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Electrochemical synthesis of diethyl fluoromethanephosphonate

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Abstract

The electrochemical reduction of diethyl chlorofluoromethanephosphonate has been studied. It has been shown that, in mildly basic media (pH 7.5–8) of water–alcohol solutions, replacement of the chlorine of the starting compound by hydrogen occurs at lead, cadmium and zinc electrodes with high selectivity. The procedure affording diethyl fluoromethanephosphonate in a yield of 85%–90% has been elaborated.© 1997 Elsevier Science S.A. All rights reserved.

Keywords: Diethyl chlorofluoromethanephosphonate; Diethyl fluoromethanephosphonate; Electrochemical synthesis

1. Introduction

In recent years, increasing attention on the roles and significance of phosphoryl transfer has resulted in the synthesis of α-fluorinated alkanephosphonates as analogues of biologically active phosphates [1,2]. Of the more interesting of these are the derivatives of monofluoromethanephosphonic acid and difluoromethanephosphonic acid [3,4], the synthesis of which may be realized in many different ways. Nevertheless, in contrast with difluoromethanephosphonates, the corresponding derivatives of monofluoromethanephosphonic acid are very difficult to prepare efficiently. There are many methods of synthesis [5] but, in our view, the most convenient and safe method for this class of compounds is the electrochemical reduction of chlorofluoroalkanephosphonates [6].

The aliphatic chloroalkanes are poorly reducible compounds with reduction potentials in the range −1.9 to −2.3 V.

Diethyl chlorofluoromethanephosphonate is active polarographically and gives, at the dropping mercury cathode, a reduction wave at $E_{1/2} = -2.18$ V vs. a saturated calomel electrode, which corresponds to the transfer of two electrons.

Thus, although this compound is relatively hard to reduce, it is possible to carry out dechlorohydrogenation in water solutions using metals giving a high overvoltage of hydrogen evolution as cathode materials.

2. Results and discussion

Cadmium, lead, zinc and amalgamated copper have been studied as cathode materials with an overvoltage of hydrogen. Preliminary tests were carried out on cadmium, lead and amalgamated copper and involved the measurement of the hydrogen generation by water–alcohol solutions of diethyl chlorofluoromethanephosphonate (Fig. 1). Lead and cadmium electrodes showed practically identical activity and the hydrogen absorption ceased after current consumption according to 2 F per mole of starting compound. On the other hand, at an amalgamated copper cathode, after the absorption of hydrogen approached 2 F per mole of starting compound, the current efficiency of hydrogen fell below 100%. Obviously, this is due to the further process of the partial substitution of the fluorine atom by hydrogen at the amalgamated copper electrode, and therefore we did not carry out the preparative electrolysis with this system.

The results obtained showed that, at zinc and cadmium electrodes, the process of reduction takes place with the selective substitution of the chlorine atom by hydrogen

$$(C_2H_5O)_2P(O)CHClF \xrightarrow{+2e^-,\ H^+} (C_2H_5O)_2P(O)CH_2F + Cl^-$$

The preparative electrolyses at lead, cadmium and zinc cathodes confirmed the high selectivity of dechlorination, and the results are summarized in Table 1. The electrolysis was also carried out using a lead cathode and various supporting electrolytes, such as potassium phosphate, sodium chloride and tetraethylammonium (TEA) chloride, the results of

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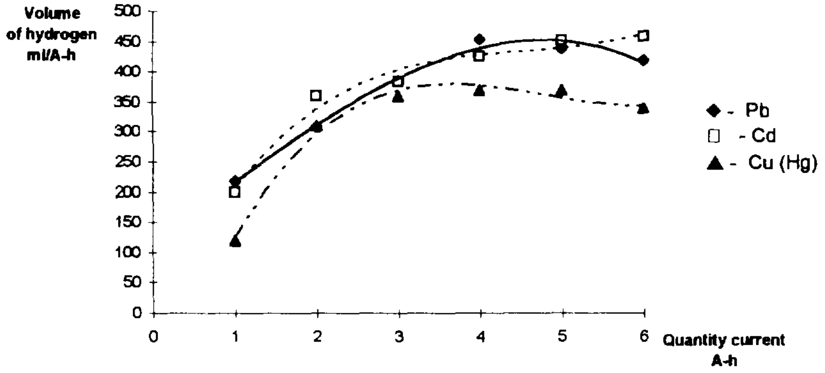

Fig. 1. Generation of hydrogen from a water–alcohol solution of diethyl chlorofluoromethanephosphonate using various cathode materials. Composition of catholyte: 0.5 N KH_2PO_4, 30 ml; ethanol, 15 ml; chlorofluoromethanephosphonate, 5.0 g.

Table 1
The influence of cathode material on the yield of diethyl fluoromethanephosphonate (catholyte: 0.5 N K_2HPO_4 (pH 8), 120 ml; ethanol, 60 ml; phosphonate, 40 g; current density, 0.10 A cm^{-2})

	Cadmium	Lead	Zinc
Yield (%)	92.30	91.12	86.49

Table 2
The influence of supporting electrolyte on the yield of diethyl fluoromethanephosphonate (cathode: lead; catholyte: 0.5 N water solution of supporting electrolyte, 120 ml; ethanol, 50 ml; phosphonate, 40 g; pH 7–8; temperature, 25–30 °C; current density, 0.10 A cm^{-2})

	$K_2H_2PO_4$	Na_2SO_4	NaCl	$(C_2H_5)_4NCl$
Yield (%)	91.12	89.07	88.93	89.12

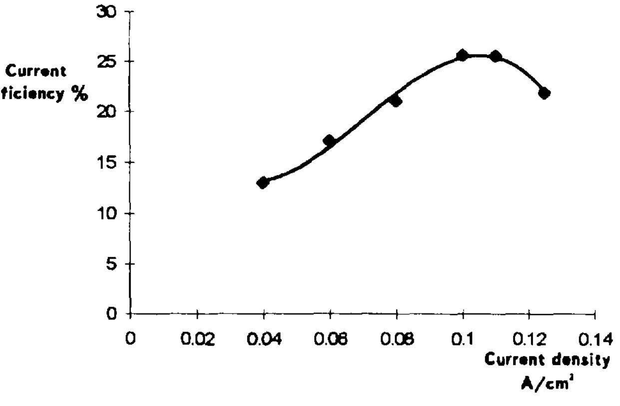

Fig. 2. The influence of the current density on the current efficiency of diethyl fluoromethanephosphonate production.

which are given in Table 2. As can be seen, the nature of the supporting electrolyte affected the process slightly, but the pH was more stable in the case of phosphate solutions. Therefore it is easy to maintain the correct pH of the solution during the electrolysis procedure. In the solution of TEA chloride, intense cathode disintegration was observed; however, this did not reduce the yield of the target product.

Further experiments were carried out to define more precise parameters for the electrolysis. Since the reduction takes place at low current efficiency, it was interesting to observe the influence of the current density on the reduction process. It has been determined that the best current densities lie in the range 0.10–0.11 A cm^{-2}. The current efficiency is about 25% at this current density (see Fig. 2). Of special importance is the acidity of the medium. The highest yield of the product was obtained at pH 6–8 and the efficiency decreased on passing to more acidic or basic media (see Fig. 3). With a lead cathode, it has been shown that the electrode surfaces must be prepared with great care to obtain reproducible data. This disadvantage can be corrected by the addition of small amounts of TEA chloride to the catholyte solution. As TEA chloride is added, disintegration of the cathode surface takes place for the first few minutes and the catholyte assumes a grey colour from the particles of lead. Then, the catholyte becomes transparent during electrolysis and a spongy lead layer covers the cathode. In this case, the cathode has a brush and it is possible to carry out the next experiment directly. The reproducibility significantly increases and it is not necessary to clean the electrode with acid after each run.

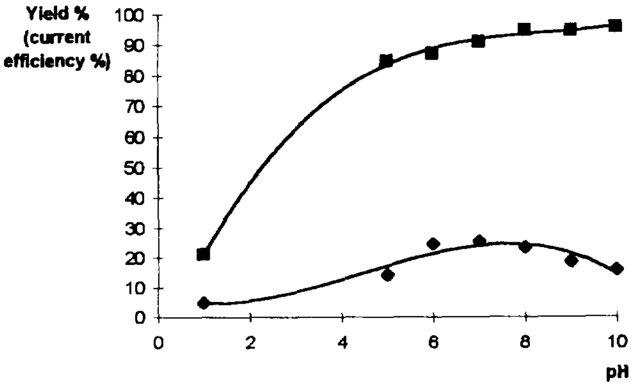

Fig. 3. The influence of pH on the yield of diethyl fluoromethanephosphonate: ◆, current efficiency (%); ■, yield (%).

3. Experimental details

The starting diethyl chlorofluoromethanephosphonate was synthesized by a known procedure [7]. It had the following characteristics: b.p., 100–104 °C/7 mmHg, $n_D^{20} = 1.4250$, $d_4^{20} = 1.2595$ g cm^{-3}; these conform with the literature data [7].

As supporting electrolytes, we used materials with a purity of better than 98%.

For electrochemical reduction, a glass cylinder electrolyser was used, which had a ceramic diaphragm, water-cooled jacket, stirrer and sampling tube for measuring the pH value during the electrolysis procedure. The volume of the catholyte compartment was 200 ml. Cathodes were perforated cylinders with an internal diameter of 45 mm and a height of 85 mm. The working area was 60 cm^2 and the anode was a platinum spiral.

3.1. General procedure

Into the catholyte compartment, 120 ml of 0.5 N aqueous potassium phosphate, 1 g (0.006 mol) TEA chloride, 60 ml ethanol and 31 g (0.162 mol) of diethyl chlorofluoromethanephosphonate were added. The anolyte was a 30% solution of orthophosphoric acid in water. Electrolysis was carried out with a current of 5.0 A (current density, 0.083 A cm^{-2}) with stirring. The temperature of the catholyte was kept in the range 25–30 °C and the pH in the range pH 7.5–8.0. After completion of electrolysis, the catholyte solution was kept under a reduced pressure of 20 mmHg at 40 °C to remove the solvent. The aqueous layer was further extracted with benzene (4×40 ml) and the combined extracts were dried ($MgSO_4$), filtered and the solvent was evaporated. The resulting liquid was distilled to give 23.8 g of diethyl fluoromethanephosphonate, yield 92.1%, b.p. 89–90 °C/20 mmHg, $d_4^{20} = 1.1510$ g cm^{-3}, $n_D^{20} = 1.4108$.

NMR (without solvent) ^1H (TMS): δ_H 1.15 (6H, t, $^3J_{HH} = 7.5$ Hz, $OCH_2\underline{CH_3}$), 3.95 (4H, dq, $^3J_{HP} = 7$ Hz, $^3J_{HH} = 7$ Hz, $PO\underline{CH_2}CH_3$), 4.61 (2H, dd, $^2J_{PH} = 6.0$ Hz, $^2J_{FH} = 46.5$ Hz, $P\underline{CH_2}F$); ^{31}P (85% H_3PO_4): δ_P 15.8 (d, $^2J_{PF} = 69.4$ Hz). m/z 171 ($M + H^+$, 100%) [8].

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