



Selective hydrodechlorination of 3,5,6-trichloropicolinic acid at an activated silver cathode: Synthesis of 3,5-dichloropicolinic acid



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ABSTRACT

Electrochemical reduction of 3,5,6-trichloropicolinic acid (3,5,6-T) at glassy carbon, Ni, Cu, and Ag cathodes in aqueous solutions at different pH values was investigated. Experiments suggest that the selectivity of the reduction strongly depends on the cathode materials used and the pH of the aqueous solutions. A high selectivity for the hydrodechlorination of 3,5,6-T to 3,5-dichloropicolinic acid (3,5-D) has been achieved exclusively at an activated Ag cathode and at pH 3: a selectivity of 95% at 42% conversion under potentiostatic mode and a selectivity of 89% at 88% conversion under intentiostatic mode. An explanation is proposed for this high selectivity.

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1. Introduction

3,5-Dichloropicolinic acid (3,5-D) is a key intermediate for some BACE1 [1] and BACE2 [2] inhibitors, and is used in the therapeutic and prophylactic treatment of Alzheimer's disease and type 2 diabetes. It can also be used as an active ingredient in some herbicidal compositions [3] that selectively control weeds growing with cereal crops. A large number of techniques, including chemical [4] or biocatalytic hydrolysis [5], KMnO_4 oxidation [6], palladium-catalysed hydroxycarbonylation [7], and lithiation reaction [8], have been reported for the synthesis of 3,5-D [8] and partially halogenated pyridine acids that resemble 3,5-D [4–7]. A key drawback of all these techniques is that their starting materials are partially halogenated pyridine compounds, mainly produced by some selective halogenation reactions. Because of the poor selectivity of the halogenation reactions [9], large-scale production of these partially halogenated pyridine compounds is usually very difficult. In addition, some of the methods suffer from several drawbacks such as the requirement of hazardous organic solvents [6–8], noble metal catalysts [8], and very low temperatures [8].

On the other hand, it is well known that electrochemical hydrodehalogenation of polyhalogenated organic compounds (POCs) is a powerful technique for the production of partially halogenated organic compounds [10–14]. Because there is no

problem with selectivity, large-scale production of POCs with high yields can be easily achieved by some halogenation reactions [15]. Advantages of the electrochemical hydrodehalogenation technique also include high selectivity [11–14], use of aqueous solutions [10–13], and no necessity for a reducing agent. In fact, this methodology has been extensively used for developing alternative synthesis routes to manufacture partially chlorinated pyridine herbicidal industrial products [11–14]. For example, electrochemical hydrodehalogenation of 3,4,5,6-tetrachloropicolinic acid, 4-amino-3,5,6-trichloropicolinic acid, and 2,3,4,5,6-pentachloropyridine has been successfully used for the manufacture of 3,6-dichloropicolinic acid (3,6-D) [11] or 3,5,6-trichloropicolinic acid (3,5,6-T) [12], 4-amino-3,6-dichloropicolinic acid [13], and 2,3,5,6-tetrachloropyridine [14], respectively.

The synthesis of 3,5-D through electrochemical hydrodehalogenation of POCs has not been reported so far. Since Ag as cathode material has remarkable electrocatalytic activity in reductive dehalogenation reactions [16–19], we report herein the first feasibility study for the electrosynthesis of 3,5-D by selective hydrodechlorination of 3,5,6-T at a Ag cathode in aqueous medium. An explanation regarding this selective hydrodechlorination is proposed. It would be illuminating for controlling the selectivity of other hydrodehalogenations.

2. Experimental

3,5,6-T, 3,5-D, 3,6-dichloropicolinic acid (3,6-D), and 3-chloropicolinic acid (3-C), with a purity of 98–99%, were obtained from Zhejiang Avilive Chemical Co., Ltd, China, and used as received. All

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solutions were prepared using H₂O with a resistivity of 18.2 MΩ cm obtained from a Millipore Milli-Q system. GC, Ni, Cu, Ag disk electrodes (2 mm diameter), a Ag disk electrode (10 mm diameter), a GC disk electrode (15 mm diameter), Ni foams (1.0 mm thickness), Cu foams (1.0 mm thickness), graphite sheets (3.0 mm thickness) were obtained from Cells Electrochemistry Experiment Equipment Co., China (www.hzcell.com). The bulk density of Ni and Cu foam are approximately 0.2 and 0.3 g/cm³, respectively. GC(p), Ni(p), Cu(p) and Ag(p) electrodes were prepared by polishing the GC, Ni, Cu, Ag disk electrodes with alumina powder (30~50 nm), whereas Cu(r) foam, Ag(r) disk and Ag(r) mesh electrodes were prepared by an oxidation-reduction cycling process (ORC process) respectively: in a 0.1 M KCl aqueous solution, at a scanning rate of 20 mV/s, in the range of -0.35 to 0.2 V vs. SCE, 50 cycles for the Cu(r); in a 0.5 M NaCl aqueous solution, at a scanning rate of 10 mV/s, in the range of -0.4 to 0.4 V vs. SCE, 4 cycles for the Ag(r) [20]. Two type of silver plated graphite, namely Ag/C and Ag(r)/C, were obtained by deposition at 0.37 V for 3 min in a 0.1 M KNO₃ + 0.01 M AgNO₃ aqueous solution and by imposing same ORC process as used for the Ag(r) electrodes on the Ag/C.

Cyclic voltammetry (CV) and preparative electrolysis experiments were carried out using a PAR 273 A potentiostat. A three-electrode cell comprised a Ag/AgCl reference electrode, a Pt (0.5 × 1 cm²) counter electrode, and a GC(p), Ni(p), Cu(p) or Ag(p) working electrode (2 mm diameter) was used for voltammetric investigations. The electrolysis experiments were carried out in a two-compartment cell, divided by a cation-exchange membrane (Nafion 117), with catholyte and anolyte volumes of 30 cm³. A 1.5 M ammonium acetate solution and a Pt plate (2 cm × 2 cm) were used as the anolyte and the anode, respectively. The electrolysis experiments were performed under stirring and under nitrogen. After the electrolysis, the catholyte was diluted 20 (Table 1) or 200 (Fig. 2) times with methanol and then was analysed by high-performance liquid chromatography (HPLC) using the mode described in Ref [21], and the dechlorinated products and unreacted 3,5,6-T were identified by comparing their retention times with those of the known samples. All the electrochemical experiments were carried out at 297 K and ambient pressure, and all the potentials (except for ORC process) are reported relative to the Ag/AgCl/saturated KCl aqueous solution reference.

3. Results and discussion

3.1. CV experiments

The effect of cathode materials and solution pH on the electrochemical reduction of 3,5,6-T was initially evaluated by a series of CV experiments. Fig. 1a shows the CV curves of the 'steady-state' cycle recorded on Ni(p), Cu(r), Cu(p), Ag(p), and GC (p) electrodes for the reduction of 3,5,6-T in a pH 3 phosphate buffer solution. The shape of the CV curves strongly depends on the working electrode material used. No obvious cathodic current response is observed for the reduction of 3,5,6-T on the Ni(p), Cu(p) and Cu(r) electrodes, which indicates that the reduction of H⁺ is favoured over that of 3,5,6-T on these three electrodes. However, on the Ag(p) and GC(p) electrodes, the current peaks corresponding to the reduction of 3,5,6-T are observed near -0.9 V. In addition, it is worth noting that the onset of the reduction of 3,5,6-T on the Ag(p) electrode occurs at a slightly more positive potential than the value observed on the GC(p) electrode. Therefore, it is likely that the Ag (p) electrode has higher electrocatalytic activity than the GC(p) electrode towards the reduction of 3,5,6-T.

Fig. 1b shows the CV curves of the 'steady-state' cycle recorded on a Ag(r) electrode in solutions with different pH values. The solution pH is found to have a significant effect on the profile of the CV curves. At pH 0.2, 3,5,6-T does not show any obvious current response in the potential range studied, whereas four and three cathodic peaks of 3,5,6-T appear at pH 3 and 7, respectively. At pH 11 and 13.3, only one irreversible cathodic peak is detected at -1.1 V. This value is more negative than the first cathodic peak observed at pH 3 and 7. These results suggest that a moderate H⁺ concentration (pH = 3–7) favours the reduction of 3,5,6-T. In addition, one finds that the cathodic peak current density of 3,5,6-T on the Ag(r) electrode is only about two times larger than the voltammetric responses generated on the Ag(p) electrode at pH 3, although the ratio of roughness factor for the two silver electrode is nearly 50 [20]. A quite similar result was observed in the dechlorination of trichloroacetic acid using same two silver electrodes in our previous work [20]. We had attributed this strange behaviour of the Ag(r) electrode to the diffusion-controlled process in the reduction of the substrate. In other words, most of active sites on the surface of Ag(r) electrode probably are not easily accessible to 3,5,6-T due to its poor mass transfer kinetics in the

Table 1

Operating conditions and results for the electrochemical reduction of 3.33 mM 3,5,6-T in a N₂-saturated 0.5 M H₂SO₄ (pH = 0.2), a 0.5 M NaOH (pH = 13.3) aqueous solution, and 0.25 M phosphate buffer solutions of three different pH values (3, 7, and 11) at 297 K on eight cathodes: Entry (1): Ni foam electrode (2.5 cm × 3 cm); (2): Cu foam electrode (2.5 cm × 3 cm); (3): Cu(r) foam electrode (2.5 cm × 3 cm); (4): Ag(p) disk electrode (Ø 10 mm); (5): GC disk electrode (Ø 15 mm); (6): fresh Ag/C sheet electrode (2.5 cm × 3 cm); (7): fresh Ag(r)/C sheet electrodes (2.5 cm × 3 cm); (8–13): Ag(r) mesh electrodes (2.5 cm × 3 cm).

Entry	Cathodes	I _{app} ^a or E _{app} ^a	Solution pH	Final product distribution (%)			Current efficiency (%) ^b	3,5-D selectivity (%) ^c	3,6-D selectivity (%) ^d
				3,5-D	3,6-D	3,5,6-T			
1	Ni foam	10 mA (1.5 mA/dm ²)	3	0	0	98	0	0	
2	Cu foam	10 mA (1.0 mA/dm ²)	3	0	0	99	0	0	
3	Cu(r) foam	10 mA (1.0 mA/dm ²)	3	0	0	98	0	0	
4	Ag(p) disk	1 mA (127 mA/dm ²)	3	2.5	0.8	95	2.5	16	
5	GC(p) disk	1 mA (57 mA/dm ²)	3	0	0	94	0	0	
6	Ag/C sheet	10 mA (133 mA/dm ²)	3	4.2	1.1	94	4.2	18	
7	Ag(r)/C sheet	10 mA (133 mA/dm ²)	3	15	1.7	82	15	9	
8	Ag(r) mesh	10 mA (580 mA/dm ²)	3	44	2.6	49	44	5.1	
9	Ag(r) mesh	-1.1 V	13	0.4	38	61	0.4	1.0	
10	Ag(r) mesh	-1.1 V	11	0.9	23	75	0.9	3.6	
11	Ag(r) mesh	-0.93 V	7	35	15	47	35	66	
12	Ag(r) mesh	-0.73 V	3	40	2.4	58	40	95	
13	Ag(r) mesh	10 mA (580 mA/dm ²)	0.2	0	0	99	0	0	

^a 2 F·mol of 3,5,6-T were consumed in the all 13 electrolysis experiments.

^b Current efficiency calculated with respect to the produced 3,5-D.

^c 3,5-D selectivity calculated with respect to the converted 3,5,6-T.

^d 3,6-D selectivity calculated with respect to the converted 3,5,6-T.

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