

Palladium-Assisted Electrodehalogenation of 1,1,2-Trichloro-1,2,2-trifluoroethane on Lead Cathodes Combined with Hydrogen Diffusion Anodes

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ABSTRACT

In this work, the efficiency and product formation in the electroreduction of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) to obtain completely dechlorinated products has been studied using constant-current electrolysis at different current densities, gas chromatography, scanning electron microscopy, and energy dispersive x-ray. While chlorotrifluoroethane was the main product obtained from CFC 113 in MeOH-water solutions containing NH_4Cl , different and suitable conditions which lead to its complete dechlorination are described in this paper. In the presence of small amounts of Pd^{2+} in solution, a very thin film of Pd black was electrodeposited on the Pb cathode and the efficiency of the CFC 113 electroreduction was about 98%. The efficiency was much smaller and the product composition very different in the absence of Pd^{2+} in solution, even in the presence of Pd black electrodeposited on the cathode. In the presence of Pd^{2+} , the main products in the gas phase were difluoroethene and trifluoroethene. Small amounts of 1,2-dichloro-1,1,2-trifluoroethane, chlorotrifluoroethene, difluoroethane, and fluoroethane were also present in the gas phase. The liquid composition was enriched in the less volatile compounds. A possible reaction pathway involving the removal of halides by successive reactions is discussed. The anode employed in these experiments was a thin Pd foil with electrodeposited Pd black, which permitted hydrogen diffusion and its further oxidation to H^+ . Because of this reaction, contamination of the working-electrolyte by other oxidation products such as Cl_2 or MeOH derivatives were avoided. This system allows new electrochemical processes along with CFC electrodegradation.

Introduction

Protection of the stratospheric ozone layer is one of the basic environmental goals which have been assumed by most countries of the world. As stratospheric ozone depletion has been related with human activities, in particular the CFC industry,¹ many governments signed the Montreal protocol, thus being in agreement to suppress their CFC production and use. As signed in this protocol, CFCs should not be produced after 1995 (together with other chlorine-containing chemical compounds such as tetrachloromethane and trichloroethane). However, there are many tons of CFCs in stock. In order to avoid residual emissions to the atmosphere, it is necessary to destroy them or even to employ them as raw materials in organic synthesis.

Different procedures for CFC destruction or transformation have been given in the literature.²⁻¹¹ Chemical degradations leading to partial or complete dehalogenation of CFCs have been proposed, for example catalytic,²⁻⁸ combustion,⁹ photochemical,¹⁰ and chemical reduction¹¹ methods. Thus, trifluoroethene (TFE) formation by catalytic hydrogenation of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) at high temperatures was already reported.⁵⁻⁸ TFE was obtained with selectivities in the range 29 to 61.5%, the CFC 113 conversion being in the range 55 to 100%. There are, however, electrochemical processes in conventional cells which use CFCs as reactants and produce partially or completely dehalogenated compounds which could be employed in other applications.¹²⁻²⁵ Thus, chlorotrifluoroethene (CTFE) can be obtained from the electroreduction of CFC 113 on Hg, Pb, Zn, Ni, Cu, Cd, and Al cathodes¹²⁻¹⁹ and wetproofed porous cathodes,^{20,21} using aqueous solutions of ammonium salts, detergents, or metal halides (in the presence or in the absence of organic solvents such as acetone or alcohols) at temperatures in the range 0 to 100°C. In particular, NH_4^+ and tetraalkylammonium ions significantly facilitate the electroreduction of CFC 113 to CTFE.^{12,21} CTFE is an industrial monomer which can be used to produce oils and waxes.²³ On the other hand, the electroreduction of CFC 114 (1,2-

dichloro-1,1,2,2-tetrafluoroethane) on Hg cathodes yields tetrafluoroethene.^{16,24} The electroreduction of CFC 12 (dichlorodifluoromethane) in 0.5 mol dm^{-3} LiClO_4 (or tetramethylammonium trifluoroacetate) solutions of organic solvents (acetonitrile, tetrahydrofuran, or ethanol) on amalgamated Cu at a temperature of -70°C leads to tetrafluoroethylene and chlorodifluoromethane (the chemical yield in terms of reacted CFC 12 attained was 25% for tetrafluoroethene and 29% for chlorodifluoromethane).²⁵ Finally, the electroreduction of CFC 11 (trichlorofluoromethane) and CFC 12 in ethanol- H_2O solutions at Hg cathodes produces different dechlorinated compounds including fluoromethane or difluoromethane.¹⁶

In preliminary work of the authors,²⁶ the complete electrodechlorination of CFC 113 has been reported. To our knowledge, TFE and difluoroethene (DFE) formation instead of CTFE by the electrochemical reduction of CFC 113 has thus been described for the first time. TFE and DFE, unsaturated compounds which may be subjected to a polymerization reaction to yield Teflon-like polymers, were produced on Cd and Pb cathodes in methanol (70% v/v)-water solutions containing NH_4Cl (0.25 and 0.75 mol dm^{-3}) and PdCl_2 (50 ppm) at 0 and 20°C with a current density of -80 mA cm^{-2} . Although the current efficiencies were not determined, higher yields were evidenced for the highest NH_4Cl concentration. A hydrogen diffusion anode based on a Pd foil with electrodeposited Pd black was employed, thus permitting the use of a single-compartment cell in the electrolysis. This anode was sufficient to support the currents needed in the process and did not lead to undesirable side reactions. In addition, the hydrogen diffusion anodes are less energy-consuming than the conventional ones.

In this work, the best conditions for an efficient CFC 113 electroreduction are pursued. A laboratory electrochemical cell in which a Pd-based hydrogen diffusion anode and a Pb cathode were employed was used. The experiments were conducted at different constant current densities, in different methanol-water mixtures containing 0.75 mol dm^{-3} NH_4Cl and different concentrations of Pd^{2+} . Parallel experiments to obtain insight into the reaction pathway of the process were also performed. The products

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of CFC 113 electroreduction were analyzed by means of gas chromatography coupled to mass spectrometry (GC-MS). The hydrogen content was quantified by GC using a thermal conductivity detector (TCD), and the Pd^{2+} content of the electrolyte was analyzed using the inductively coupled plasma technique (ICP). The surface of the cathode was examined by SEM and EDX.

Experimental

Cell and electrolytes.—The experimental cell consisted of a single-compartment chamber of about 100 cm^3 in volume in which the anode was downward facing and the cathode upward facing (see Fig. 1). The gas evolved on the cathode was collected by means of a graduated tube, placed in parallel with the anode support. The gas samples were collected with a syringe through the septum of this tube.

The anode consisted of a Pd foil 0.025 mm thick with 4 mg cm^{-2} of Pd black electrodeposited on it, and was prepared as previously described Ref. 27. The Pd foil was first polished with alumina, rinsed in an ultrasonic bath, and degreased with ethyl alcohol. The Pd foil was then cathodically polarized in 5% KOH at a current density of -15 mA cm^{-2} up to the formation of a curtain of bubbles on its surface. Afterward, Pd black was electrodeposited on both faces of the foil from a 2% PdCl_2 solution acidified to pH 0 with HCl, at a current density of -15 mA cm^{-2} at 50°C for 8 min. Subsequently, the electrode was rinsed in Millipore Milli Q quality water, dried in warm air, and mounted in a cylindrical support, opposite to the hydrogen inlet. In this form, the hydrogen contained in the inner part of the cylinder, at a pressure of 1 atm, permeates through the foil to the Pd/electrolyte interface, where it is oxidized. The section of the Pd electrode exposed to the working solution was 0.5 cm^2 .

The cathodes were made of high-purity lead. They were cut as rods having sections of 0.04 and 0.08 cm^2 (the lowest area was used for the electrolysis at -200 and -140 mA cm^{-2} and the highest for -40 and -80 mA cm^{-2}). One base of the rod was connected to a copper wire. Then, the entire rod was embedded in a cylinder of epoxy resin. Before the experiments, the epoxy cylinder was polished to expose the base of the metallic rod (which was the electrode area offered to the working solution). The area of the

anode was about ten times greater than that of the cathode in order to assure its stability during electrolysis. The anode stability was proved by Pd^{2+} analysis of the electrolyte during the experiments in the absence of added Pd^{2+} . No cation release from the anode was found.

The electrolyte consisted of $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$ dissolved in a methanol (50 to 80% v/v)-water mixture, to which a small amount of PdCl_2 was added (concentrations in the range 0 to 75 ppm). The experiments were conducted at 20°C without stirring. Before the electrolysis, the methanol-water solution was saturated with CFC 113 to form a layer of it in the bottom of the cell (which was always present during the experiment) and the graduated tube was completely filled with the working solution. Afterwards, a constant current density was applied to the cathode in the range from -40 to -200 mA cm^{-2} by means of a Solartron 1286 potentiostat-galvanostat. Gas volumes less than 25 cm^3 were collected from the cathode after suitable times of electrolysis (normally 8 to 14 h). The effect of the addition of Pd^{2+} to the working electrolyte was tested by the addition of a volume of 2% PdCl_2 solution acidified to pH 0 with HCl or eventually with HNO_3 . The effect of a Pd black layer freshly electrodeposited on the Pb cathode was also tested. In this case, a Pd black layer of 4 mg cm^{-2} was electrodeposited on a recently polished Pb electrode using the same solution and conditions as in the preparation of the Pd anodes (see above).

Chemical analysis.—The analysis of the products was carried out by gas chromatography (HP 5890, Series II, electron impact) coupled with mass spectrometry (GC-MS), using HP-5 and DB-624 capillary columns, the gas carrier being He (5 psi). The oven temperature was held at 30°C for 5 min and then increased to 250°C at $10^\circ\text{C min}^{-1}$. Different ranges of molecular weights were measured to deconvolute the overlapping peaks. The liquid solution was analyzed after extracting the organic compounds in chloroform. In this case, the procedure was to add 1 cm^3 of chloroform to 5 cm^3 of the liquid solution of the cell (cooled to 0°C). The chloroform-rich phase was separated by the addition of an excess of cold Milli-Q water. The resulting products were identified by means of the corresponding mass spectra (McLafferty data base). The analysis of Pd^{2+} in solution during the electrolysis was performed collecting small volumes of the electrolyte. The organic compounds of such samples were mineralized with $\text{HNO}_3\text{-HClO}_4$. After evaporation and dissolution with HNO_3 , the Pd^{2+} content was determined by the inductively coupled plasma technique using a Perkin-Elmer ELAN 6000 ICP-MS.

The compositions of the products in the gas and in the liquid are given, excluding H_2 , in relative amounts (mol percent) determined by the area-normalization method. The relative amounts were not corrected for the response factors, because at this stage the main object was the analysis of the dechlorinated compounds and the conditions with higher efficiencies. Such relative amounts (R) were sufficient to identify the main CFC 113 derivative appearing, in the gas and in the liquid, under the different experimental conditions. The H_2 content of the gas evolved from the cathode was determined by GC (HP 5890) using a thermal conductivity detector (TCD) and a 15 ft Supelco 60-80 Carboxen 1000 column. The oven temperature was 35°C and the N_2 flow was set at $30 \text{ cm}^3 \text{ min}^{-1}$. The quantitative analysis was carried out with standards of different compositions. The efficiency of the CFC 113 electroreduction could then be calculated by the difference between the total charge employed in the electrolysis and that employed in Pd electrodeposition (calculated from the Pd^{2+} analysis of the electrolyte) and in H_2 formation (H_2 in the gas evolved from the cathode plus H_2 absorption in the electrodeposited Pd).

SEM observations.—The surface and the transverse section of the cathode were examined by scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDX) after constant-current electrolysis in the presence

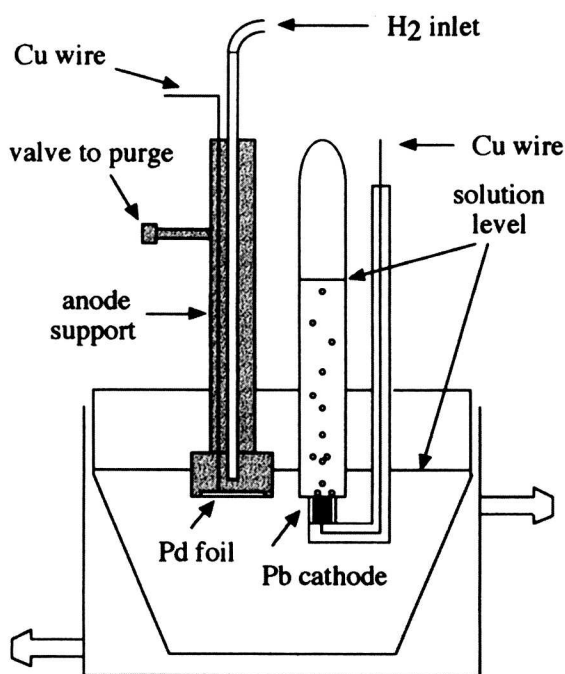


Fig. 1. Diagram of the cell used to collect the gas evolved from the cathode.

of Pd^{2+} in solution. The cathodes to be observed by SEM were rinsed with ethanol, dried in air, and stored under high vacuum. The transverse sections were cut after embedding the cathode in epoxy resin and were covered by a sputtered thin film of carbon.

Results and Discussion

Identification of the processes and efficiencies of CFC 113 electroreduction.—As indicated above, the results of the analysis of the gas and of the liquid are given in relative amounts [$R/\text{mol percent (m/o)}$] of each product, considering all products of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) electroreduction and excluding H_2 , CFC 113, and solvents. The different values of R will provide the best conditions for the electrosynthesis of a particular CFC derivative. The results of different electrolyses are shown in Fig. 2. In Fig. 2a, b, and c, bars 1 correspond to the MeOH (70% v/v)- H_2O solution containing $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$ and 50 ppm PdCl_2 , bars 2 to the same solution in the absence of Pd^{2+} , and bars 3 and 4 to the use of a Pb/Pd cathode in the absence of Pd^{2+} in solution. The Pb/Pd cathode consisted of a Pb cathode with a thin film of Pd black electrodeposited previously. 1,2-dichloro-1,1,2-trifluoroethane (DCTFE) and chlorotrifluoroethane (CTFE) together with completely dechlorinated compounds were obtained. For reasons of simplicity when presenting the experimental results, the completely dechlorinated compounds are referred to as CDCs and the values of R of the CDCs mean the sum of the values of R of the different CDCs formed. However, CDC compositions are also given separately.

In order to first study the effect of the presence of Pd^{2+} in solution for $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$, the analyses of the gas and of the working electrolyte were performed after different electrolyses using solutions differing only in the cation content. The bars 1 and 2 of Fig. 2a-c clearly show that both in the gas and in the liquid, the relative amounts of CTFE and that of CDCs after a constant-charge electrolysis are opposite in the presence and in the absence of Pd^{2+} . In the gas phase, CTFE is the main product obtained in the absence of Pd^{2+} , whereas CDCs are the main products in the presence of Pd^{2+} . The main CDCs in the presence of Pd^{2+} were 1,1-DFE and 1,2-DFE. The relative amounts of DFEs were 58 and 60% for current densities of -80 and -200 mA cm^{-2} , respectively. The corresponding relative amounts of TFE for the same current densities were 17 and 13%. Small quantities of difluoroethane and fluoroethane were also found. It should be noted that small amounts of TFE and DFE were also found in the absence of Pd^{2+} (bars 2 in Fig. 2a and c), but TFE was dominant with respect to DFE and the main product was CTFE.

The product analysis of the liquids always gave the same organic compounds as those found in the gas, in agreement with previous results.²⁶ Formation of Cl_2 and MeOH oxidized derivatives, as should be formed with conventional anodes, were thereby avoided.

To determine the efficiency of CFC 113 electroreduction, the different processes taking place at the same time must be known. Aside from CFC 113 electroreduction, these could be hydrogen evolution and Pd electrodeposition.

It is interesting to note that after the experiments in the presence of Pd^{2+} , a certain quantity of Pd black was electrodeposited on the Pb cathode (Fig. 3). Figure 3a is the secondary electron image (SEI) of the surface of the cathode after long-time electrolysis (experiment with $Q = -386 \text{ C}$ in Table I) and shows the fractal nature of the Pd electrodeposit, while Fig. 3b shows the backscattered electron image (BEI) of the same region as that of Fig. 3a. This latter image permits an estimation of the Pd film thickness. At 20 kV voltage acceleration, the electron beam promotes metal ionization up to a depth of about $1 \mu\text{m}$, while x-ray emission is estimated to proceed from a depth of about $1.5 \mu\text{m}$ (because of the secondary ionization). In the BEI mode, the brighter areas correspond to the regions where the atomic number of the element is higher, *i.e.*, where the Pb under the Pd film is detected by the electron

beam (this was confirmed by EDX microanalysis). Thus, at 20 kV, the bright regions must correspond to Pd film thicknesses thinner than about $1.5 \mu\text{m}$. The bright area increased with the acceleration voltage. Therefore, the thicker regions should not exceed a few microns (for instance, the star-shaped Pd structure in the middle of Fig. 3a). In any case, the Pd black electrodeposit is far from being a compact film. This is clearly demonstrated in Fig. 3c, where the transverse section of the Pd film is

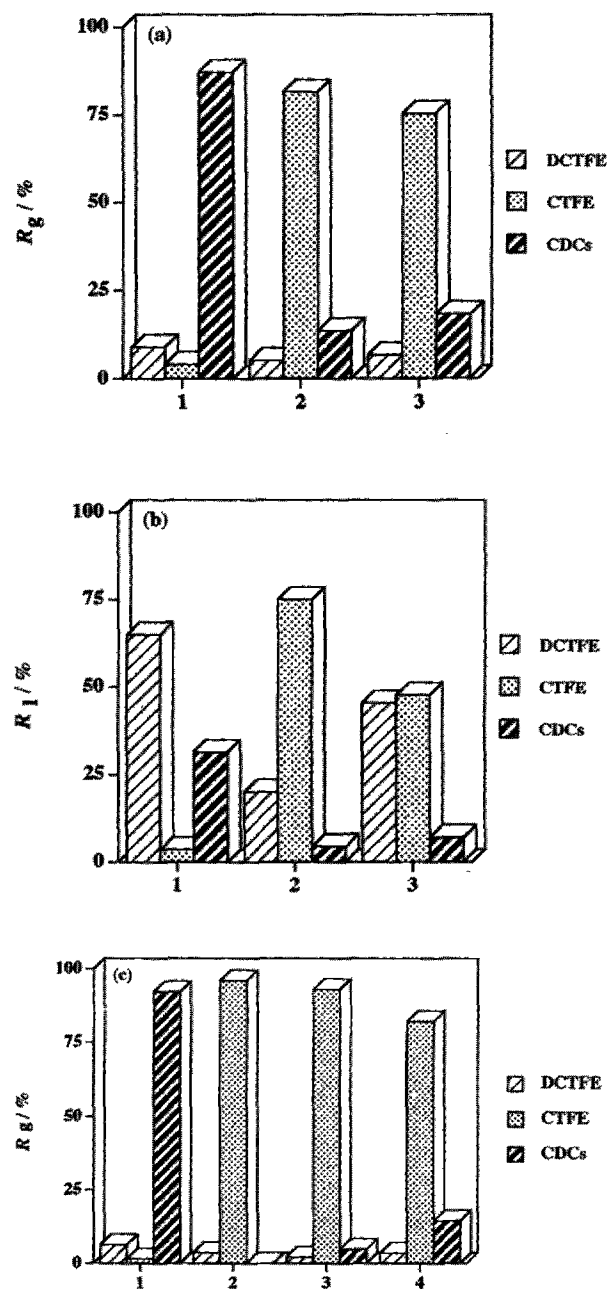


Fig. 2. Relative amounts [R (w/o)] of the products of the electroreduction of CFC 113 in MeOH (70% v/v)- H_2O solution containing $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$. In these figures, bars 1 correspond to working solutions containing 50 ppm PdCl_2 , bars 2 to working solutions in the absence of Pd^{2+} , and bars 3 and 4 to the use of a Pb/Pd cathode (Pb cathode with a thin film of electrodeposited Pd black), also in the absence of Pd^{2+} in solution. Bars 3 correspond to a Pb cathode with a thin film of Pd black electrodeposited in a previous CFC electrolysis. Bars 4 correspond to a Pb cathode with a 4 mg cm^{-2} film of freshly electrodeposited Pd black. (a) gas phase, -80 mA cm^{-2} ; (b) liquid, -80 mA cm^{-2} ; (c) gas phase, -200 mA cm^{-2} . The total cathodic charges, Q , were -160 C for all the experiments.

shown. The Pd coating then consists of a thin Pd film on Pb and star-shaped nuclei on it. The white square cursor shows a cavity free of Pd.

On the other hand, the total quantity of Pd in the cell was 3.0 mg (corresponding to a PdCl_2 concentration of 50 ppm). A cathodic charge of 5.4 C should be necessary to electrodeposit all of the Pd^{2+} present in the cell, and a compact film thickness of about 28 μm should be obtained (assuming a Pd density of 12.0 g cm^{-3} , *i.e.*, that of the bulk Pd). However, the thickness of the electrodeposit was far below 28 μm (see Fig. 3c). For this reason, the Pd^{2+} content of the solution during electrolysis was determined. After an electrolysis at -200 mA cm^{-2} for sufficient time to consume a cathodic charge of 348 C (see Table I), it was found

that the Pd^{2+} content of the solution changed from 28 to 23 ppm. The equivalent to 5 ppm is then expected to be electrodeposited, which corresponds to a homogeneous film thickness of about 5 μm . In the case of -80 mA cm^{-2} , the equivalent of 6 ppm was electrodeposited after a 386 C electrolysis, which corresponds to a homogeneous film thickness of about 6 μm , thus being consistent with the SEM observation of Fig. 3c.

Apart from the charge employed in the Pd electrodeposition, it is necessary to know the charge employed in H_2 evolution in order to evaluate the efficiencies of CFC electroreduction. As indicated in the Experimental section, the H_2 present in the gas phase evolved from the cathode was determined by the corresponding quantitative analysis of H_2 in this gas. In addition, it is well documented that hydrogen is strongly absorbed into Pd.²⁷⁻³⁰ In the case of proton reduction on Pd cathodes, a certain quantity of hydrogen is also expected to be absorbed in it.²⁸ The total quantity of hydrogen absorbed is not known exactly. However, a good estimation can be made assuming the relation of one hydrogen atom per two Pd atoms.³⁰ In this case, a charge of about 0.3 C is needed for the 6 μm thick Pd film obtained in this work. Note that this charge is much smaller than those employed in the process (see the *Q* values in the Table I).

It can be claimed that protons can be continuously reduced on the electrodeposited Pd black while atomic hydrogen is undergoing a chemical reaction with the halogenated compounds, as suggested by Cleghorn *et al.*²⁸ for the cathodic hydrogenation of other organic molecules (aromatic nitrogroups, some alkynes, alkenes, and aldehydes, etc.). In this case, the current would be also employed (although indirectly) in CFC 113 dehalogenation. So, no additional correction accounting for this contribution should be made in the calculation of the efficiency.

The efficiencies of the CFC 113 electroreduction, calculated as indicated above, under the different conditions studied, *i.e.*, presence of Pd^{2+} in solution, concentration of methanol, nature of the cathode, current density, and cathodic charge, are listed in Table I. The first result to be noted is that efficiencies of about 98% are obtained only when MeOH concentrations are 70 to 80% and Pd^{2+} is present in the electrolyte. In addition, not only is the efficiency for the CFC 113 electroreduction much higher in the presence of this cation, but also the formation of the CDCs is strongly favored (see Fig. 2).

Another question can be raised in relation to the role of Pd and Pd^{2+} in CFC electroreduction. It is known that Pd black acts as a catalyst in the reduction of organic substances in protic media.²⁸ For this reason, different experiments using electrodeposited Pd black on Pb in a previous electrolysis (we refer to this electrode as the Pb/Pd cathode) and without Pd^{2+} in the electrolyte were performed. The Pb/Pd cathode was prepared by two different procedures: (i) Pd black electrodeposition in a previous electrolysis using the Pb cathode in the working electrolyte itself (methanolic solution containing NH_4Cl and Pd^{2+}) or (ii) fresh electrodeposition of a 4 mg cm^{-2} (about 3.5 μm thick) film of Pd black (see the Experimental section). These results are presented and compared with those obtained in the presence and in the absence of Pd^{2+} (Fig. 2). The bars marked 3 in Fig. 2a-c show that when the first electrodeposition procedure was used, the relative amounts of CDCs were slightly higher than those obtained in the absence of Pd^{2+} (bars marked 2). Note that the efficiencies for CFC electroreduction decreased when this Pb/Pd electrode was employed in the absence of Pd^{2+} in the electrolyte (Table I). This result means that the current leading to H_2 evolution is quite high. In addition, the relative amounts of the products did not change significantly when the cathodic charge was increased to -210 C .

A slight further increase in the relative amount of CDCs was found when the Pd black was electrodeposited by the second procedure (bar 4 in Fig. 2c). However, CTFE was also dominant. Moreover, the CFC 113 electroreduction efficiency was found to be the same as that found for the

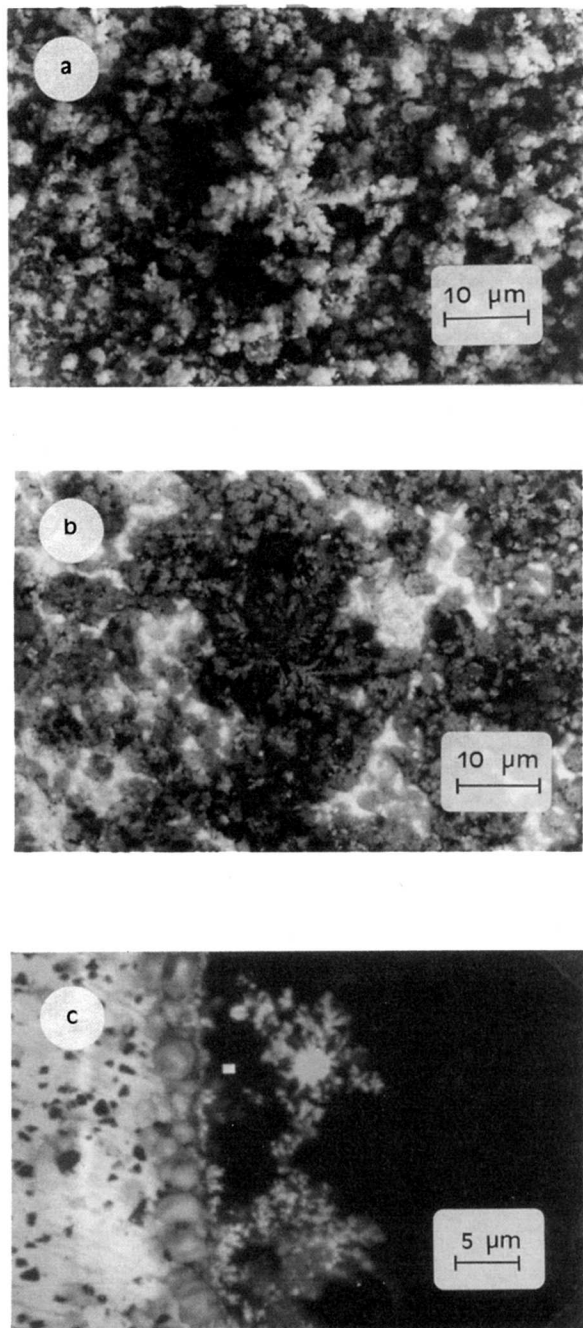


Fig. 3. SEI (a) and BEI (b) of the surface of a Pb cathode showing the fractal electrodeposition of a very thin film of Pd black after the experiment at -80 mA cm^{-2} with total cathodic charge of -386 C described in Table I. Both micrographs correspond to the same sample area. Fig. 3c is the SEI of a section of the Pd film shown in Fig. 3a.

Table I. Current efficiencies (ϵ) of CFC 113 electroreduction on Pb cathodes under different conditions (MeOH concentration, current density, in the presence and in the absence of Pd^{2+}) in MeOH-H₂O solutions containing 0.75 mol dm⁻³ NH₄Cl, calculated from the volume and H₂ concentration ([H₂]) of the gas evolved from the cathode, considering Pd electrodeposition (ICP-MS analysis) and hydrogen absorption by the electrodeposited Pd (one hydrogen atom per two Pd atoms).^c

Cathode	[MeOH] (% v/v)	[Pd ²⁺] (ppm)	-j (mA cm ⁻²)	-Q ^a (C)	[H ₂] (% v/v)	ϵ (%)
Pb	70	50	80	386	0.0	98
id ^d	id	—	id	145	29	83
Pb/Pd ^b	id	—	id	161	44	61
Pb	id	50	200	348	3.5	98
id	id	—	id	131	49	58
Pb/Pd ^b	id	—	id	210	54	50
Pb	50	50	80	209	46	55 to 58 ^b
id	60	id	id	325	37	76 to 78 ^b
id	80	id	id	277	2.0	97 to 99 ^b

^a Cathodic charges employed in the corresponding experiment.

^b Pb/Pd refers to a Pb cathode with a thin film of Pd black, which was electrodeposited in a previous experiment using the same electrolyte with 50 ppm PdCl₂.

^c Pd electrodeposited was not determined and thus the minimum and the maximum values are given, corresponding, respectively, to complete Pd electrodeposition and no Pd electrodeposition.

^d id = identical.

experiment of bar 3 in Fig. 2c. By comparing bars 3 and 4 in Fig. 2c, some effect of the cathode history is observed. However, it is clear that the presence of Pd²⁺ in the electrolyte exerts a positive effect on the efficiency of CFC 113 electroreduction and leads to greater amounts of the completely dechlorinated products. Such a comparison also indicates that, apart from the existence of some hydrogenation by Pd(H), *i.e.*, the surface catalysis mechanism, a significant part of the overall process should proceed via a different mechanism.

Effect of cathodic charge.—To obtain further insight into the effect of the presence of Pd²⁺ in solution, analyses of the gas and the liquid for different times of electrolysis (and thus cathodic charges) at -200 mA cm⁻² were carried out (Fig. 4) in different experiments. The determination of the relative amounts of dechlorinated products in the gas phase, Fig. 4a, and in the liquid, Fig. 4b, allows one to follow the change in the composition of the products which are being formed during the electrolysis. In the gas phase, it is interesting to note that the relative amount of DCTFE increases slightly with time but remains at a low level (*R* about 10%). As shown in Fig. 4b this compound is very

soluble in the liquid. CTFE formation in the gas phase and in the liquid is dominant at the beginning of the electrolysis. However, the relative amounts of CTFE in both phases decrease down to about 2% during the electrolysis. In contrast, the CDCs contents, even though small in the gas and in the liquid at the beginning of the experiment, suddenly present a sharp increase to be dominant in the gas (*R* near 90%) and important in the liquid (*R* about 30%). This behavior can be explained by the solubility of the partially or totally dechlorinated products in the liquid, the multicomponent system evolving continuously to a liquid-gas equilibrium during the course of the electrolysis. The most volatile compounds are less soluble in the liquid, thus being mostly found in the gas, whereas DCTFE is mainly found in the liquid.

The volume of gas evolved on the cathode *vs.* charge in these experiments is plotted in Fig. 5 (curve a) together with the equivalent plots for the Pb electrode in the absence of Pd and Pd²⁺ (curve b) and the Pb/Pd electrode in the absence of Pd²⁺ (curve c). The same curve c was obtained using the two electrodeposition procedures described before (fresh electrodeposition and electrodeposition during a previous electrolysis). The curve a in Fig. 5

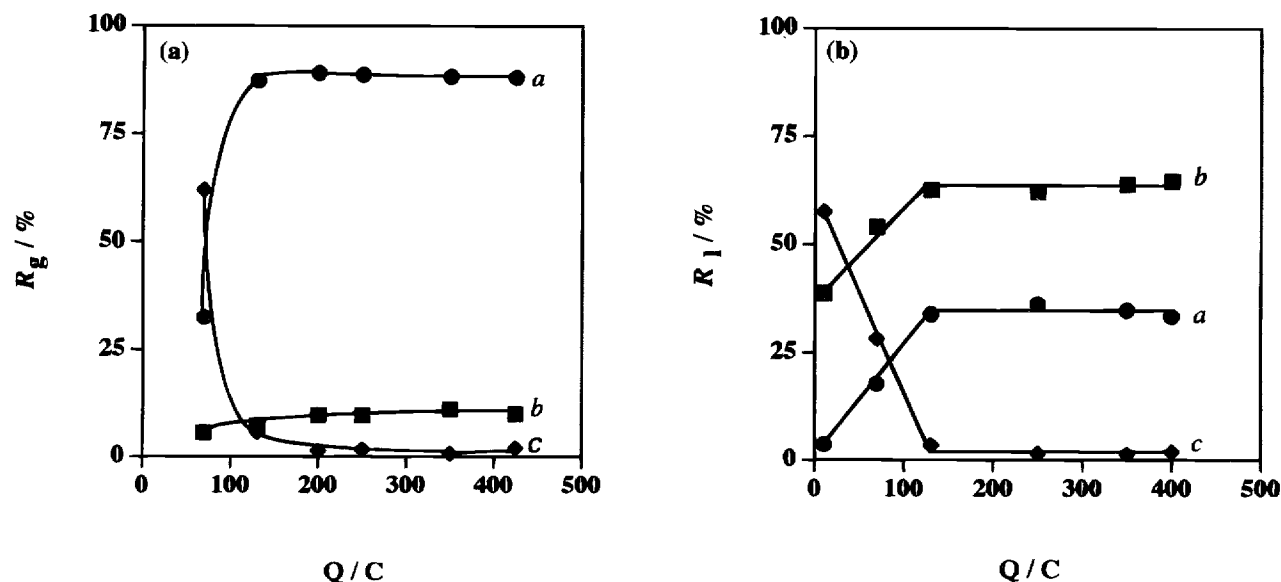


Fig. 4. Relative amounts in the gas phase, R_g (m/o) (a), and in the liquid, R_l (m/o) (b), of the products of the CFC 113 electroreduction in MeOH (70%)-H₂O containing 0.75 mol dm⁻³ NH₄Cl and 50 ppm PdCl₂ at a current density of -200 mA cm⁻². Curve a in Fig. 4a and b refers to CDCs, curve b to DCTFE, and curve c to CTFE.

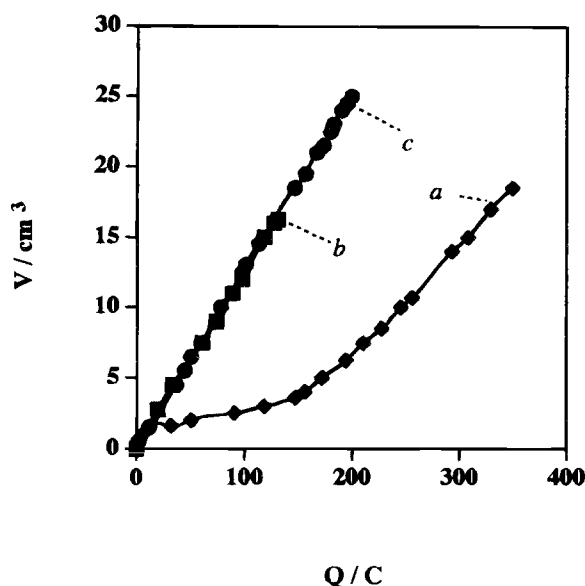


Fig. 5. Volume (V) vs. charge (Q) plots of the gas evolved on the cathode during the electroreduction of CFC 113 at -200 mA cm^{-2} in MeOH (70%)- H_2O containing $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$. a: The working solution contains 50 ppm PdCl_2 ; b: Pb cathode in the absence of Pd^{2+} ; c: Pb/Pd cathode (the same curve was obtained for both a Pb cathode with a thin film of Pd black electrodeposited in a previous CFC electrolysis and for a Pb cathode with a thin film of Pd black freshly electrodeposited).

grows following an almost parabolic shape, whereas linear plots are obtained for curves b and c. These latter plots can be explained considering that the volume of gas evolved is proportional to the volume of H_2 produced (see Table I). Hydrogen is not soluble in the electrolyte, but the products of the CFC 113 electroreduction present a certain solubility. The increase in volume of curve a could be due to a gradual increase in H_2 formation. However, the efficiency for CFC 113 electroreduction after the total time of electrolysis was 98% (Table I) and thus, such a gradual increase must be related to the continuous increase in the CFC degradation products concentrations until the electrolyte becomes saturated. In particular, the CDCs formed are transferred to the gas phase, since they are the most volatile products.

Effect of the MeOH concentration.—In Table I, the efficiencies of CFC 113 electroreduction at a current density of -80 mA cm^{-2} in the MeOH- H_2O solution containing 50 ppm PdCl_2 , for different concentrations of MeOH, are also listed. It can be seen that the efficiencies increase with the MeOH concentration. At a concentration of 50%, the efficiency was 55 to 58% whereas efficiencies of 97 to 99% were achieved at MeOH concentrations of 70 to 80% v/v. This can be interpreted considering the solubility-transport phenomena of these organic compounds. As previously reported by Savall *et al.*¹² the saturation concentration of CFC 113 in a MeOH (70% v/v)- H_2O solution containing $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$ is about 0.17 mol dm^{-3} , whereas in the solution containing 50% v/v MeOH, it is only about 0.02 mol dm^{-3} . Thus, under potentiostatic control, the reduction of CFC 113 to CTFE on a rotating zinc disk was mass-transfer limited when the MeOH concentration was lower than 70% v/v.¹² The relative amounts in the gas phase as a function of MeOH concentration are presented in Fig. 6a and b. As shown in Fig. 6a the most relevant result is that much higher concentrations of CDCs are found in the gas when the MeOH concentrations are 70 and 80%. It is also proved that in the liquid phase, the concentrations of CDCs also increased with MeOH concentration. In Fig. 6b, the relative amounts of the different CDCs are represented. These relative amounts are referred

to the total amount of CFC derivatives present in the gas phase, that is curve a in Fig. 6a is the sum of all the curves in Fig. 6b. As shown in this figure, the CDCs contain DFE, TFE, and small quantities of difluoroethane and fluoroethane. The most important effect of MeOH is seen for DFE (curve d). It should be noted that DFE, the most abundant CDC, was either in the form of 1,1-DFE or 1,2-DFE. Therefore, it is concluded that MeOH concentrations in the range 70 to 80% are suitable to obtain the CDCs reported here.

Effect of current density.—The effect of current density on the product distribution was also studied. Different experiments at a constant charge of -160 C were performed at current densities in the range from -40 to -200 mA cm^{-2} . Figure 7 shows that no significant differences in the relative amounts of DCTFE, CTFE, and CDCs were found. The relative amounts of CDCs were about 87% for all of the current densities studied. DFE, TFE, difluoroethane, and fluoroethane were found in the gas

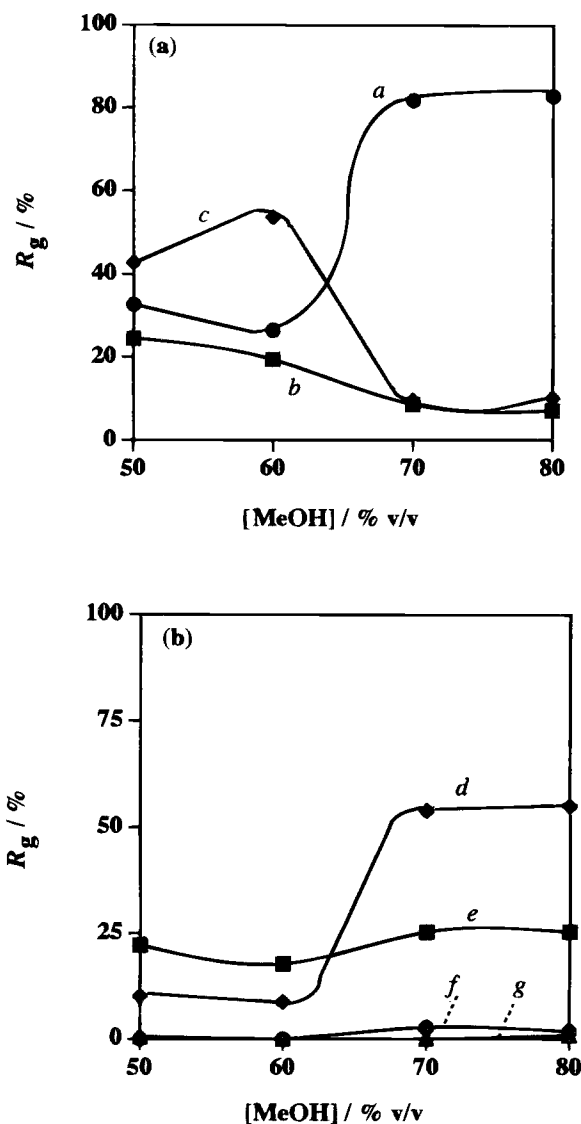


Fig. 6. Relative amounts in the gas phase, R_g (m/o) of the products of the CFC 113 electroreduction at -80 mA cm^{-2} in MeOH- H_2O solution containing $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$ and 50 ppm PdCl_2 . The cathodic charges for MeOH concentrations of 50, 60, 70, and 80% v/v were 210, 325, 386, and 386 C, respectively. (a) Curve a refers to CDCs, curve b to DCTFE, and curve c to CTFE. (b) Curve d refers to DFE, curve e to TFE, curve f to difluoroethane, and curve g to fluoroethane.

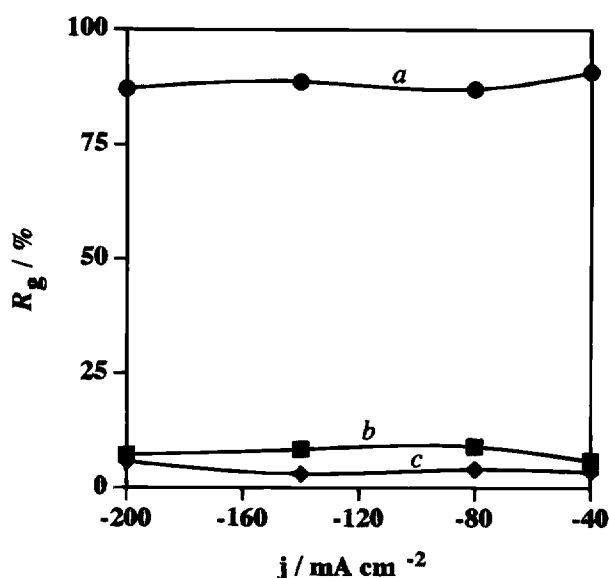


Fig. 7. Relative amounts in the gas phase, R_g (m/o) of the products of the CFC 113 electroreduction at different current densities in MeOH (70%)-H₂O containing 0.75 mol dm⁻³ NH₄Cl and 50 ppm PdCl₂. Curves a, b, and c refer to CDCs, DCTFE, and CTFE, respectively.

phase. The relative amount of DFE was about 62% for all current densities, whereas that of TFE decreased from 25% at -40 mA cm⁻² to 12% at -200 mA cm⁻². Within the same current density limits, the relative amounts of difluoroethane increased from 1 to 6%, whereas that of fluoroethane, from 2 to 7%. Thus, the formation of the most defluorinated compounds were slightly favored when the current density increased. The same CDCs were also found in the liquid, although at smaller concentrations because of their solubility/volatility. The relative amount of DFE was about 25%, whereas those of TFE, fluoroethane and difluoroethane were smaller than 10%.

Discussion on the possible reaction pathway.—The experiments described above show that the presence of Pd²⁺ in solution is essential to produce DFE and TFE from CFC 113 with high efficiencies, because the Pd black electrodeposited alone basically yields CTFE with lower efficiencies. Other parallel experiments at -200 mA cm⁻² were performed as a first approach for understanding the mechanism of the process. These experiments explored the use of different PdCl₂ concentrations, the use of HCl together with NH₄Cl and the use of NH₄NO₃ or HCl instead of NH₄Cl.

The effect of PdCl₂ concentration is shown in Fig. 8a and b, the first corresponding to the gas and the second to the liquid. It is shown that the compositions of the gas and of the liquid do not depend on the PdCl₂ concentration in the range 25 to 75 ppm. The important change appears when this concentration is changed from 0 to 25 ppm, the product composition changing from CTFE to the CDCs as main compounds in the gas phase. In addition, the gas volumes collected in these experiments ($Q = -131$ C) were 14.5 cm³ in the absence of PdCl₂ and 3.5 cm³ in the presence of PdCl₂, the latter volume being independent of PdCl₂ concentration. Thus, the efficiency in the absence of PdCl₂ was 58% (Table I) and in the presence of PdCl₂ it was 98% and did not change with PdCl₂ concentration in the concentration range studied. This is in agreement with the above-mentioned analysis of Pd²⁺ in solution over the course of the experiment, because only a very small quantity of Pd was electrodeposited on Pb.

The relative amounts of products in the gas phase for the experiments with solutions containing different additives are shown in Fig. 9. Bars 1 show the effect of the change from NH₄Cl to NH₄NO₃ at the same concentration. In this

case, 50 ppm PdCl₂ additions were added. However, this salt was acidified with HNO₃ instead of HCl in order to prevent the formation of the complex PdCl₄²⁻,³¹ at least at the beginning of the experiment (the dechlorination reaction leads to the formation of chloride ions). After the electrolysis, a rather bright Pd electrodeposit was observed instead of the black electrodeposit formed with NH₄Cl. The volume of gas formed with -165 C was only 1 cm³, thus indicating a very high efficiency of CFC 113 electroreduction. Even in the case that the evolved gas was pure H₂, which is not possible, the efficiency should be about 95%. As shown in the bars 1 of Fig. 9, CTFE was the main product obtained and therefore, the presence of excess chloride is necessary to yield CDCs as the main products.

Bars 2 and 3 in Fig. 9 show that in the presence of 0.75 mol dm⁻³ of NH₄Cl and 1.2 mol dm⁻³ HCl, the presence of Pd²⁺ in solution is again essential for the preferential formation of CDCs. The efficiencies were only 30 to

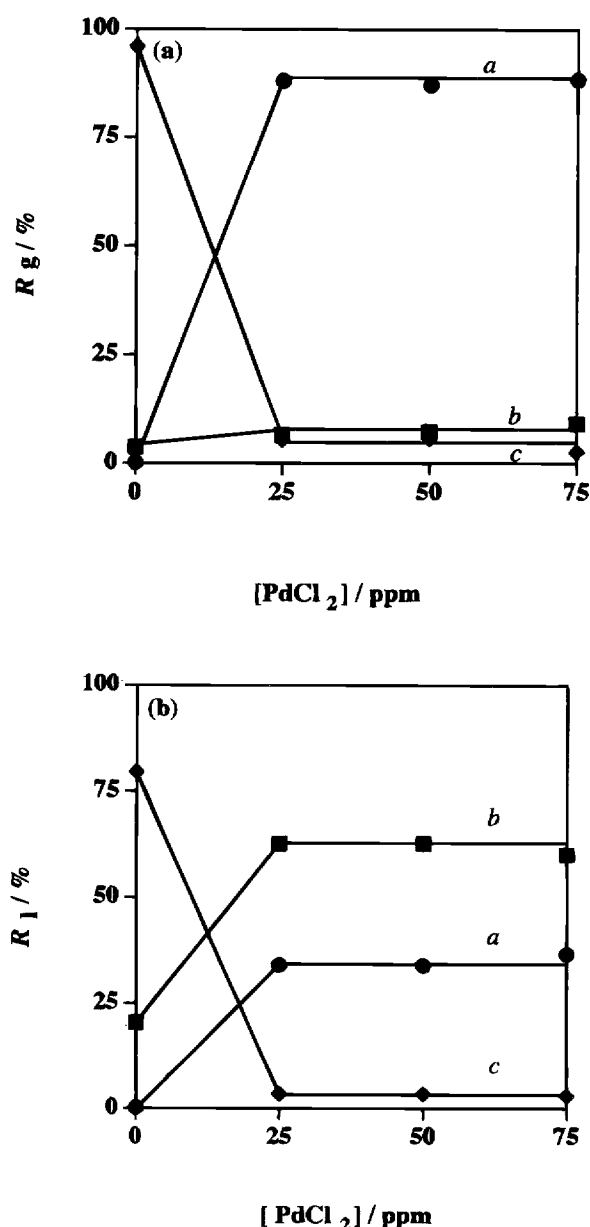


Fig. 8. Relative amounts in the gas phase R_g (m/o) (a), and in the liquid, R_l (m/o) (b), of the products of the CDC 113 electroreduction at -200 mA cm⁻² and different PdCl₂ concentrations in MeOH (70%)-H₂O containing 0.75 mol dm⁻³ NH₄Cl. Curves a, b, and c refer to CDCs, DCTFE, and CTFE, respectively. $Q = -131$ C.

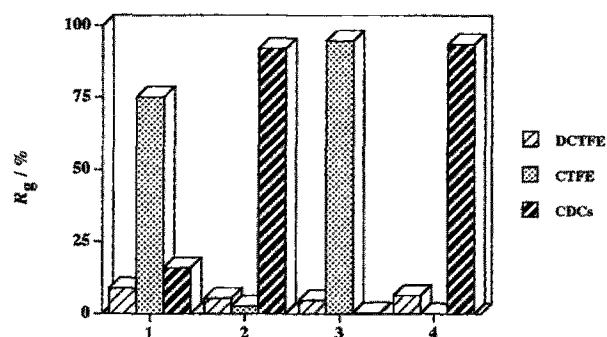
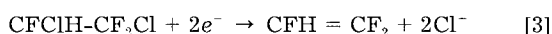
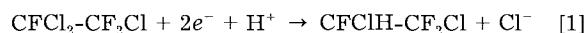


Fig. 9. Relative amounts R (m/o) of the products of the CFC 113 electroreduction in MeOH (70% v/v)-H₂O with different additives. $Q = -165$ C. Bars 1 correspond to: 0.75 mol dm⁻³ NH₄NO₃, 50 ppm PdCl₂, and -200 mA cm⁻²; bars 2: 0.75 mol dm⁻³ NH₄Cl, 1.2 mol dm⁻³ HCl, 50 ppm PdCl₂, and -80 mA cm⁻²; bars 3: 0.75 mol dm⁻³ NH₄Cl, 1.2 mol dm⁻³ HCl, in the absence of Pd²⁺ and -80 mA cm⁻²; and bars 4: 0.75 mol dm⁻³ HCl, 50 ppm PdCl₂, in the absence of ammonium salts, at -200 mA cm⁻².

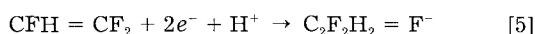
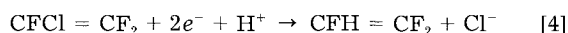
35% in the presence of Pd²⁺ and 53% in the absence of Pd²⁺. It is shown consistently that hydrogen formation is strongly increased in the presence of HCl. The efficiency was also low when the electrolyte consisted of 0.75 mol dm⁻³ HCl and 50 ppm PdCl₂ (bars 4 in Fig. 9), because 23.5 cm³ were collected for $Q = -165$ C. Therefore, an increase in the acidity of the solution favored hydrogen evolution and the use of the ammonium salt is then more adequate.

Despite the fact that further work is being performed to delve more deeply into the mechanism of CFC 113 dehalogenation under the different conditions studied, a sequence of reactions with a gradual halide removal can be proposed to explain the results of our work.

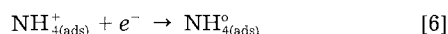
For Pb cathodes in the absence of Pd²⁺ in solution, the suggested sequence is



and/or



Reactions 1 to 5 account for the DCTFE, CTFE, TFE, and DFE formation, although the only major product was CTFE. Under these conditions, reaction 2 is dominant and agrees with previous results in the literature for different cathodes.¹² Reaction 3 is similar to that reported for CF₂Cl-CF₂Cl dechlorination which leads to CF₂ = CF₂ + 2 Cl⁻.¹⁶⁻²⁴ Although to study the catalytic effect of NH₄⁺ has not been the object of this work, we have confirmed that the effect of NH₄⁺ on product distribution cannot be due to its ability to act as proton donor to intermediate carbanions, and we may also suggest, in agreement with the study of Savall *et al.* on Zn cathodes,¹² that reaction 2 is in this case also catalyzed through the reduction of adsorbed NH₄⁺

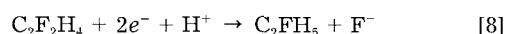
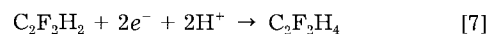


which may react with CFC 113 (by electron transfer from the NH₄⁺ adsorbed species) or lead to hydrogen gas formation.

When Pb/Pd cathodes are employed instead of Pb, TFE and DFE formation is slightly favored (see Fig. 2), thus showing the surface catalytic activity of electrodeposited Pd black. However, the effect of the surface nature appears not to be essential in the product distribution resulting

from the total process. In this case, the electrochemical reactions 1-6, some of them favored by the surface catalytic mechanism, can also explain our experimental results.

The most interesting result of the present work is the great increase in the reduction efficiency to lead to CDCs in the presence of Pd²⁺ in solution. Reactions 1-5 can be invoked to explain DCTFE, CTFE, TFE, and DFE formation. In addition, difluoroethane and fluoroethane can be formed through the following reaction sequence



Although the quantity of Pd electrodeposited in the presence of NH₄NO₃ was not determined, the coating in this case was not black, thus suggesting a different and more facile electrodeposition pathway. In another experiment, an electrolysis for $Q = -330$ C was performed at -200 mA cm⁻² in the methanolic solution containing 0.75 mol dm⁻³ NH₄Cl and 50 ppm PdCl₂, but in the absence of CFC. Only the equivalent of 7.5 ppm was electrodeposited. All of these results suggest that the presence of PdCl₄²⁻ determines (partially precluding) Pd electrodeposition. In addition, a previous paper showed that the mechanism of deposition of this complex did not involve previous dissociation.³²

In short, there is evidence for the surface catalytic activity of electrodeposited Pd black (see Fig. 2). However, this does not appear to be the only mechanism in the electroformation of CFC 113 derivatives. The presence of PdCl₄²⁻ in solution is necessary to strongly favor CFC dehalogenation, possibly being the catalyst of reactions 4, 5, and 7. It is known that Pd is able to form complexes with ethylene derivatives.³³⁻³⁶ In view of our experimental results we suggest that Pd complexes could be formed with Cl⁻ ligands and some of the ethylene derivatives mentioned here as intermediates.³⁵ Intramolecular electron transfer from Pd to the adjacent olefin could yield some of the products described along with halide removal. The resulting oxidized Pd-chloride complex would then accept new electron(s) from the cathode, thereby acting as an efficient charge transfer relay.

Conclusions

In this work, new electrochemical reduction processes of CFC 113 are explored for application in the electrosynthesis of organic compounds and CFC electrodehalogenation. While chlorotrifluoroethene (CTFE) has been the unique product described in the literature resulting from the electrochemical reduction of CFC 113 in conventional cells, suitable conditions for the complete dechlorination of CFC 113 together with the formation of new products are reported herein.

The electroreduction of CFC 113 on Pb in MeOH-H₂O solutions containing 0.75 mol dm⁻³ NH₄Cl essentially leads to the formation of CTFE with current efficiencies in the range 58 to 83% for current densities between -200 and -80 mA cm⁻², respectively. In this case, the relative amount of CTFE in the total quantity of electroreduction products in the gas phase was in the range 81 to 96%, whereas in the liquid it was 75 to 79%. Small amounts of completely dechlorinated compounds (CDCs) were found together with 1,2-dichloro-1,1,2-trifluoroethane (DCTFE). However, when the electrolysis was performed in the presence of 50 ppm PdCl₂, a small amount of Pd black film was electrodeposited on the cathode and the CDCs were dominant in the gas phase (relative amounts of 87% in the total amount of the electroreduction products). In this case, small amounts of DCTFE and CTFE were also formed. The most relevant result was that the efficiency for CFC 113 electroreduction in the presence of Pd²⁺ in solutions containing 70 to 80% v/v MeOH was 98%, in contrast with the much lower efficiencies in the absence of Pd²⁺.

The efficiencies of CFC 113 electroreduction on Pb cathodes covered by a thin Pd black film (electrogenerated in a previous experiment), in the absence of Pd²⁺ in solution,

were much lower than in the presence of Pd^{2+} in solution, the total amount of CDCs in the gas and in the liquid also being much lower. Thus, the presence of Pd^{2+} in solution expands the possibilities in the field of electrosynthesis from CFC 113.

In this work, the effects of MeOH concentration in MeOH- H_2O mixtures, of the current density and of a new anode instead of the conventional anodes were also studied. The most suitable MeOH concentrations were 70 to 80% v/v, much lower current efficiencies being obtained at lower concentrations because of CFC solubility. In addition, no significant differences in the gas and in the liquid compositions were found in the current range between -40 and -200 mA cm^{-2} for MeOH concentrations of 70% v/v. Finally, the use of hydrogen diffusion anodes, *i.e.*, thin Pd foils with electrodeposited Pd black, appear to be more suitable in electrosynthesis and CFC electrodehalogenation because H_2 is oxidized to H^+ instead of the formation of secondary and undesirable products such as Cl_2 or MeOH derivatives.

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REFERENCES

- M. J. Molina and F. S. Rowland, *Nature*, **249**, 810 (1974).
- G. M. Bickle, T. Suzuki, and Y. Mitarai, *Trans. IChemE*, **70B**, 44 (1992).
- S. Okazaki and A. Kurosaki, *Chem. Lett.*, 1901 (1989).
- S. Imamura, H. Shimizu, T. Haga, S. Tsuji, and K. Utani, and M. Watanabe, *Ind. Eng. Chem. Res.*, **32**, 3146 (1993).
- Y. Murikawa, T. Ikawa, and W. Ueda, JP 05 09,138 [93 09,138].
- L. Lerot, V. Wilmet, and J. Piroton, EP 355,907 (1990).
- T. Saiki, M. Sumida, S. Nakano, and K. Murakami, EP 471,320 (1992).
- B. Berthe and J. M. Cognion, EP 485,246 (1992).
- K. Tokuhashi, Y. Urano, S. Horiguchi, and S. Kondo, *Combust. Sci. Technol.*, **72**, 117 (1990).
- H. Saikai, K. Sato, and K. Takeuchi, JP 04,112,842 [92,112,842].
- A. Oku, K. Kimura, and M. Sato, *Chem. Lett.*, 1789 (1988).
- A. Savall, R. Abdelhedi, S. Dalbéra, and M. L. Bouguerra, *Electrochim. Acta*, **35**, 1727 (1990).
- A. Savall, S. Dalbéra, R. Abdelhedi, and M. L. Bouguerra, *J. Appl. Electrochem.*, **20**, 1045 (1990).
- K. M. Smirnov, A. P. Tomilov, L. G. Feoktistov, and M. M. Gol'din, *Zh. Prikl. Khim.*, **51**, 703 (1978).
- K. Yagii and H. Oshio, Ger. Offen. 2,818,066 (1977).
- Montecatini Edison S.p.a. Ital. 852,487 (1969).
- S. Dapperheld, EP 334,796 (1989).
- S. Wawzonek and S. Willging, *This Journal*, **124**, 860 (1977).
- H. Matschiner, R. Voigtlaender, and B. Hesse, *Z. Chem.*, **17** (1977).
- V. L. Kornienko, M. A. Kedrinskii, N. V. Kalinichenko, G. V. Kornienko, Yu. G. Chirkov, M. M. Gol'din, L. G. Feoktistov, and N. S. Stepanova, USSR SU 702,702 (1983).
- V. L. Kornienko, G. A. Kolyagin, G. V. Kornienko, and Yu. V. Saltykov, *Soviet Electrochem.*, **28**, 412 (1992).
- G. A. Kolyagin, G. V. Kornienko, and I. S. Vasil'eva, *Russ. J. Electrochem.*, **32**, 277 (1996).
- D. Goerrig and H. Jonas, Ger. Pat. 937,919 (1956).
- K. M. Smirnov, A. P. Tomilov, L. G. Feoktistov, and M. M. Gol'din, *Zh. Prikl. Khim.*, **51**, 701 (1978).
- N. S. Stepanova, M. M. Gol'din, and L. G. Feoktistov, *Soviet. Electrochem.*, **12**, 1070 (1976).
- P. L. Cabot, M. Centelles, L. Segarra, and J. Casado, *J. Electroanal. Chem.*, In press.
- A. J. Hartner and M. A. Vertes, U.S. Pat. 3,393,098 (1968).
- S. J. C. Cleghorn and D. Pletcher, *Electrochim. Acta*, **38**, 425 (1993).
- C. Iwakura, T. Abe, and H. Inoue, *This Journal*, **143**, L71 (1996).
- Handbook of Chemistry and Physics* CRC, D. R. Lide, Editor, p. 421, CRC Press, Boca Raton, FL (1995).
- J. F. Llopis and F. Colom, Palladium, in *The Encyclopedia of the Electrochemistry of the Elements*, pp. 253-275, Marcel Dekker, New York (1976).
- G. W. Watt and J. A. Cunningham, *This Journal*, **110**, 716 (1963).
- B. Trost and T. R. Verhoeven, in *Comprehensive Organometallic Chemistry*, Vol. 8, p. 799, Pergamon Press, Oxford (1982).
- N. Gragor and P. M. Henry, *J. Am. Chem. Soc.*, **102**, 681 (1981).
- P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).
- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, pp. 919, 1276, Wiley, New York (1988).