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Electrocatalytic Dehydrochlorination of Pentachlorophenol to Phenol or Cyclohexanol

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The electrocatalytic hydrogenolysis of pentachlorophenol (PCP) was carried out under galvanostatic control, in an aqueous 1 M NaOH solution in which PCP is fully soluble, and on particles of palladium or rhodium supported on alumina ($Pd(5\%)/Al_2O_3$ or $Rh(5\%)/Al_2O_3$) and entrapped in a reticulated vitreous carbon (RVC) electrode. On Pd/Al_2O_3 and at 75 °C, the conversion was complete (>99%) after 16 mol of electrons per mol of substrate (16 F mol^{-1}) were consumed, and phenol was the sole product formed in 98% yield (61% current efficiency). On Rh/Al_2O_3 and 25 °C, 100% conversion was reached after 24 F mol^{-1}, and cyclohexanol was obtained in 98% yield with some 2% of cyclohexanone (62% current efficiency). The ease of electrocatalytic hyrogenolysis was found to increase in the following order: PCP < 2,6-dichlorophenol < 4-chlorophenol.

Introduction

Chlorophenols are used as pesticides (PCP) (*1*−*3*) and are formed during industrial operations such as the bleaching of pulp with chlorine (*4*−*6*), hydrolysis of chlorinated phenoxyacetic acid herbicides (*7, 8*), and oil refining (*9*). Due to their high toxicity, their persistence, and their bioaccumulation in aquatic organisms, their disposal has become a major environmental concern. A large number of techniques have been suggested for the treatment of wastewater containing chlorophenols. Among them are biodegradation (*10*), ultraviolet and gamma irradiation (*11*), oxidative processes such as ozonolysis (*12, 13*), reductive processes using chemical reducing agents (*14*), and catalytic hydrogenation (*15*−*17*).

More recently, interest in environmental electrochemistry, an emerging technology, has increased (*18, 19*), and possible applications for the treatment of effluents from industrial or municipal plants can be envisaged. In particular, electrochemical processes have been developed for the destruction of carbon−halogen bonds. They include direct electrooxidations (*20*), mediated electrochemical oxidations (*21*), and cathodic processes (*22*−*25*). In the oxidation processes, undesired reactions may arise due to the formation of reactive radicals either on the electrode surface or in the solution. Most of the cathodic processes were carried out on high hydrogen overvoltage electrodes such as lead or carbon in order to minimize the hydrogen evolution reaction, but low current efficiencies were obtained. Recent studies have shown that dechlorination of 4-chlorophenol by electrocatalytic hydrogenation (ECH) on a palladized carbon cloth or on graphite (*26*) and of chlorophenoxy acetic acids on palladium-loaded carbon felt (*27*) can be performed with good efficiencies.

ECH, a process in which chemisorbed hydrogen is generated at the electrode surface by electrolysis of water, is indeed a very useful tool for the hydrogenation and hydrogenolysis of organic molecules (*28*−*31*) and presents several advantages over catalytic hydrogenation and classical electroreduction (see refs *28* and *29*). The mechanism of the electrocatalytic hydrogenolysis of a carbon−halogen bond (R−X molecule) is described by eqs 1−4. First, chemisorbed hydrogen is formed on the cathode surface by reduction of water

$$2H_2O + 2e^- + M \rightarrow 2(H)_{ads}M + 2OH^- \qquad (1)$$

$$R{-}X + M \rightleftharpoons (R{-}X)_{ads}M \qquad (2)$$

$$(R{-}X)_{ads}M + 2(H)_{ads}M \rightarrow (R{-}H)_{ads}M + HX \qquad (3)$$

$$(R{-}H)_{ads}M \rightleftharpoons R{-}H + M \qquad (4)$$

(eq 1 where M is the metallic surface and $(H)_{ads}M$, chemisorbed hydrogen). Hydrogenolysis of the C−X bond then proceeds as in catalytic hydrogenation, that is by reaction of the adsorbed substrate with chemisorbed hydrogen (eq 3, adsorption step shown in eq 2) followed by desorption of the product (eq 4). It is important to point out that the efficiency of ECH of a given organic compound depends on the relative rates of the hydrogenation step (eq 3, hydrogenolysis in this particular case) and of hydrogen desorption (see eqs 5 and(or) 6 below) (*28*−*31*). If the hydrogenation step (eq 3) is too slow with respect to hydrogen desorption (eqs 5 and(or) 6), only hydrogen evolution occurs.

$$(H)_{ads}M + H_2O + M + e^- \rightarrow H_2 + 2OH^- \qquad (5)$$

$$(H)_{ads}M + (H)_{ads}M \rightleftharpoons H_2 \qquad (6)$$

The concentration of chemisorbed hydrogen can be controlled by adjusting the current density or the electrode potential. Among the factors affecting the ECH efficiency, the nature of the electrode material and the nature of the surface (which depends inter alia on the technique used to prepare the electrode) are of a prime importance (*28*−*31*). Most of the studies on the ECH of organic compounds have been carried out on electrodes constituted of a spongy transition metal or of Raney nickel. Recently, we have shown that the ECH of an organic compound can be successfully and efficiently carried out on an electrode consisting of particles which are active in catalytic hydrogenation and which are entrapped in a reticulated vitreous carbon (RVC) matrix even when these particles consist of a transition metal dispersed on a nonconducting support such as alumina (*31*).

We report in this paper the results of a study of the ECH of pentachlorophenol (PCP), 2,6-dichlorophenol, and 4-chlorophenol on such electrodes with, as catalyst, particles of palladium or rhodium dispersed on charcoal (Pd/C and Rh/

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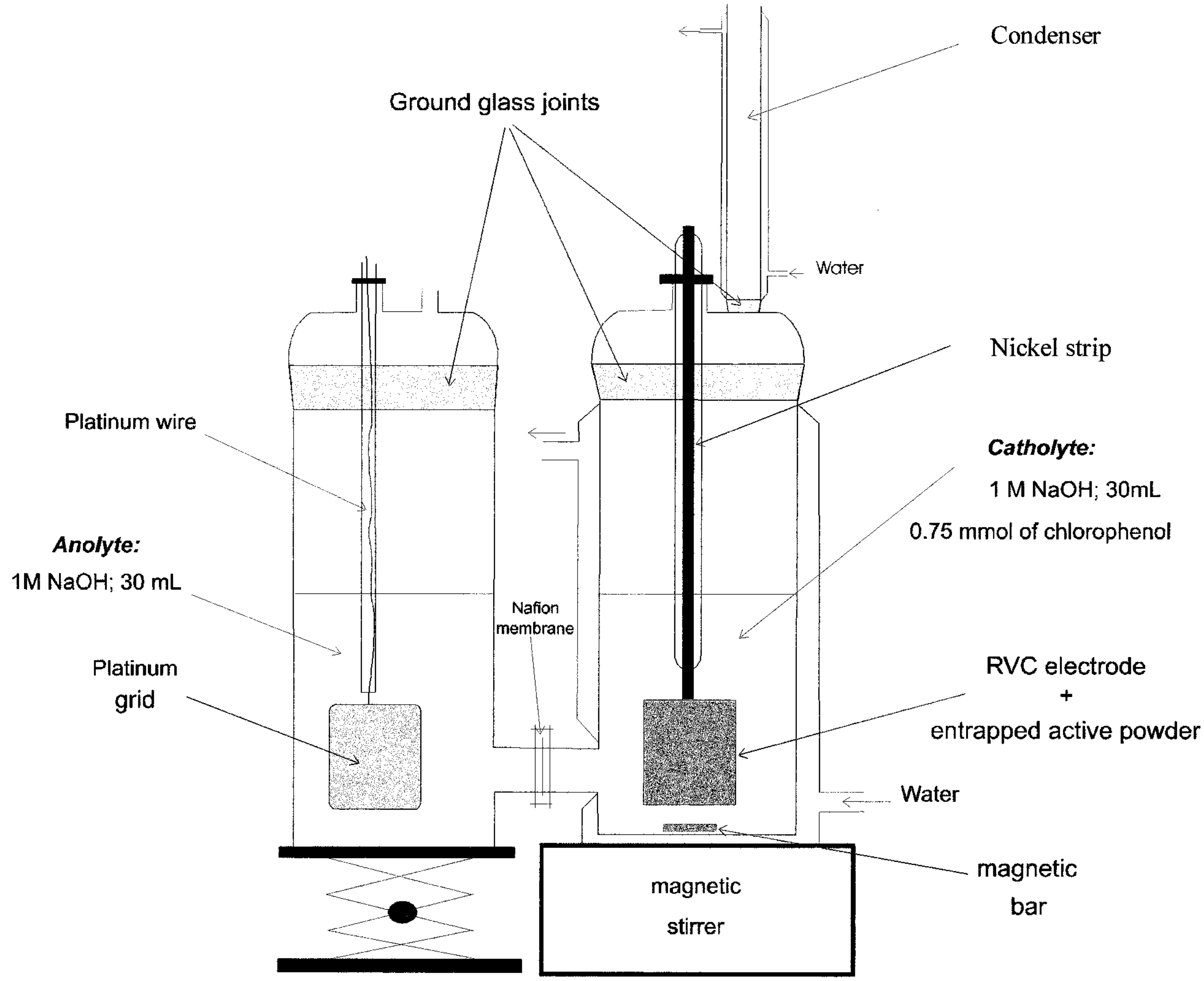

FIGURE 1. Two-compartment cell used for the electrolyses.

C) or on alumina (Pd/Al_2O_3 and Rh/Al_2O_3). The effect of various parameters on the efficiency of ECH of PCP was investigated: catalyst support, PCP concentration, current intensity, supporting electrolyte, and temperature.

Experimental Section

Electrolyses. The electrolyses were carried out in a two-compartment jacketed glass H-cell (volume of electrolyte in each compartment: 30 mL) having a Nafion-324 (E.I. duPont de Nemours & Co) membrane (1.8 cm^2) as separator and equipped with a condenser, which was connected to a constant temperature circulating bath (Haake 1) (see Figure 1). The cathode was a piece of RVC (from Electrosynthesis Company, $2.5 \times 2 \times 0.6$ cm^3, 100 ppi) to which a nickel strip for electrical contact was fixed and into which the catalyst powder was embedded in the following way. The powder (0.2 g) was introduced in the cathodic compartment containing the solvent and supporting electrolyte. Upon stirring the catholyte, the catalyst powder was forced inside the pores by convection and remained in the pores throughout the electrolysis. The anodic compartment was filled with a 1 M NaOH solution (BDH). The counter electrode was a platinum gauze. After less than half an hour of polarization, almost all the particles were entrapped in the RVC matrix, and 7.5×10^{-4} mol of PCP (Aldrich) was then added to the catholyte. The electrolyses were performed under a constant applied current using an Electrosynthesis Company (ESC) 410 potentiostat connected to an ESC 640 digital coulometer. The electrolyses of 2,6-dichlorophenol and of 4-chlorophenol (both from Aldrich) were carried out under the same conditions.

Electrocatalysts. The following electrocatalysts purchased from Aldrich were used as such in this study: Pd(5% w/w)/C, Pd(5% w/w)/Al_2O_3, and Rh(5% w/w)/Al_2O_3.

Product Analysis. After the electrolysis, the reticulated vitreous carbon electrode was thoroughly rinsed successively with 1 M NaOH and distilled ethanol. The solution was filtered, saturated with NaCl, acidified to pH $\approx$ 1 with 1 M HCl, and extracted with ethyl acetate. The compounds were analyzed by gas−liquid chromatography (GLC) and high-performance liquid chromatography (HPLC) and identified by comparison of their retention times with those of authentic samples. The GLC analyses were carried out on a Hewlett-Packard (HP) 5790a chromatograph equipped with a FID detector using a 30-m long DB-5 fused silica column, and the HPLC analyses were carried out on a system composed of a C_{18} column packing, Beckman 100A pumps, a Beckman 420 controller, a Hitachi 100-40 spectrophotometer set at $\lambda = 272$ nm, and a HP3390A integrator.

Results and Discussion

In Table 1 are summarized the results of the electrochemical reduction of PCP in 1 M aqueous sodium hydroxide and under galvanostatic control, at a RVC electrode (entry 1) and at electrodes consisting of Pd(5%))/C (entry 2), Pd(5%)/Al_2O_3 (entries 3−9), or Rh(5%)/Al_2O_3) (entries 10−12) particles entrapped in the RVC electrode. Under such basic conditions,

TABLE 1. Electrocatalytic Dehydrochlorination of PCP under Various Electrolysis Conditions

entry	catalyst	*Q*, F mol$^-$	*T*, °C	*C*, mmol L^{-1}	*i*, mA	pentachlorophenol, %	phenol, %	cyclohexanone	cyclohexanol
1	none[a]	10	50	2.5	25	90 (6)[b]	0		
2	Pd (5%)/C	10	50	2.5	25	1.5	71[c]		
3	Pd (5%)/Al_2O_3	10	25	2.5	25	34	60		
4	Pd (5%)/Al_2O_3	10	50	2.5	25	18	77		
5	Pd (5%)/Al_2O_3	10	75	2.5	25	8	92		
6	Pd (5%)/Al_2O_3	16	75	2.5	25	≤1	98		
7	Pd (5%)/Al_2O_3	10	50	7.5	25	7 (7)[b]	82		
8	Pd (5%)/Al_2O_3	10	50	2.5	10	16	79		
9[d]	Pd (5%)/Al_2O_3	10	50	2.5	25	13 (6)[b]	67		
10	Rh (5%)/Al_2O_3	16	25	2.5	25	11	44	6	40
11	Rh (5%)/Al_2O_3	24	25	2.5	25	0	0	2	92
12	Rh (5%)/Al_2O_3	16	50	2.5	25	≤1	43	5	30

[a] Electrolysis performed on the RVC electrode in the absence of transition metal catalyst. [b] Yield of tetrachloro- plus trichlorophenol. [c] Low material balance (72%) due to strong absorption of phenol on activated charcoal (see text). [d] Electrolysis performed in 1 M NH_4OH.

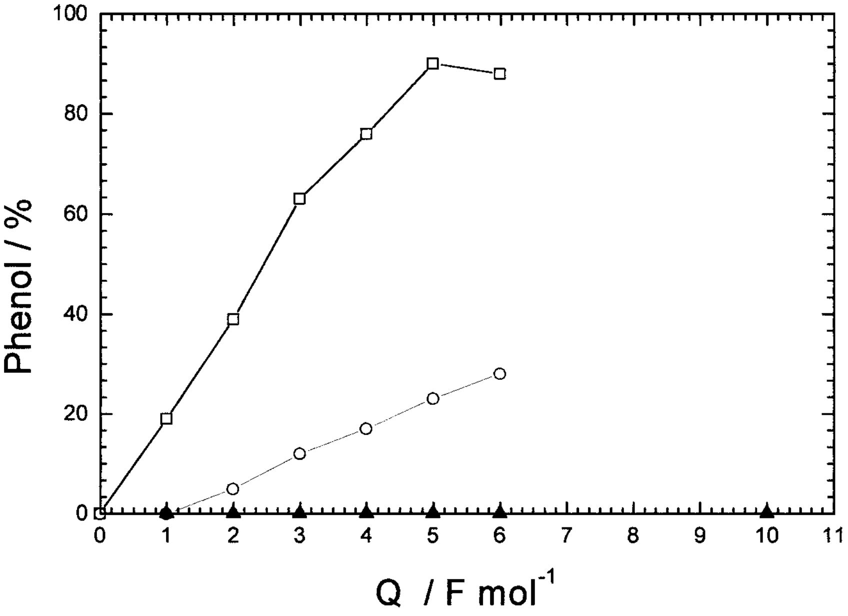

FIGURE 2. Yield of phenol formed in the electrolysis of 4-chlorophenol (□), 2,6-dichlorophenol (○), and PCP (▲) on a RVC electrode under galvanostatic conditions (i = 25 mA) in 1 M NaOH at 50 °C.

chlorophenols and phenols exist as their sodium salts which are soluble in water.

In the absence of a transition-metal catalyst and at 50 °C (entry 1), hydrogen evolution was the main process taking place since only about 10% of PCP was converted to give a mixture of tetra- and trichlorophenols after a charge corresponding to 10 mol of electrons per mol of substrate (10 F mol^{-1}). As reported previously (*31*), ECH does not occur on a RVC electrode because chemisorption of hydrogen on vitreous carbon is very weak or nonexistent. Therefore, the tetra- and trichlorophenols must have been formed by classical electroreduction (electronation-protonation) of PCP. As shown in the electrolyses of Figure 2 carried out on a RVC electrode and at 50 °C in aqueous alkali, the ease of electronation of chlorophenols decreases with the number of chlorine atoms on the aromatic ring. Indeed, after a charge corresponding to the theoretical amount of electrons required for the cleavage of all the carbon−chlorine bonds, the yield of phenol was 39% with 4-chlorophenol (after 2 F mol^{-1}), 17% with 2,6-dichlorophenol (after 4 F mol^{-1}), and 0% with PCP (after 10 F mol^{-1}). After a charge corresponding to 6 F mol^{-1}, the yield of phenol was 85% with 4-chlorophenol and 25% with 2,6-dichlorophenol.

In contrast to the results of entry 1 (Table 1), the results of entries 2−12 show that, in the presence of a transition-metal catalyst entrapped in the RVC electrode, there was extensive hydrogenolysis of PCP to phenol. Therefore, hydrogenolysis must have occurred by an ECH mechanism (eqs 1−4). On Rh/Al_2O_3 (entries 10−12), sodium phenolate, which is not reducible by electronation, was even hydrogenated further to cyclohexanone and cyclohexanol. In only two cases (entries 7 and 9), tetra- and trichlorophenols were present in small amounts (6−7% yield) in the reaction mixture, and no dichlorophenols nor chlorophenols were detected. This suggests that the electrocatalytic hydrogenolysis of the carbon−chlorine bond becomes easier as the number of chlorine atoms on the aromatic ring decreases as a result of a weaker carbon−chlorine bond and maybe also because of a less favorable adsorption of the more highly chlorinated phenols on the catalyst surface. One cannot exclude the possibility that some of the dehydrochlorination of the lesser chlorinated phenols did occur by direct electronation on the RVC matrix.

With palladium as supported catalyst, the effect of catalyst support, PCP concentration, current intensity, supporting electrolyte, and temperature on the electrocatalytic hydrogenolysis efficiency was investigated (entries 2−9). The conversion rate appears higher with Pd/C (entry 2) than with Pd/Al_2O_3 (entry 4). However, the material balance was lower with the former (72% compared to 94% with the latter) due to strong adsorption of phenol (and maybe also of PCP) on charcoal as previously observed in the electrocatalytic hydrogenolysis of phenoxyphenol (*31*). This shows once more the advantage of using alumina instead of activated charcoal as support material for ECH in aqueous medium (*31*). A 3-fold increase of the initial concentration of PCP (from 2.5 to 7.5 mmol L^{-1}) had a beneficial effect on the efficiency of the electrocatalytic hydogenolysis (about 77% current efficiency in entry 4 compare to about 87% in entry 7). This is related to an increase of the rate of the hydrogenation step (eq 4) with substrate concentration as previously discussed (*30*). In previous studies, it was found that increasing the current density over a certain value, depending on the conditions and the substrate, did cause a decrease in the ECH efficiency due to an increase in the rate of the electrochemical desorption of chemisorbed hydrogen (eq 5), the effect on the rate of the hydrogenation step (eq 4) being less important (*28*−*30*). For the electrocatalytic hydrogenolysis of PCP at Pd/C, an applied current of 25 mA was below the value where the current has an effect on the efficiency since decreasing the current to 10 mA had no influence (compare entries 4 and 8). The electrocatalytic hydrogenolysis was slightly less efficient with ammonium hydroxide as supporting electrolyte (entry 9: 67% yield of phenol, 86% material balance) than with sodium hydroxide (entry 4: 77% yield of phenol, 95% material balance). In contrast, dehydrochlorination of PCP by catalytic hydrogenation was found much less efficient in an ammonium hydroxide than in a sodium hydroxide solution (*17*). Finally, increasing the temperature from 25 to 75 °C (see entries 3−5) favored hydrogenolysis (eq 2) over hydrogen desorption (eqs 5 and(or) 6) as shown by the increase in conversion rate (from 66% to 92%) and in yield of phenol (from 60% to 92%). Hence and interestingly, at 75 °C, it was possible to reach complete hydrogenolysis of PCP to phenol (98% yield) after 16 F mol^{-1} (61% current efficiency) (entry 6).

We have shown recently that Rh(5%)/Al_2O_3 entrapped in a RVC electrode is very efficient for the ECH of phenol in aqueous alkali (*31*). Indeed, after 10 F mol^{-1} (corresponding to the theoretical charge for complete hydrogenation of phenol), all the phenol had been hydrogenated to cyclohexanol (97% yield, 60% current efficiency). No hydrogenation occurred on the RVC electrode in the absence of catalyst, showing that the ECH process does not take place on vitreous carbon and that the phenolate anion is not reducible by electronation in aqueous alkali as already pointed out. In entries 10−12 of Table 1, it can be seen that electrocatalytic hydrogenolysis of PCP to phenol is also efficient on Rh/Al_2O_3 and that the phenol is further electrohydrogenated as expected from the previous studies. The lower material balance at 50 °C (entry 12: 78%) than at 25 °C (entry 10: 100%) was due to the loss of cyclohexanol by evaporation during the electrolysis even if the cell was equipped with a water-cooled condenser. Indeed, when a 0.025 M solution of cyclohexanol was put in the cell under the electrolysis conditions (except that no current was applied), its concentration diminished gradually, and there was none left after 12 h. There was no loss of cyclohexanol at 25 °C. It is noteworthy that it was possible to convert PCP completely to cyclohexanol (92% yield) with some residual cyclohexanone (2%) at 25 °C with a charge corresponding to 24 F mol^{-1} (about 62% current efficiency) (entry 11).

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