatics on Palladium-loaded Carbon Felt Cathode in Aqueous Medium

Andrey I. Tsyganok, Ichiro Yamanaka, and Kiyoshi Otsuka*

Department of Chemical Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152

(Received December 24, 1997; CL-970966)

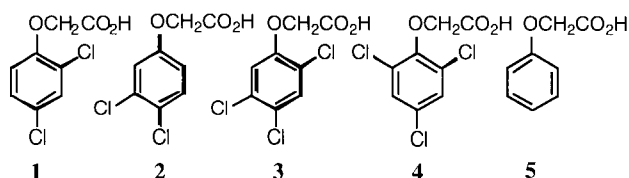
The selective dechlorination of highly toxic chloroaromatic herbicides based on phenoxyacetic acid was successfully achieved under mild experimental conditions in aqueous medium by electrocatalytic reduction at palladium-loaded carbon felts. Such cathode material is in principle available for dechlorination of chloroaromatics having different molecular structure.

Both the efficient removal of chlorinated aromatics from contaminated waters and consequent method for disposal of such highly stable toxic compounds are the urgent problems of environmental chemistry nowadays. Electrochemical reductive dehalogenation at modified carbon cathodes is considered as a convenient alternative to adsorption treatment of wastewaters by granular activated carbon with subsequent oxidative destruction of contaminated material by incineration. The reductive approach avoids the formation of dioxin-like compounds and allows to achieve the selective dechlorination of organochlorine pollutants under mild experimental conditions.¹⁻⁴

Recently we reported the selective electrochemical dehalogenation of 2,4-D (1) in MeCN with different bare carbons.⁵ This method, however, required the use of organic solvent and high cathodic overvoltage. Therefore, the objective of this work was to find the electrochemical system facilitating dehalogenation of stable chloroaromatics in aqueous medium *in situ*.

We found very recently that exhaustive dechlorination of 1 to phenoxyacetic acid (5) could be achieved in aqueous solution by using palladium-modified carbon felt cathode.⁶ Such a compound was completely converted to 5 within 7 h of constant current electrolysis under relatively low cathodic polarization of -1.4 V vs Ag/AgCl reference electrode. Instead, the electrochemical reaction performed at bare carbon felt revealed low efficiency of 2,4-D dechlorination showing 0.7% conversion after 4-h electrolysis. In addition, to provide the felt electrode with the stated current density (-111 mA/cm²) the potential more negative than -5 V was required.

In this work, we report the comparative results on electrocatalytic dechlorination of 3,4-D (2), 2,4,5-T (3), and 2,4,6-T (4) which are also employed in agriculture as effective herbicides.



Dehalogenation was achieved under the constant current electrolysis by using Teflon membrane-separated flow-through cell with permeable carbon felt cathode (superficial area of 9 cm²)

loaded with palladium,⁷ and Pt-foil anode. Quantitative analysis of dechlorinated products and unreacted substrate was performed by reverse-phase HPLC-UV. The current efficiency (CE) of the

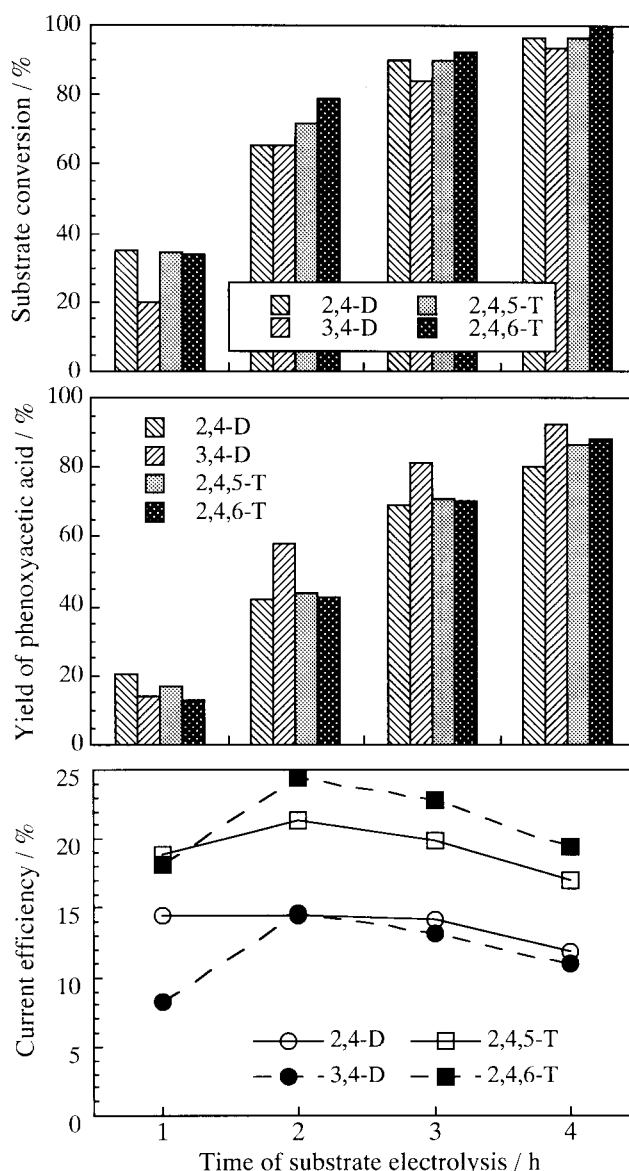





Figure 1. Electrocatalytic dehalogenation of chlorinated phenoxyacetic acids in aqueous medium. Catholyte (100 mL; 18–20 °C) contained 50 mM of substrate, 0.50 M *n*-Bu₄NBr, 0.50 M CF₃CO₂H, 40% MeOH (v/v); flow rate 100 mL/min. Cathode: Pd(5 wt. %)/FE-600 carbon felt; applied current density -111 mA/cm².

$$\text{1-4} \xrightarrow{+ 2\text{ne}^-, + 2\text{nH}^+} \text{5} + \text{nHCl}$$

Few other chlorine-containing aromatic compounds of different molecular structure (**6-8**) were also screened to estimate the electrocatalytic performance of the Pd/C system described above:

Substrate loading / μmol	Chlorine-free product / μmol^b	Yield / % ^c	CE/ % ^d
6	Biphenyl	24.5	1.3
1017	249		
7	Naphthalene	44.1	2.4
1007	444		
8 ^c	1,1-Diphenylethene	1.5	0.34
1048	16		

The financial support of this work by the Ministry of Education, Science and Culture of Japan (Monbusho) is gratefully acknowledged.

- 1 J. F. Rusling, S. Schweizer, S. Zhang, and G. N. Kamau, *Colloids and Surfaces A*, **88**, 41 (1994).
- 2 S. Zhang and J. F. Rusling, *Environ. Sci. Technol.*, **29**, 1195 (1995).
- 3 S. M. Kulikov, V. P. Plekhanov, A. I. Tsyganok, C. Schlimm, and E. Heitz, *Electrochim. Acta*, **41**, 527 (1996).
- 4 I. F. Cheng, Q. Fernando, and N. Korte, *Environ. Sci. Technol.*, **31**, 1074 (1997).
- 5 A. I. Tsyganok, K. Otsuka, I. Yamanaka, V. Plekhanov, and S. Kulikov, *Chem. Lett.*, **1996**, 261.
- 6 Presented at the 72nd Annual Meeting of the Chemical Society of Japan, Tokyo, 1997, Abstr., 2D232, and at the 80th Annual Meeting of the Catalysis Society of Japan, Ueda, 1997, Abstr., 4B17.
- 7 Polyacrylonitrile-based carbon felt FE-600 ($S_{\text{BET}} \sim 1400 \text{ m}^2/\text{g}$) was obtained from TOHO Rayon Co., Ltd. Palladium was supported due to ion-exchange by immersion of carbon felt sample into $\text{MeOH}-\text{CF}_3\text{CO}_2\text{H}$ solution of PdCl_2 . Before addition of substrate to catholyte, the supported Pd was electrochemically reduced with current density $-111 \text{ mA}/\text{cm}^2$ for 2 hours.
- 8 p,p'-DDE (2,2-bis(4-chlorophenyl)-1,1-dichloroethylene) is known as the main non-degradable metabolite of pesticide DDT extensively used over the decades.