

Electrodegradation of Chlorofluorocarbons in a Laboratory-Scale Flow Cell with a Hydrogen Diffusion Anode

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Trichlorofluoromethane (CFC 11) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) have been cathodically reduced in a laboratory-scale flow cell at room temperature. The electrodes, 10 cm^2 in section, were a Cu cathode and a H₂-fed gas diffusion electrode. The cell reservoir contained 0.5 dm³ of methanol-water mixture with NH₄Cl, perchlorate of tetrabutylammonium (PTBA), or both. In the case of CFC 113, 50 ppm PdCl₂ was also added to the electrolyte. Electroreduction took place with the formation of dechlorinated derivatives by steps, methane and difluoroethene being the last derivatives for CFCs 11 and 113, respectively. The current efficiency in NH₄Cl was about 75%. It was improved for CFC 11 to 90-95% when PTBA was employed, both with NH₄Cl or alone. The use of PTBA for CFC 113 was unsatisfactory, because it interfered with Pd electrodeposition and the current efficiency diffusion anode appeared to be chemically stable during the process, although some concave deformation after prolonged hydrogen oxidation leading to an increase in the interelectrode gap was apparent. The improvement of its dimensional stability is discussed.

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The use of chlorofluorocarbons (CFCs) for industrial purposes since around 1930 has lead to emissions and further accumulation of these compounds in the atmosphere, destroying stratospheric ozone and contributing to the greenhouse effect in the troposphere. Although the production of CFCs was stopped since 1996 as a result of international agreements, there are still large amounts in stock. The estimated amount of banked CFCs are 2.25 Mton, about 45% being trichlorofluoromethane (CFC 11) and about 45% dichlorodifluoromethane (CFC 12).¹

In order to avoid eventual emissions, different destruction processes such as incineration, pyrolysis, hydrolysis, catalytic oxidation, catalytic hydrogenation, plasma destruction, UV destruction, and destruction using high-energy radiation, have been proposed. However, destruction methods require energy and waste removal, and therefore, conversion of CFCs into useful products appears to be more attractive, since it combines synthesis with degradation. This can be done using chemical or electrochemical reactions. As an example of the former, Pd black has been applied as a model catalyst for the high-temperature hydrogenolysis of CFC 12 into CH₂F₂ (HFC 32), which appears to be a new technology refrigerant.¹

Electroreduction of CFCs appears to be adequate for such a combination of electrodegradation and electrosynthesis, because chloride is easily removed from the molecule in this way. Diverse compounds such as chlorotrifluoroethylene $(CTFE)^{2-7}$ and tetrafluoroethylene^{4,8} can be produced from 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) and from 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC 114), respectively, using a variety of electrodes and electrolytes. More recently, difluoroethene (DFE) and trifluoroethene (TFE) have also been obtained from CFC 113 on Pb cathodes in methanol-water mixtures containing different electrolytes and PdCl₂ dissolved at the parts per million level,⁹⁻¹¹ which catalyzed the formation of the most dechlorinated derivatives. It has also been shown that HFC 32 and/or tetrafluoroethene are formed in the electrochemical reduction of CFC 12 in aqueous^{12,13} or organic media¹⁴⁻¹⁶ using lead,^{15,16} silver,^{12,14} or Pb-supported gas diffusion electrodes (GDEs).¹⁴

The authors have employed a conventional laboratory closed cell to dechlorinate CFC 11 (trichlorofluoromethane) and CFC 113 in methanol-water mixtures containing $\rm NH_4CL^{9,10,17}$ The electrodes were a Pb cathode and a Pd-based hydrogen diffusion anode. In the hydrogen diffusion anode, only one side is in contact with the elec-

trolyte, whereas H_2 is fed from the opposite side. Hydrogen absorbed in Pd is then transported to the electrolyte side, where it is electrochemically oxidized to proton. This electrode made the use of separators unnecessary and it avoided the formation of polluting by-products. Different dechlorinated compounds including completely dechlorinated ones were obtained with electroreduction efficiencies up to 98% at high current densities. However, significant Pb corrosion and current efficiencies of 25-50% were found in sodium acetate and current densities of about 1 mA cm^{-2,11} thus justifying further effort to characterize corrosion phenomena and current efficiency in different electrode-electrolyte systems.

In this work, a new small-scale flow cell with a Pd-based H₂-diffusion anode and a copper cathode in parallel has been built and tested. Methanol (70 vol %)-water mixtures containing NH₄Cl, PTBA, or both have been employed. The selection of cathode and electrolytes was based on the efficient electroreduction of CFC 113 to CTFE on Cu cathodes in NH₄Cl-containing methanol-water mixtures² and on the catalytic effect of PTBA in the electroreduction of CFC 113 in wetproofed carbon-black porous cathodes.¹⁸ The conversion of CFCs 11 and 113, the current efficiencies, and the stability of the electrodes at current densities of about 10 mA cm⁻² have been determined using different analytical techniques.

Experimental

The cathodes were 2 mm thick Cu disks having 4.6 cm diam. The Cu composition, in weight %, was 0.013 Pb, 0.005 Sn, 0.002 Ni, and 0.031 P, Al, Sb, As, Bi, and Fe, being less than 0.001%. Before the experiments it was cleaned with 50 vol % HNO_3 .

The anode was built using a 150 μ m thick Pd-30 Ag foil from Goodfellow, activated with a layer of Pd black (2 mg cm⁻²) and an external layer of Pt black (2 mg cm⁻²). The first layer was electrochemically generated, as indicated previously, but reducing the deposition time to the half.⁹ Afterward, Pt black was electrodeposited on it from a solution containing 3% H₂PtCl₆ · 6H₂O and 0.02% Pb(AcO)₂ · 3H₂O (both Merck for synthesis), at -15 mA cm⁻² and 50°C for 8 min, as indicated elsewhere.¹⁹ It was fed with commercially pure H₂ from Air Products and Chemicals at atmospheric pressure.

The electrodes were coupled to a two-electrode undivided flow cell made of stainless steel (SS) and polymethylmethacrylate (PMMA). Figure 1 shows a side view, with two SS bodies, for the anode (SA) and the cathode (SC). The latter was solid whereas the former was perforated to allow the H_2 arrival at the anode. The anode gas chamber was closed with a PMMA window (PW), thus allowing observation of the foil, and had a H_2 inlet and a purge.

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Figure 1. Side view of the undivided two-electrode flow cell, with two steel bodies to press the cathode (SC) and the anode (SA), respectively, onto the electrolyte compartment (EC). A PMMA window (PW) to observe the gas chamber is also shown.

Each SS body had a terminal for electrical connection. The SS bodies of the anode and the cathode, together with the electrodes described previously were pressed onto the electrolyte compartment (EC) using Viton O-rings and SS screws. The electrolyte compartment was also made with PMMA, with inlet and outlet allowing the electrolyte circulation. The electrodes were placed vertically, face to face, with an interelectrode gap of 4 mm. The electrode sections to be exposed to the electrolyte were 10 cm² both for the anode and the cathode.

The cell was integrated in the system depicted in Fig. 2, where it can be seen on the right of the figure (C). An electrolyte volume of 0.5 dm^3 was placed in a closed glass reservoir (R), which in turn was immersed in a water bath at 20°C (W). From the reservoir the electrolyte was circulated through the cell at a flow rate of 25 mL



Figure 2. Scheme of the laboratory-scale experimental setup for the CFCs electrodegradation. The electrolyte is recirculated from a glass reservoir (R), immersed in a water-bath (W), to the cell (C), by means of a peristaltic pump (P). A magnetic stirrer (S) and a key for sample extraction (E) are also shown.

 \min^{-1} by means of a peristaltic pump (P), and then it was returned to the reservoir. The electrolyte was mildly stirred during the electrolyses by means of a magnetic stirrer (S) for homogenizing its composition and temperature. The system also had a key for extracting liquid sample (E). The extraction of gas samples was performed by means of a syringe through the septum on the top of the reservoir.

The working electrolytes were prepared in methanol (70 vol %)water mixtures. They contained $0.75 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$, 0.1 mol dm^{-3} PTBA, or 0.75 mol dm^{-3} NH₄Cl + 0.05 mol dm^{-3} PTBA. The water was Millipore of Milli-Q quality. Methanol and NH₄Cl were Panreac PRS, and PTBA, Fluka, electrochemical grade. Amounts of CFC 11 and CFC 113 of about 0.1 mol were added to the electrolyte in different experiments. They corresponded to about the half the saturation concentration of CFC 11,17 and near saturation concentration of CFC 113,9 at 20°C. For CFC 113 electrodegradation, PdCl₂ (Merck for synthesis) was also used at a concentration of 50 ppm. It was added to the electrolyte as a small volume of concentrated PdCl₂ solution acidified with HCl (reagent grade Merck) to pH 0. These solutions were not deaerated prior to the experiments in order to avoid the loss of volatile compounds and to study the behavior of the system in the presence of dissolved O_2 , which can be useful in the case of a higher scale application.

The electrolyses were performed controlling the cell voltage in the range 1-5 V to obtain quasi-steady currents of about 100 mA, using an HP-6643A power supply, up to a significant CFC electrodegradation. They were periodically stopped for the electrode examination. In these stops, the electrolyte of the cell was transferred to the reservoir, the cell was removed, and the electrolyte bypassed in order to avoid electrolyte and gas losses. Afterward, the electrodes were examined, carefully rinsed in methanol and water, and dried.

To study the possible metal corrosion and release in solution, the electrolyte was analyzed by inductively coupled plasma (ICP) and mass spectrometry (MS) detection, both during CFC electrodegradation and in open-circuit conditions. The organic compounds of small electrolyte volumes were mineralized with HNO₃-HClO₄. After evaporation and dissolution with HNO₃, the copper, palladium, and platinum contents were determined using a Perkin-Elmer ELAN 6000 ICP-MS. The surface of the cathode was also analyzed by X-ray diffraction (XRD) using a Bragg-Brentano $\theta/2\theta$ Siemens D-500 diffractometer.

As shown in Fig. 2, a gas phase over the electrolyte was always present during the electrolyses, and then a product distribution of CFC and its derivatives between the liquid and the gas according to their solubility/volatility was expected. The identification of the derivatives was performed by MS coupled to gas chromatography (GC) using a HP 5890 GC chromatograph with an HP-624 capillary column of 60 m and an HP 5989A MS detector. The routine analyses were performed using an HP 6890 chromatograph with the same column and a thermal conductivity detector (TCD). The gas carrier was He and the column flow was 1.0 mL min⁻¹. The temperature program for the oven was 20 min at 30°C, a temperature ramp of 15°C min⁻¹ to 200°C, and then the temperature was held at 200°C for 5 min. All the organic compounds were detected during the 20 min period of constant temperature of the oven. The analyses of the gas phase were performed by direct injection of 400 µL of it to the chromatograph by means of a syringe. The analyses of the liquid were performed after extracting the corresponding organic compounds in chloroform, as indicated previously.⁹ As some of the standards needed were not available, the amount of derivatives formed during the electrolyses together with the remaining amounts of CFC, both in the gas and in the liquid, were obtained correcting the chromatographic areas by the relative molar response (RMR) factors. The results of the analyses are given in relative amounts of CFC and its derivatives, excluding evolved hydrogen and solvent vapors, in the electrolyte, R_1 , and in the gas, R_g . Such relative amounts allowed calculating the CFC conversion and the product distribution, and they were also employed to determine the current efficiency. The RMR factors were calculated from the molecular diameter approach, which gives accurate results for halogenated organic compounds,^{20,21} being 112.3, 94.5, 78.4, 57.3, and 42.5, for CFC 11, dichlorofluoromethane (DCFM), chlorofluoromethane (CFM), fluoromethane (FM), and methane, respectively, and 138.9, 123.8, 101.2, 84.9, and 74.7 for CFC 113, 1,2-dichloro-1,1,2-trifluoroethane (DCTFE), CTFE, TFE, and DFE, also respectively. The pH values of electrolyte samples were measured using a Metrohm 632 pH meter.

Results and Discussion

Electroreduction of CFC 11.-The electrolyses in 0.75 M NH₄Cl was performed at a constant cell voltage of 1.0 V. In the first 7 h, the cell current decreased from 100 to 70 mA and afterward it slowly increased. The cell current was quasi-steady and ca. 120 mA after about 13 h from the beginning of the experiment. The analyses of the electrolyte and of the gas showed the preferential formation of DCFM and CFM. FM was scarcely detected in the electrolyte, whereas it was found to significant amounts in the gas. In addition, small amounts of methane, difficult to quantify, were also determined in the latter. These compounds except methane were also previously found when a Pb¹⁷ or Hg cathodes⁴ were employed. Therefore, Cu has certain ability for defluorination. This capacity has also been evidenced during the electroreduction of chlorotrifluoromethane (CFC 13) and CFC 12 on Cu-supported GDEs in aqueous media.^{13,22} Pb-supported GDEs induced only dechlorination of CFC $12.^{13}$

The results of the analyses of the electrolyte and of the gas over the latter during the electroreduction of CFC 11 in NH₄Cl are shown in Fig. 3a and b, respectively. Figure 3a shows the evolution of the electrolyte composition in CFC and its derivatives together with the conversion of CFC 11 into DCFM and CFM, in front of the charge consumed. Fig. 3b shows the same in the gas phase, although with the addition of FM, which was scarcely found in the electrolyte. As indicated previously, methane could not be adequately quantified and therefore, it has not been included in this figure. CFC 11 and its derivatives were volatile and therefore appear to be distributed in the gas and in the electrolyte according to their volatility. As FM is more volatile than its related compounds with more Cl atoms, it is mainly found in the gas phase. CFM is present in the gas in smaller amounts than FM, but it dominates over the latter in the electrolyte. Therefore, we may conclude that the relative amounts of CFC derivatives resulting from the electrolysis decrease in the order DCFM > CFM > FM > methane. This is in agreement with a stepped removal of Cl atoms from CFC during the electrolysis, following the sequence

$$CFCl_3 + 2e^- + H^+ \rightarrow CFCl_2H + Cl^-$$
 [1]

$$CFCl_2H + H^+ + 2e^- \rightarrow CFClH_2 + Cl^-$$
[2]

$$CFClH_2 + H^+ + 2e^- \rightarrow CFH_3 + Cl^- \qquad [3]$$

$$CFH_3 + H^+ + 2e^- \rightarrow CH_4 + F^- \qquad [4]$$

A stepped removal of Cl was also found when using Pb cathodes,^{11,17} although no methane was released in such conditions. The derivatives having fewer Cl atoms are found in a smaller concentration due to the also smaller concentrations of the corresponding reactants. The dominance of the most dechlorinated compounds should be obtained for much longer electrolysis time to allow a significant conversion of DCFM. The electrolysis was stopped at Q = 12.2 kC, whereas a charge of about 69.5 kC (0.090 \times 8F, where F is the Faraday constant) should be necessary for a complete conversion of 0.090 mol CFC 11 into methane, assuming that only Reactions 1-4 are taking place. They are not the only reactions because hydrogen gas can be evolved¹¹ and oxygen dissolved can be reduced. A rough estimation of the current efficiency for the conversion of CFC 11 can be done assuming that most of the derivatives formed are in the liquid phase, as shown elsewhere.¹¹ When the electrolysis was stopped, the R_1 values of CFC and derivatives in



Figure 3. Relative molar composition of CFC 11 and its derivatives DCFM, CFM, and FM (indicated) in (a) the liquid, R_1 , and (b) the gas, R_g , in front of the charge Q utilized in its electrolysis in methanol (70 vol%)-water mixture containing 0.75 mol dm⁻³ NH₄Cl.

the electrolyte were 49.8% CFC 11, 48.4% DCFM, and 1.8% CFM. The corresponding amounts of products are listed in Table I, where the results of the main experiments of this work are summarized. As shown in Reactions 1 and 2, DCFM needs 2F per mol, whereas CFM needs 4F per mol. The charge required for this conversion was 9.0 kC, thus indicating a mean current efficiency of about 74%.

As shown in Fig. 3b, CFC 11 concentration in the gas phase is much higher than in the liquid (its R_g being about 75% at the end of the electrolysis). This is in contrast with the results of the analysis of the liquid (its R_g being 48.4%). The dominance of the most volatile compounds in the gas is expected if we assume phase equilibrium and the absence of great deviations from the ideal behavior of the mixtures. Therefore, we may suspect that no phase equilibrium is attained in the system in the absence of suitable mixing of gas and electrolyte. Note that a greater amount of volatile compounds were being produced with time, thus requiring the use of adequate pressurized systems to avoid losses during operation and extraction of liquid and gas samples. This has to be considered in further work.

The surface of the cathode was periodically revised after about 7-8 h in order to follow its evolution. It was seen that the cathode surface gradually became brown, loosing its peculiar brightening

Table I. Summary of the results obtained for the main experiments of electrodegradation of CFCs 11 and 113 indicating the amount of CFC consumed (n_c) , amount of products (n_p) , consumed charge (Q), current efficiency (ε) , initial potential (V_0) , and mean corrosion rate of the Cu cathode (v_{cor}) . The initial electrolyte volume was always 0.5 dm³.

Electrolyte	$n_{\rm c} ({\rm mol})$	$n_{\rm p} \ ({\rm mol})$	Q (kC)	ϵ (%)	V_0 (V)	$v_{\rm cor} ~(\mu g ~ h^{-1} ~ {\rm cm}^{-2})$
$0.75 \text{ mol } \text{dm}^{-3} \text{ NH}_4\text{Cl}$	4.52×10^{-2}	DCFM:4.36 \times 10 ⁻² CFM:1.62 \times 10 ⁻³	12.2	74	1.0 ^a	12
$0.1 \text{ mol } \text{dm}^{-3} \text{ PTBA}$ +0.095 mol CFC 11	5.81×10^{-2}	$DCFM: 1.02 \times 10^{-2}$ $DCFM: 5.63 \times 10^{-2}$ $CFM: 1.81 \times 10^{-3}$	12.2	95	4.0	0.8
$0.75 \text{ mol } dm^{-3} \text{ NH}_4\text{Cl} + 0.05 \text{ mol } dm^{-3} \text{ PTBA}$	1.82×10^{-2}	DCFM:1.77 \times 10 ⁻² CFM:5.23 \times 10 ⁻⁴	3.96	91	1.0	3.5
+0.095 mol CFC 11 0.75 mol dm ⁻³ NH ₄ Cl +50 ppm PdCl ₂	4.33×10^{-2}	DCTFE: 3.53×10^{-2} CTFE: 2.77×10^{-3}	12.8	80	1.0 ^a	8.5
+0.084 mol CFC 113 $0.1 \text{ mol } dm^{-3} \text{ PTBA}$ +50 ppm PdCl ₂ +0.084 mol CFC 113	8.48×10^{-3}	$\begin{array}{c} \text{TFE:} 6.55 \times 10^{-3} \\ \text{DFE:} 4.54 \times 10^{-3} \\ \text{DCTFE:} 2.60 \times 10^{-3} \\ \text{CTFE:} 3.36 \times 10^{-3} \\ \text{TFE:} 2.52 \times 10^{-3} \end{array}$	4.10	52	2.7	1.0

^a Experiment at constant potential.

and color, presenting sometimes some small blue spots. This indicated some Cu corrosion during the electrolysis, because the electrode was rinsed and dried when the electrolysis was stopped. The examination of the cathode surface by XRD showed only small amounts of Cu2O as Cu oxidized species, and therefore, some amount of copper could be dissolved into the solution. This became evident by the slight blue color of the electrolyte after sufficient time of electrolysis. ICP analysis of the electrolyte showed a copper amount equivalent to a Cu corrosion rate of about 12 μ g h⁻¹ cm⁻² This shows that a cathodic current density of *ca*. 10 mA cm⁻² appears to be insufficient to avoid the cathode corrosion. Dissolved oxygen plays a role in the copper corrosion in aqueous media. However, copper oxidation by CFC 11 and/or its derivatives, as in the case of Fe with CCl_4 ,²³ could not be discarded at first. For this reason, a parallel experiment of Cu corrosion for about 9 h was performed using the same system as that employed for the CFC 11 electrodegradation, except that no current flowed between the electrodes. In this case, the amount of copper in the electrolyte was equivalent to a Cu corrosion rate of about 86 μ g h⁻¹ cm⁻², *i.e.*, much higher than that found during electrodegradation. In addition, the analysis of the electrolyte showed the formation of DCFM, as in the electrodegradation process, indicating that CFC 11 could oxidize copper through the following redox reaction

$$CFCl_3 + Cu + H^+ \rightarrow CFCl_2H + Cu^{2+} + Cl^-$$
[5]

We may therefore conclude that oxygen and CFC 11 are able to oxidize Cu and that Cu corrosion could probably be avoided at sufficiently negative potentials, with higher cathodic current densities. However, to study the effect of the electrolyte in Cu corrosion, CFC 11 (0.095 mol) was electrolyzed in 0.1 mol dm⁻³ PTBA at the same current densities as in NH₄Cl. In this case, the cell voltage to obtain a quasi-stationary current of about 100 mA was higher than for the latter electrolyte. The initial cell voltage was 4.0 V and it was decreased with time to 1.9 V, at the end of the electrolysis (see curve a in Fig. 4). These higher cell voltages were most probably due to the higher resistance of the electrolyte. Although the decrease in potential to keep constant the cell current could be attributed to different reasons, we feel that the main one was the increase in conductivity due to the decrease of pH. Figure 5 shows such a pH decrease during the electrolyses in this experiment (curve a). A pH decrease also took place when NH₄Cl was employed as supporting electrolyte (curve b), thus justifying the increase in current density with time at constant potential in such conditions. This net acidification clearly resulted from the anodic process, because two H⁺ ions were produced per 2F

$$\mathrm{H}_2 \to 2\mathrm{H}^+ + 2\mathrm{e}^- \qquad [6]$$

and only one H^+ ion is consumed per 2F in each one of Reactions 1-4.

The plots of R_1 and R_g for CFC 11 and its derivatives in PTBA had the same shape as in NH₄Cl. However, a greater CFC conversion in PTBA was apparent, because the values of R_1 for CFC 11, DCFM, and CFM at the end of the electrolysis were 38.9, 59.3, and 1.9%, respectively. This means a required charge of 11.6 kC, which corresponds to a mean current efficiency of about 95% (see Table I). In this case, the corrosion rate of Cu was *ca*. 0.8 μ g h⁻¹ cm⁻², about one order of magnitude smaller than in NH₄Cl (no blue color in the electrolyte was appreciated). The visual inspection of the Cu cathode clearly indicated that it was cleaner than in NH₄Cl, and the XRD analyses of its surface showed only Cu metal. The use of PTBA has the penalty of a higher cell voltage, but the current efficiency of CFC11 electrodegradation is greater and Cu corrosion much smaller than in NH₄Cl and PTBA in the corrosion rate and the



Figure 4. Cell voltage, *V*, *vs*. consumed charge, *Q*, for different experiments at constant cell current of 100 mA using (a) 0.1 mol dm⁻³ PTBA with CFC 11 and (b) 0.1 mol dm⁻³ PTBA with 50 ppm acidic PdCl₂ and CFC 113.



Figure 5. Measured pH vs. consumed charge, Q, for different experiments using (a) 0.1 mol dm⁻³ PTBA with CFC 11, (b) 0.75 mol dm⁻³ NH₄Cl with CFC 11, (c) 0.1 mol dm⁻³ PTBA with 50 ppm acidic PdCl₂ and CFC 113, and (d) 0.75 mol dm⁻³ NH₄Cl with 50 ppm acidic PdCl₂ and CFC 113.

current efficiencies can be found in the hydrophobic character of the tetrabutylammonium cations. It is known that they can be strongly adsorbed at the electrode,²⁴ thus propitiating more suitable conditions for the CFC 11 reduction.

As in the case of NH_4Cl , a parallel experiment of 6 h without current flow was performed. The electrolyte containing PTBA and CFC was circulated through the cell at open-circuit conditions. The period extraction of electrolyte samples showed increasing amounts of DCFM with time, thus indicating that Reaction 5 also takes place with PTBA. The amounts of DCFM were smaller, but significant, being about 3.5% of the DCFM formed when the quasi-stationary current of 100 mA was applied.

The PTBA concentration employed was near saturation and this precluded using higher concentrations. As expected, higher cell voltages had to be applied to obtain currents of about 100 mA when its concentration decreased. Thus, an initial cell voltage of 5.5 V was required to obtain a cell current of about 100 mA in 0.05 mol dm⁻³ PTBA. Therefore, this salt was employed in combination with NH₄Cl and 0.095 mol CFC 11. The corresponding results are also shown in Table I. The cell voltage to maintain a quasi-stationary current of about 100 mA was in the range 1.0-1.2 V, in agreement with the experiment using NH₄Cl. The corrosion rate of Cu (3.5 µg h⁻¹ cm⁻²) and the current efficiency (91%), intermediate between NH₄Cl and PTBA, makes NH₄Cl + PTBA preferable in front of NH₄Cl alone.

The gas pressure over the electrolyte increased during the electrolyses. This was assigned to the formation of the most volatile compounds, methane, and even hydrogen. Such a pressure increase did not indicate continuing the electrolyses because the system was not specially prepared for this. Therefore, a new system, prepared to sustain high pressures, has to be built up to study greater CFC conversions in CFC-concentrated electrolytes.

Electroreduction of CFC 113.—Figures 6a and b show the distribution of CFC 113 and its derivatives, in the electrolyte and in the gas, respectively, during the electrolysis of 0.084 mol CFC in 0.75 mol dm⁻³ NH₄Cl plus 50 ppm of acidic PdCl₂ at a constant cell voltage of 1.0 V. The initial cell current was about 100 mA and it presented a net increase with time to about 130 mA. The initial pH of the electrolyte, curve d in Fig. 5, was smaller than that of NH₄Cl with CFC 11, curve b, because of the addition of acidic PdCl₂. As in



Figure 6. Relative molar composition of CFC 113 and its derivatives DCTFE, CTFE, TFE, and DFE (indicated), in (a) the liquid, R_1 , and (b) the gas, R_g , in front of the charge, Q, employed during its electroreduction in methanol (70 vol %)-water mixture with 0.75 mol dm⁻³ NH₄Cl and 50 ppm acidic PdCl₂.

the previous experiments with CFC 11, the pH of the electrolyte decreased with time due to the net acidification produced by the anodic reaction. The increase in the cell current with time may then be attributed to a slight increase in the electrolyte conductivity. The XRD analyses of the surface of the cathode at the end of the electrolysis showed the formation of electrodeposited Pd, a PdCu alloy, together with very small amounts of Cu_2O .

As the great part of CFC and its derivatives are in the liquid, the R_1 values of Fig. 6a show that the amount of products formed decrease in the order DCTFE > DFE > DFE > TFE. This sequence is also found for the R_g values of the same derivatives except for DCTFE (Fig. 6b), because the latter is the less volatile product, and it is expected to be mostly in the electrolyte. The formation of DCTFE and CTFE can be explained by two different two-electron reductions of CFC 113⁹

$$CFCl_2-CF_2Cl + 2e^- + H^+ \rightarrow CFCIH-CF_2Cl + Cl^-$$
 [7]

$$CFCl_2 - CF_2Cl + 2e^- \rightarrow CFCl = CF_2 + 2Cl^-$$
[8]

where Reaction 8 is the main reaction taking place without $PdCl_2$ in solution.² As discussed elsewhere,^{9,10} electrodeposited Pd and subvalent Pd complexes may catalyze the consecutive hydrogenation of ethylene derivatives according to the following reaction stoichiometries

$$CFCl = CF_2 + 2e^- + H^+ \rightarrow CFH = CF_2 + Cl^-$$
 [9]

$$CFH = CF_2 + 2e^- + H^+ \to C_2F_2H_2 + F^-$$
[10]

We also suggested the formation of TFE by the two-electron reduction of DCTFE⁹ in a similar reaction, producing tetrafluoroet-hylene from CFC $114^{4,8}$

$$CFCIH-CF_2Cl + 2e^- \rightarrow CFH = CF_2 + 2Cl^-$$
[11]

The relative amount of DFE was higher than that of TFE and CTFE. This indicates a relatively rapid transformation of CTFE into TFE (Reaction 9) and a more rapid transformation of TFE into DFE (Reaction 10). This is also supported by the initial increase and the further decrease in the relative amount of CTFE both in the electrolyte (Fig. 6a) and in the gas (Fig. 6b), although it is more apparent in the latter. Note, however, that the use of higher current densities favored the formation of the most dechlorinated derivatives on the Pb cathode.^{9,10}

The electroreduction efficiency was calculated from the liquid composition, as in the case of CFC 11 (see Table I). The conversions into DCTFE, DFE, CTFE, and TFE, were 42, 5.4, 3.3, and 0.78%, respectively (R_1 values corresponding to Q = 12.8 kC in Fig. 6a). According to Reactions 7-11, the charge employed in such a conversion was 10.2 kC, thus corresponding to a current efficiency of about 80%. The corrosion rate of Cu was 8.5 μ g h⁻¹ cm⁻², somewhat smaller than that found for CFC 11, probably due to the partial protection of the Cu surface by electrodeposited Pd black. No Cu corrosion in open circuit was studied for CFC 113, because no Pd electrodeposition was expected in this condition and therefore the cathode would not be the same. The Cu corrosion may vary during Pd electrodeposition, *i.e.*, at different Pd black coverage. In fact, this opens a new study of CFC degradation in open circuit, where the CFC can be reduced on Pd whereas Cu is being oxidized in an overall process similar to Reaction 5. However, it is out of the scope of the present paper.

The different derivatives formed during the electrolysis of 0.084 mol CFC 113 in 0.1 mol dm⁻³ PTBA with acidic PdCl₂ presented similar relative amounts as in NH₄Cl, in the range 3-4%, except DFE, which was much smaller (see Table I). This could be due to the different form of Pd black electrodeposition in NH₄Cl and in PTBA, because $PdCl_4^{2-}$, which is generally involved in the Pd electrodeposition,²⁵ was not present with PTBA. Adherence problems of Pd black were evident, because small black particles appeared in the electrolyte and the XRD analysis of the cathode surface at the end of the electrolysis scarcely showed the presence of Pd, in contrast with XRD analysis of the cathode when NH₄Cl was employed. The visual inspection also indicated that Pd electrodeposition was deficient, because the color of Cu only changed to be dark, not black as in NH₄Cl. However, some completely dechlorinated derivatives were still produced. With the use of PTBA, greater cell voltages than in NH₄Cl were also found to obtain quasistationary cell currents of about 100 mA (see curve b in Fig. 4). The cell voltages were smaller, however, than for the electrolysis of CFC 11 (curve a). This can be explained again by the electrolyte pH, which was higher in the electrolyte with CFC 11 (curve a in Fig. 5) than in the electrolyte with CFC 113 (curve c in Fig. 5), because acidic PdCl₂ was added to the latter. It is interesting to observe that the corrosion rate in PTBA was only 1.0 μ g h⁻¹ cm⁻², thus confirming its positive effect against the cathode corrosion. However, the current efficiency was only about 52%.

Electrolysis of CFC 113 in $NH_4Cl + PTBA$ led to the same Pd electrodeposition problems as in the case of PTBA. The deposit was

loosely adhered and the amount of CFC derivatives in the electrolyte was smaller than in NH₄Cl alone. DFE was scarcely detected in the liquid and the current efficiency was comparable to that obtained in PTBA. This salt then appears to interfere with Pd black electrodeposition and to reduce the current efficiency of its electrodechlorination when compared with NH₄Cl alone, thus being undesirable for CFC 113 electrodegration with dissolved PdCl₂.

Anode behavior.--As indicated previously, one of the objects of this paper was to study the behavior of the Pd-30Ag foil of the hydrogen diffusion anode after prolonged hydrogen oxidation. A couple of anodes were employed in the electrolyses reported here. The ICP analyses of the electrolyte did not show significant Pd or Pt release from the foils. In addition, no methanol derivatives were found in the GC analyses. This shows that the essential reaction in the hydrogen diffusion anode is hydrogen oxidation, the oxidation of Pd, Pt, or methanol being insignificant. However, the Pd-30Ag foil suffered some deformation. The foil, initially flat, became concave, its concavity being quite regular and slowly increasing with time. The interelectrode gap increased in the central part of the electrodes as a result and the electrodes could not become shorted. A 25 μ m thick Pd foil with a section of about 0.5 cm² was employed in previous experiments of CFC electrodegradation9,11,17 and the foil deformation was much less apparent because of the electrode size. Use of a greater size electrode in this work then magnifies this effect so that it is much more apparent.

The deformation of the Pd-30Ag foil can be explained by the inner pressures developed in the foil due to the hydrogen dissolution. It is known that volumes of hydrogen much higher than a given volume of Pd can be dissolved in it.²⁶ In this process, two palladium hydride phases are formed at room temperature, the relative stresses appearing in the region between such phases leading to the deformation of the thin Pd foils. As indicated elsewhere,²⁶ only one hydride phase is formed at temperatures over 77°C in Pd-30Ag foils, and therefore, electrodegradation of CFCs at these temperatures has to be explored in order to study the stability of such foils under these conditions. Use of a mechanical reinforcement at the hydrogen side of the foil can be suggested. A temperature increase is expected to lead to a greater loss of volatiles from the electrolyte, thus increasing the pressure in the gas phase over the electrolyte. Therefore, the use of a new system, especially prepared to support high pressures, appears necessary. This has to be tested in further work.

Conclusions

A laboratory-scale flow cell was built to study the behavior of the electrodes and the formation of the derivatives during the electrodegradation of CFCs 11 and 113. The electrolyte was nondeaerated 0.75 mol dm⁻³ NH₄Cl, 0.1 mol dm⁻³ PTBA, or 0.75 mol dm⁻³ NH₄Cl + 0.05 mol dm⁻³ PTBA, adding 50 ppm PdCl₂ only for CFC 113. The electrolyte volume of the cell was 0.5 dm³ and it was circulated at 25 mL min⁻¹ between a Cu cathode and a H₂-fed Pd-30Ag hydrogen diffusion anode activated with Pd + Pt blacks, the interelectrode gap being 4 mm. The electrolyses were performed at current densities of *ca.* 10 mA cm⁻². A gas chamber was enabled over the electrolyte, which permitted the distribution of the CFC derivatives in both phases according to their volatility.

CFC 11 was electrodechlorinated in the different electrolytes, gradually losing its Cl atoms up to CH_4 . The current efficiency in NH_4Cl was *ca.* 74%. It increased in PTBA + NH_4Cl and PTBA to *ca.* 91 and 95%, respectively, although the cell voltage had to be considerably higher to obtain the same current density as in NH_4Cl . The use of PTBA significantly reduced the cathode corrosion.

The electroreduction of CFC 113 in NH₄Cl led to different dechlorinated derivatives, their amounts decreasing in the order DCTFE > DFE > CTFE > TFE, and the current efficiency being about 80%. The cathode corrosion was smaller than for CFC 11 because of the Pd black electrodeposition. PTBA also decreased the cathode corrosion, but Pd black electrodeposition was poor and the current efficiency decreased to about 50%.

The increasing amount of volatile derivatives with time increased the pressure in the cell, thus suggesting building up a system prepared to support inner pressures significantly over the atmospheric one.

In spite of its chemical stability, the Pd-30Ag foil of the hydrogen diffusion anode presented some concave deformation, which increased the interelectrode gap during prolonged H₂ oxidation. The dimensional stability of the anode needs improvement and its longtime operation has to be studied in depth.

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References

- E. J. A. X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum, and J. A. Moulijn, Appl. Catal., A, 155, 59 (1997).
- 2. A. Savall, R. Abdelhedi, S. Dalbéra, and M. L. Bouguerra, Electrochim. Acta, 35, 1727 (1990)
- 3. A. Savall, R. Abdelhedi, S. Dalbéra, and M. L. Bouguerra, J. Appl. Electrochem., 20, 1045 (1990).
- 4. Montecatini Edison S.p.a., Italian Pat. 852,487 (1969).
- 5. K. M. Smirnov, A. P. Tomilov, L. G. Feoktistov, and M. M. Gol'din, Zh. Prikl. Khim. (S.-Peterburg), 51, 703 (1978).
- S. Wawzonek and S. Willging, J. Electrochem. Soc., 124, 860 (1977).
 V. L. Kornienko, G. A. Kolyagin, and G. V. Kornienko, Russ. J. Electrochem., 33, 7 896 (1997).

- 8. K. M. Smirnov, A. P. Tomilov, L. G. Feoktistov, and M. M. Gol'din, Zh. Prikl. Khim. (S.-Peterburg), 51, 701 (1978).
- 9. P. L. Cabot, M. Centelles, L. Segarra, and J. Casado, J. Electrochem. Soc., 144, 3749 (1997).
- 10. P. L. Cabot, M. Centelles, L. Segarra, and J. Casado, J. Electroanal. Chem., 435, 255 (1997).
- 11. P. L. Cabot, L. Segarra, and J. Casado, Electrochem. Solid-State Lett., 6, B15 (2003).
- 12. E. Delli, S. Kouloumtzoglou, G. Kyriacou, and C. Lambrou, Chem. Commun. (Cambridge), 1998, 1693.
- 13. N. Sonoyama and T. Sakata, Environ. Sci. Technol., 32, 375 (1998).
- 14. A. Schizodimou, G. Kyriacou, and Ch. Lambrou, J. Electroanal. Chem., 471, 26 (1999).15. N. Georgolios, G. Kyriacou, and G. Ritzoulis, J. Appl. Electrochem., 31, 207
- (2001). 16. N. Sonoyama, K. Ezaki, H. Fujii, and T. Sakata, Electrochim. Acta, 47, 3847
- (2002). 17. P. L. Cabot, M. Centelles, L. Segarra, and J. Casado, J. Electrochem. Soc., 147,
- 3734 (2000) 18. V. L. Kornienko, G. A. Kolyagin, G. V. Kornienko, and Yu. V. Saltykov, Sov.
- Electrochem., 28, 412 (1992). 19. P. L. Cabot, E. Guezala, J. C. Calpe, M. T. Garcia, and J. Casado, J. Electrochem. Soc., 147, 43 (2000).
- 20. M. J. Height, E. M. Kennedy, and B. Z. Duglogorski, J. Chromatogr., A, 841, 187 (1999)
- 21. E. F. Barry, R. S. Fischer, and D. M. Rosie, Anal. Chem., 44, 1559 (1972).
- N. Sonoyama and T. Sakata, Environ. Sci. Technol., 32, 4005 (1998).
- 23. M. M. Scherer, J. C. Westall, M. Ziomek-Moroz, and P. G. Tratnyek, Environ. Sci. Technol., 31, 2385 (1997).
- 24. H. Lund and O. Hammerich, in Organic Electrochemistry, 4th ed., p. 275, Marcel Dekker, New York (1991).
- 25. J. F. Llopis and F. Colom, in The Encyclopedia of the Electrochemistry of the Elements, pp. 253-275, Marcel Dekker, New York (1976).
- 26. J. N. Armor, CHEMTECH, 1992, 557.