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

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(Received December 24, 1997; CL-970966)

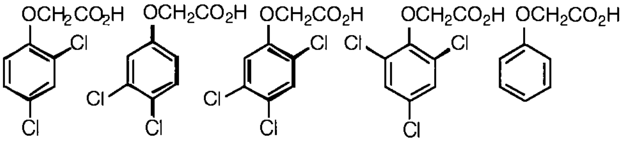
The selective dechlorination of highly toxic chloroaromatic herbicides based on phenoxyacetic acid was successfully achieved under mild experimental conditions in aqueous medium by electrocatalytic reduction at palladium-loaded carbon felts. Such cathode material is in principle available for dechlorination 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/cm^2) 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.



1 **2** **3** **4** **5**

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 cm^2) 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

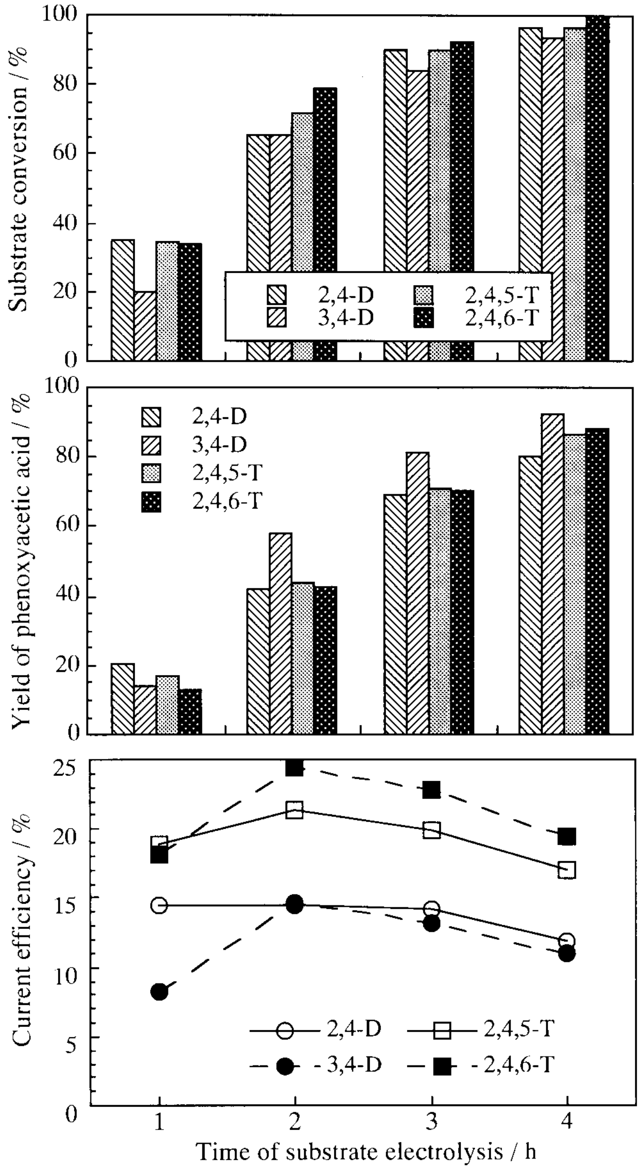
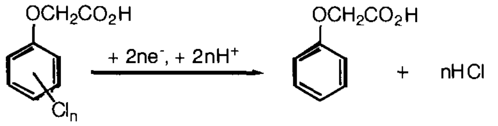


Figure 1. Electrocatalytic dehalogenation of chlorinated phenoxyacetic acids in aqueous medium. Catholyte (100 mL; 18~20 °C) contained 50 mM of substrate, 0.50 M n-Bu_4NBr, 0.50 M CF_3CO_2H, 40% MeOH (v/v); flow rate 100 mL/min. Cathode: Pd(5 wt.%)/FE-600 carbon felt; applied current density -111 mA/cm^2.

dechlorination reaction was calculated as the percentage of the charge passed that was used to convert the starting material to the products according to the following scheme:



1 - 4 **5**

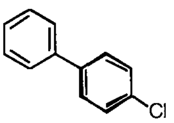
Figure 1 shows the substrate conversion, yield of final chlorine-free product **5**, and current efficiency as functions of time of substrate electrolysis. After 4 hours of reaction all the compounds tested underwent more than 90% conversion and 80 to 93% yield of **5**. Furthermore, although the main electrochemical reaction occured was the copious evolution of hydrogen from water decomposition, the electrocatalytic dechlorination proceeded with fairly high current efficiencies.

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 discribed above:

Table 1. Electrocatalytic dechlorination of chloroaromatics at Pd(5 wt.%)/FE-600 carbon felt cathode in water-MeOH medium[a]

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

[a] Catholyte (100 mL; 18-20 °C) contained 0.50 M *n*-Bu_4NBr, 0.50 M CF_3CO_2H, 40% MeOH (v/v); flow rate 100 mL/min. Applied current density -111 mA/cm^2, corresponding potential did not exceed -2.0 V *vs* reference of Ag/AgCl. [b] Determined in catholyte by HPLC after 1-h electrolysis. [c] Based on initial substrate loading. [d] Calculation based on the amount of corresponding chlorine-free product assuming $2e^-$ and $2H^+$ consumption per every chlorine removed as Cl^-. [e] Catholyte contaned 0.50 M *n*-Bu_4NBr and 80% MeOH (v/v) to increase the solubility of **8**.



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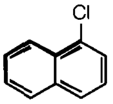

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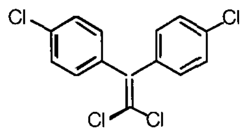

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The results obtained are listed in Table 1. It is seen that the formation of chlorine-free products occured as well. For the dechlorination of large planar molecules of **8**[8] (318.02 g/mol), it should be stressed that both the aromatic chlorines and the other ones attached to the conjugated C=C bond can be cleft, though the yield of 1,1-diphenylethene and current efficiency were low. We believe such characteristics of dechlorination can be significantly improved by varying the composition of catholyte and modifying the cathode electrocatalysts. Further research toward these aims is currently in progress.

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

References and Notes

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7 Polyacrylonitrile-based carbon felt FE-600 ($S_{BET} \sim 1400\ m^2/g$) was obtained from TOHO Rayon Co., Ltd. Palladium was supported due to ion-exchange by immersion of carbon felt sample into MeOH-CF_3CO_2H solution of $PdCl_2$. Before addition of substrate to catholyte, the supported Pd was electrochemically reduced with current density -111 mA/cm^2 for 2 hours.
8 p,p'-DDE (2,2-bis(4-chlorophenyl)-1,1-dichloroethylene) is known as the main non-degradable metabolyte of pesticide DDT extensively used over the decades.