Selective Electrochemical Dehalogenation of 2,4-Dichlorophenoxyacetic Acid in MeCN at Room Temperature

Andrey Tsyganok,[†] Kiyoshi Otsuka,[*] Ichiro Yamanaka, Vasilii Plekhanov,[†] and Sergei Kulikov[†]
Department of Chemical Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152
[†]*Institute of Chemistry of Natural Organic Materials, Krasnoyarsk, 660036, Russia*

(Received December 15, 1995)

2,4-Dichlorophenoxyacetic acid (commercial pesticide 2,4-D) can be dechlorinated by electrochemical reduction at different carbon materials under mild conditions to give phenoxyacetic acid with 80% selectivity at 75% conversion of 2,4-D (current efficiency 10~14%).

Chlorinated organic compounds are widely used in a variety of applications as reagents for chemical industry, pesticides for agriculture, transformer oils and fire-retardants for electrical equipment, etc. As a result of their wide spread, they are known to belong to the priority organic pollutants of environment.

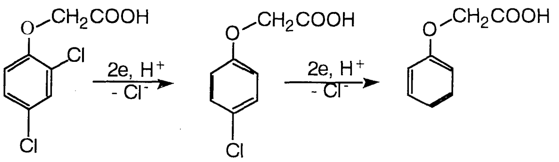
It is known that dehalogenation of such compounds leads to the decrease of its toxicity and makes it possible to utilize these products by other convenient methods (biodegradation, for an example).

Electrochemical reductive dechlorination can be recognized as one of possible detoxification methods and is proposed as a practical technology for PCB removal.[1-3] The subject of our interest is another group of synthetic organohalogen products which are based on phenoxycarboxylic acids and known to be effective herbicides (2,4-D, 2,4-DP, 2,4,5-T, etc.).

In this communication, we wish to report the results of electrochemical reductive dehalogenation of 2,4-dichlorophenoxyacetic acid (**I**) in MeCN solution at different carbonaceous materials (carbon cloths[4] and graphite[5]).

The experiments were carried out using a thermostated glass electrolytic cell divided by ion-exchange membrane into two compartments with geometric surface area of cathode about 0.3 cm^2. Quantitative analysis of dechlorination products was performed by reverse-phase HPLC-UV.

First of all, we should note that for all cathode materials tested and potential values used the electrochemical dechlorination of **I** proceeded with consecutive removal of chlorine atoms. The interesting feature of this process is the fact that the product of mono-chlorine elimination from **I** is 4-chlorophenoxyacetic acid (**II**) only. No detectable amount of 2-chlorophenoxyacetic acid has been observed. Then, inspite of high values for cathodic polarization, neither products of reduction of carboxy group of **I**, nor compounds of phenolic structure have been observed. Based on monography[6] and all these data, we suggest the dechlorination scheme for **I** in MeCN as follows:



I **II** **III**

Table 1. Electrochemical reductive dechlorination of 2,4-D in MeCN at different carbon materials

Cathode Material	Charge Passed (C)	Polarization (V)	Conversion of I (%)	Selectivity of **III** Formation (%)	Current Efficiency (%)	Current Density (mA/cm^2)
(1) Busofit	272.9	-5	75.5	82	9.6	37
(2) Busofit	151.2	-5	53.6	63	12.7	[c]
(3) Busofit	149.8	-3	70.6	47	12.8	[c]
(4) Busofit	127.8	-2.5	1.8	0	0.4	[c]
(5) Ural	187.2	-3	62	34	8.6	55
(6) Ural	189	-5	46.1	60	5.7	130
(7) Viskum	158	-3	66.8	62	14.1	55
(8) Viskum	182.9	-5	47.5	74	5.9	72
(9) Busofit[a]	151.9	-5	51	67	7.8	[c]
(10) Graphite spectral[b]	164.2	-3.5	40	87	10.8	[c]

Electrolysis conditions: C_0^{I} 9.9~12.7 mM, supporting electrolyte 0.25 M Et_4NBr, atmospheric pressure, 20 °C.

[a] 0.25M of $(n\text{-Bu})_4NBr$ as supporting electrolyte. [b] Destruction of cathode during electrolysis. [c] Not determined.

The quantitative results for the electrochemical dechlorination of **I** are shown in Table 1. The nature of carbon material (graphitization extent, conductivity, specific surface area and porous structure) essentially effects on the dechlorination process. Thus, carbon cloth Busofit, which had shown the specific surface area about 900 m^2/g and the lowest conductivity among all the carbon materials tested, has demonstrated almost the same current efficiency (CE) at different polarization values ((2), (3)), small decrease of CE during electrolysis (from 12.7 to 9.6% for (2) and (1)) and low current density at high cathodic polarization (-5 V, compare (1) with (6) and (8)). At the same time, the change of Et_4NBr to a supporting electrolyte with larger volume cation ($(n\text{-Bu})_4NBr$) does not influence essentially on **I** dechlorination. In turn, the destruction of the graphite cathode has been observed even at -3.5 V polarization.

The increase of absolute potential value leads to the same tendency for selectivity of **III** formation for all the used carbon cloths. But, on the other hand, it results in the decrease of both the conversion of **I** and CE for dechlorination reaction. This can be explained by the effect of side reactions at the electrode (reduction of solvent and supporting electrolyte) of which role at high cathodic polarizations becomes predominant.

As a conclusion, one can emphasize that 2,4-dichlorophenoxyacetic acid can be selectively dechlorinated by electrochemical reduction at different carbonaceous materials with maintaining carbon skeleton and functional groups of initial molecule.

References and Notes

1 U.S. Patent No. 4659443. 9 pp. (21 Apr. 1987).

2 U.S. Patent No. 4702804. 8 pp. (27 Oct. 1987).

3 S. Zhang and J. F. Rusling, *Environ. Sci. Technol.*, **29**, 1195 (1995).

4 All used activated carbon cloths (Busofit, Ural, and Viskum) are polyacrilonitrile (PAN)-based ones and produced by "Khimvolokno (Chemical Fibers)" Co., Svetlogorsk, Belorussia.

5 Graphite cathode was prepared from a rod of high purity graphite used ordinarily in arc furnaces.

6 Organic Electrochemistry: an introduction and guide, ed by H. Lund and M. Baizer. 3rd ed., rev. and expanded. Marcel Dekker, Inc. (1991).