Spectroelectrochemical study of perchloroethylene reduction at copper electrodes in neutral aqueous medium

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Abstract.-

The potential-dependent chemical reaction of perchloroethylene (PCE) on copper in neutral noncomplexing aqueous media is explored by means of surface-enhanced Raman spectroscopy (SERS), linear sweep voltammetry and preparative electrolysis at controlled potential. Voltammetric peaks associated with copper oxide reduction in Na₂SO₄ solution in the presence and the absence of Cl⁻ are correlated with simultaneously acquired SER spectra. Perchloroethylene undergoes a dechlorination process at potentials at $E \leq -0.3$ V vs Ag/AgCl/KCl(3M), as shown by the emergence of an intense Cu-Cl stretching band at 290 cm⁻¹ and a C-H stretching band together with the presence of Cl⁻ in the catholyte. In the potential region between 0 and -0.9 V vs Ag/AgCl/KCl(3M) a broad band assigned to -C≡C- structures is observed in the triple-bond region (~ 1900 cm⁻¹, fwhm = 180 cm⁻¹). In addition, dichloroethylene (DCE) is detected (but not trichloroethylene (TCE)) in this potential region during preparative electrolysis. At potentials lower than -1 V vs Ag/AgCl/KCl(3M) carbon residues are the main product, detected on the copper surface by SERS (and confirmed by XPS), whereas in solution higher levels of dichloroethylene and trichloroethylene are detected with a DCE/TCE ratio below 1.

Keywords: perchloroethylene, copper, SERS, electroreduction, acetylene

Introduction.-

There is a continuous interest in the electrochemical reduction of halogenated organic compounds, especially in the elucidation of mechanistic details about the cleavage of the carbon-halogen bond. The reduction reaction of compounds with potential leaving groups (Cl, Br, I, SO₂,....) was extensively studied in terms of hydrogenolysis or/and formation of acetylenes in the 80s and 90s [1, 2]. Several general rules can be found in literature[3,4], establishing that: (i) polyhalogenated compounds are easier to reduce than monohalogenated compounds; (ii) iodides are easier to reduce than bromides and chlorides, being the latter the most difficult; (iii) tertiary alkyl halides are easier to reduce than secondary, which are in turn easier to reduce than primary alkyl halides. Different electrochemical behavior can be found depending on the electrode material used. On one hand, with electrodes such as mercury, lead, silver and tin [5], the radical species can interact strongly with the cathode metal, which can enhance the reduction of the halogenated compound and can result in the formation of organometallic compounds. On the other hand, by using carbon cathodes, which cannot form organometallic compounds, it is possible to observe the cleavage of carbon-chloride bonds in some alkyl monochlorides [6]. Recently, it has been reported the use of alloys as cathodic materials for the catalytic cleavages of carbon-halide bonds, focusing special attention on the palladiated copper interfase [7]. However, most of this information has been obtained in organic solvents [8-10].

Recently, the electrochemical technology is being investigated for the degradation of these persistent pollutant compounds [11-15]. Despite the potential advantage in the

electrochemical treatment by reduction and oxidation, the halocompounds present only acceptable results by electroreduction [16], especially in aqueous media. In this latter reference, it is established that i) the electroreduction takes place at potentials close to those for the reduction of the background working solution, decreasing the current efficiency, and ii) that the mechanism usually follows a radical pathway, whose intermediates undergo other reactions. However, it is not obvious that reduction of a carbon-chloride bond follows a radical pathway. In almost every instance, the process (which occurs at very negative potentials) involves two electrons to form a carbanion intermediate [1].

Because of sluggish kinetics, little attention has been paid to fundamental studies of the electrochemical behavior of chlorinated compounds in aqueous media. From the large group of chlorinated compounds, chloroform has been routinely the molecule most studied by electrochemical methods. It was stated that the carbon-halogen bond cleavage follows a general scheme involving loosely and strongly adsorbed species and methane was obtained as the major final product with platinum cathodes [17]. With Ag, Zn, Cu and Pd cathodes, both methane and dichloromethane were obtained [18]. Dichloromethane was found as a final product for Pb and Sn electrodes [18]. Carbon tetrachloride has been also degraded by Criddle et al. [19] using silver as cathode in the electrochemical route. Chloroform, dichloromethane and CO were obtained as final products. They concluded that carbon tetrachloride can undergo parallel transformation: by hydrogenolysis and by hydrolytic reduction in aqueous solutions.

Chlorinated ethylenes are another group frequently studied and different approaches can be found in the literature. On one hand, the metal-catalyzed degradation of chlorinated ethylenes by interaction of these compounds with metal surfaces is of great interest, but

only a limited amount of work on metal surfaces such as Ag, Cu, Pd, and Pt has been reported [20-24]. On the other hand, electrochemical approaches are also being investigated. Special attention merits the work done by Liu et al. [25]. For perchloroethylene (PCE), trichloroethylene (TCE) was the major intermediate and trans-dichloroethylene (DCE) and acetylene were intermediates at the trace level. Ethene and ethane were the major products together with minor quantities of propane, C₄ and C₆ hydrocarbons, which indicates that free radicals are produced during the electroreduction at nickel electrodes. They concluded that sequential hydrogenolysis is the major reaction pathway for chlorinated alkenes. Farrell et al. [26] reported that TCE is indirectly reduced by atomic hydrogen and PCE undergoes direct reduction, but, in any case, ethene was the major reaction product.

In spite of the fact that perchloroethylene is a widely used solvent in many areas of industry and it has been reported as a major intermediate in the degradation of other chlorinated compounds, to our knowledge, there is not an extensive fundamental study of the electrochemical degradation of this compound. We present here for the first time a combined spectroscopic (SER) and electrochemical study on perchloroethylene reduction in aqueous medium, examining the catalytic reactions occurring on the electrode surface. This system is studied on a copper substrate, due not only to the good performance of this material for SER analysis but also owing to the large possibilities we can foresee, having exceptional catalytic properties as common metal or alloy [7]. In this paper, it has been shown that electroreduction of perchloroethylene may occur at very high electrode potential (-0.3 V vs Ag/AgCl/KCl(3M)). Besides, the fruitful combination of SER analysis and electrochemistry is highlighted, especially for the analysis of systems whose

electrochemical behavior is difficult to analyze only by means of electrochemical techniques.

This article is organized as follows. First, the voltammetric behavior of the background system (aqueous sodium sulphate/copper electrode) is presented followed by a parallel SER study as reference. Then, perchloroethylene is added to the system and the same combined study is carried out: the voltammetric behavior is analyzed in static and enhanced mass transport conditions (RDE experiments). This study is completed with an analysis of the SER spectra recorded at different electrode potentials. For this SER analysis, a specific combined study (spectroelectrochemical and voltammetry analysis) of the background system now in presence of Cl^- anion and SER analysis in D_2O solvent in presence and absence of perchloroethylene were also carried out. The combination of all these results reveals a strong surface activity of the perchloroethylene with the appearance of several new bands. Finally, comparison between chemical reduction trials and preparative electrolysis for the PCE electroreduction gave qualitative information about the process. All this information, complemented by that found in the literature, allows both a systematic assignment of the new bands and to monitor the electroreduction of PCE.

Experimental.-

Materials. The background electrolyte, 0.05 M Na₂SO₄ aqueous solution, was prepared with purified water obtained from a Milli-Q UV Plus system (18.2 MΩ cm resistivity) and Na₂SO₄ (Merck p. a.). For electrochemical experiments, this background electrolyte was Ar-purged in the electrochemical cell. After that, due to the volatility of PCE, all ports were carefully sealed and PCE (99.9% (Aldrich) without any further purification) was then added to obtain the desired concentration (c.a. 50 ppm). On one hand, in the voltammetric experiments, the electrochemical cell was kept under argon atmosphere from then on, to avoid oxygen entrance. On the other hand, in the preparative electrolysis experiments, a gas balloon was connected to collect the gas products. The solution was stirred to dissolve PCE prior to the electrochemical experiments.

A copper wire (0.07 cm² active surface) from Goodfellow and a copper disk (0.196 cm²) Radiometer Copenhagen were used as working electrodes in the voltammetric experiments and RDE experiments respectively. A copper sheet (3x2x0.1 cm) was used in the preparative electrolysis experiments. Two treatments were applied to the electrode surface. In order to get a fresh copper surface, we have polished the surface with decreasing size alumina powder (1, 0.3 and 0.05 μm) until a mirror finish was obtained. After that, the electrode was thoroughly rinsed with ultrapure water (treatment 1). The copper electrodes employed in SERS experiments and in voltammetric experiments related with SERS, were polished and activated by anodic dissolution at 0.5 V for 40 s and subsequent reduction at -0.8 V for 10 s in 0.2 M CuSO₄ +0.4 M H₂SO₄ [27] (treatment 2). This treatment renders the rough metal surface needed for SERS experiments.

Experimental setup. A three-compartment electrochemical cell was used for voltammetric studies and an all-glass two-compartment cell for preparative electrolysis. Figure 1 shows the spectroelectrochemical PTFE cell designed to acquire *in situ* Raman spectra. The electrochemical experiments were carried out using an Autolab PGSTAT30 and the spectroelectrochemical experiments using a Electrochemical Analyzer, model CHI600C frp, CH Instruments, USA. In both cases, the counter electrode was a spiral wound platinum wire and all electrode potentials were measured and quoted vs Ag/AgCl/KCl (3M) electrode (Crison, model 52 40).

For the spectroelectrochemical experiments, the Cu working electrode, pretreated by the method previously indicated, was mounted in the spectroelectrochemical PTFE cell. A fused silica window separates the microscope objective from the electrolytic solution. PCE solutions were introduced into the spectroelectrochemical cell at controlled potential. Raman spectra were obtained with a LabRam spectrometer (from Jobin-Yvon Horiba). The slit and pinhole employed were 200 nm and 600 nm, respectively. The excitation line was provided by a 17 mW He-Ne laser at 632.8 nm. The laser beam was focused through a 50x long-working distance objective (0.5 NA) into a 2- μ m spot at the electrode surface. The spectrometer resolution was better than 3 cm^{-1} , the detector was a Peltier cooled charge-couple device (CCD) (1064 x 256 pixels) and typical acquisition times of 5 s were employed. All the spectra shown in this paper are presented as obtained and no baseline correction was applied. The SER spectra at different potentials were recorded point by point by varying the electrode potential stepwise in the negative-going direction from the

initial anodic one, followed by shifting of the potential to a new value and recording of SERS spectrum.

Analysis. For the detection of the products of preparative electrolysis, the sample analyses were carried simultaneously by both HPLC and gas chromatography in order to follow the organic products from the PCE reduction. The chloride ion content was determined by potentiometric titration with 0.002M AgNO₃ solution. All sample aliquots were analyzed immediately after collection. The XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer, by using the Mg /K// α / (1253.6 eV) radiation of twin anode in the constant analyser energy mode with pass energy of 50 eV.

Results and discussion.-

Spectroelectrochemical analysis of the system aqueous Na₂SO₄-Cu electrode

First, the spectroelectrochemical behavior of a SERS-activated copper electrode (treatment 2) in contact with 0.05 M Na₂SO₄ aqueous solution was studied. Figure 2 shows (A) the linear voltammetric profile obtained in the typical electrochemical cell and (B) a set of spectra acquired at different potentials. The cleanliness of the spectroelectrochemical cell was checked by comparing the blank voltammogram, obtained prior to the acquisition of Raman spectra, to the voltammetric profile obtained in a standard voltammetric glass cell (Figure 2A).

The shape of the broad peaks located between -0.36 and -0.9 V in Figure 2A indicate that they are not related to a mass-transport controlled process but to one limited by the surface. These broad peaks are followed by a short potential window with a low current density prior to the onset of hydrogen evolution at potentials more negative than -1.0 V. SER spectra recorded at different electrode potentials provide useful information in order to analyze the voltammetric profiles shown in Figure 2A. Spectrum (a) in Figure 2B was recorded at -0.1V where a net anodic current density is observed. A set of bands ranging from 250-600 cm⁻¹ related to copper oxides, and a clear band located at 964 cm⁻¹ from symmetric stretching vibration of sulphate anion, are displayed. In the same way, other authors such as Chan et al [28] have studied the oxide film formation and oxygen adsorption on copper in aqueous media by SERS, in alkaline and neutral media. In spite of the unbuffered nature of the neutral pH electrolyte (pH 6), which precludes a detailed potential analysis of the spectra, they assigned the peaks at 625 and 525 cm⁻¹ to Cu₂O thin films and a weak SERS feature at 460 cm⁻¹ was tentatively assigned to Cu(OH)₂. In any

case, an increase in the cathodic contribution of the net current density is detected at more negative potentials (points *b* and *c* in Figure 2A) linked to a decrease in intensity of the copper oxide bands (Figure 2B). The copper oxide reduction is pointed out by the observation of a net cathodic current density at potentials more negative than -0.36V (Figure 2A) in agreement with spectrum (c) in Figure 2B.

Spectroelectrochemical analysis of the system aqueous PCE- Na_2SO_4 -Cu electrode

Figure 3 summarizes in a first approach the voltammetric behavior of the PCE- Na_2SO_4 -Cu electrode system in static conditions (Figure 3A) and under enhanced mass transport conditions (Figure 3B). In static conditions, two different electrode surface treatments and initial potentials have been chosen for analysis: (i) copper treated by method 1 in order to decrease the disturbance resulting from the possible presence of copper oxide and $E_i = -0.3\text{V}$ (inlet plot in Figure 3A) and (ii) $E_i = 0\text{ V}$ and SERS-activated copper electrode by treatment 2 (main plot in Figure 3A). In the inset ($E_i = -0.3\text{V}$), the comparison of the voltammetric profile in the presence of PCE with the background electrolyte profile clearly demonstrates that PCE is reduced at fresh Cu surface at potentials lower than -0.3V. With this previous result, we can analyze the voltammetric profiles obtained with $E_i = 0\text{ V}$ in Figure 3A. As the electrode potential decreases, the reduction of PCE is favored, especially when copper oxide is simultaneously reduced, and the voltammetric profile shows the overlapping of the two processes (PCE and copper oxide reduction). The low concentration of PCE and the simultaneous reduction of the surface oxide do not allow any quantitative analysis of the curve profile. Finally, there is an increase of the negative current in the hydrogen evolving region, compared to the background electrolyte profile. As we have mentioned in the introduction, it has been proposed that some chlorinated

compounds can be reduced by indirect reaction with atomic hydrogen and this could be a reasonable explanation for this increase in the cathodic current density at potentials in the hydrogen evolution range.

As indicated above, the solubility of PCE in water is very low, so the mass-transport limitations are analyzed in Figure 3B showing the voltammetric profile in RDE experiments in the presence and absence of PCE (inset), and at two different rotation rates in presence of PCE (main plot). As we can see, the PCE electroreduction onto a fresh copper surface is increased by the mass-transport enhancement of PCE from the bulk solution, throughout the whole potential region investigated. Special attention should be paid to the voltammetric responses at $E > -0.3\text{V}$ showed in Figure 3. In static conditions (Figure 3A) addition of PCE enhances the anodic current observed. In contrast, at enhanced mass transport conditions (Figure 3B), the addition of PCE implies an increase of the cathodic current density contribution at potentials less negative than -0.3V .

Voltammetric analysis can be clarified with additional information provided by SERS. Figure 4 shows a set of spectra acquired at different potentials obtained by adding 2 ml of a saturated PCE aqueous solution (solubility: 150 mg L^{-1} , at 20°C) to the background electrolyte, initially kept at $+0.15\text{ V}$. The final concentration of PCE was approximately 10 ppm. In the low-frequency range a band centered at 290 cm^{-1} appears between $+0.05\text{ V}$ and -0.8 V , varying its intensity with a maximum at -0.05 V . It is reported in the literature that adsorbed chloroethylenes, other than vinyl chloride, undergo C-Cl bond scission on Cu(100) [22] and Cu(110) [21, 29], and the dominant product in all cases is acetylene. Pettinger et al. [30] performed a study of the potential dependence of the SER spectra for

metal-halide vibrations and assigned the band at 292 cm^{-1} to the $\nu[\text{Cu-Cl}]$. Eltsov et al. [31] in a SERS study on chlorinated Cu(111) observed a band centered at 294 cm^{-1} that was assigned to the $\nu[\text{Cu-Cl}]$. Finally, Jugnet et al. [32] in a HREELS investigation of the adsorption of trans-dichloroethylene on Cu(110) found a band at 310 cm^{-1} assigned to the Cu-Cl stretching. In order to check this assignment in our experimental system and the possible role of the Cl^- anion in the copper oxide/PCE reduction, an experiment was performed in which a 1 mM NaCl aqueous solution was added into the electrolyte solution at 0 V. Figure 5 displays (A) the linear voltammetric profile and (B) the spectra registered and their evolution with the potential applied to the working electrode. As we can see in Figure 5A, there is little influence in the voltammetric profile due to the presence of Cl^- anion, decreasing the oxidation of copper at potentials higher than -0.36 V. Besides, looking at Figure 5B, a strong band appears at 290 cm^{-1} and according with Chan *et al.* [28] the observed band is assigned to the presence of a CuCl phase film formed during metal dissolution. Consequently, when PCE is added to the background electrolyte, the observed band at 290 cm^{-1} proofs that PCE undergoes a dehalogenation process. It is also interesting to highlight that an unexpected band appears at 2920 cm^{-1} whose intensity varies in the same way as the 290 cm^{-1} band does. It can be noticed that at potentials more negative than -1 V, the intensities of these two bands are insignificant. The assignment of this band is difficult. Due to the absence of any carbon compound in the $\text{NaCl} + \text{Na}_2\text{SO}_4$ aqueous solution, this band should arise from surface molecular complexes composed of water, chloride ions and copper (ad)atoms [30]. A band in this spectral region was also observed but not explained by Storey et al. [33] in a blank SERS spectrum of an activated copper electrode in 0.1 M KBr solution. It is also interesting to note that, at 0 V, spectrum (a)

Figure 5B, copper oxide bands are displayed but the clear band located at 964 cm^{-1} from sulphate anion is not displayed, maybe due to the strong adsorption of Cl^- anion. Similar competition has been detected by other authors [34]. As the electrode potential becomes more negative, copper oxide bands disappear and at very negative potentials (-1 V), close to the hydrogen evolution reaction, the peak related to coadsorbed Cl^- anions disappears too.

Let us return again to the Figure 4. In addition to the band at 290 cm^{-1} other ones can be observed: bands centered at 1900 cm^{-1} and 2920 cm^{-1} and a broad feature that appears between 1100 and 1650 cm^{-1} . In this feature, bands between 1500 and 1580 cm^{-1} are clearly observed and would indicate the presence of double $\text{C}=\text{C}$ bonds on the surface. Net Raman spectra of chlorinated ethylenes show bands in this spectral range [35]. On the other hand, the intensity and persistence of the band centered at 2920 cm^{-1} (that is also present in spectra shown in Figure 5B), at potentials more negative than -1 V , could support the existence of C-H stretching. Nevertheless, in order to check the presence of C-H bonds, an experiment with D_2O was performed. Figure 6 shows a set of SER spectra recorded under these experimental conditions. Now, a new band appears at 2130 cm^{-1} which is the wavenumber expected for a C-D stretching, but the band at 2920 cm^{-1} is still present. Thus, such a band should have a component due to C-H stretching and, consequently, species containing C-H bonds are present on the electrode surface and C-H bending modes would be included as a component in the broad band around 1300 cm^{-1} [35].

Another spectral feature shown in Figure 4 is at 1900 cm^{-1} ($\text{fwhm} = 180\text{ cm}^{-1}$). It is reported in the literature that dechlorination of chloroethylenes on $\text{Cu}(110)$ [21, 29, 32] produces mainly acetylene. Yang et al. [22] in their study of the chemistry of chloroethylenes on $\text{Cu}(100)$ found that TCE dissociation generates acetylene and deposits a

carbon residue on the surface. Abrantes et al. [36] observed in the SER spectrum of phenylacetylene adsorbed on copper a broad complex band in the spectral range 1800 – 2000 cm^{-1} . This complex band was assigned to the $\nu[\text{C}\equiv\text{C}]$ of adsorbed phenylacetylene at different crystal faces. They also concluded that adsorption onto copper occurs via the $\text{C}\equiv\text{C}$ bond. The low $\nu[\text{C}\equiv\text{C}]$ frequency would indicate that a π bonding between this triple bond and Cu exists. Donation would occur from filled π orbitals on the adsorbate to vacant σ orbitals on the metal, accompanied by back donation from filled metal d_{xy} orbitals to empty π^* orbitals on the adsorbate. For silver this broad band is slightly shifted to higher frequencies, indicating a weaker π interaction of the triple bond. Weaver et al. [37] reported the SER spectra in electrochemical systems of acetylene and simple alkynes adsorbed on silver and gold. For acetylene, the main band is observed at 1910 cm^{-1} for Au and at 1975 cm^{-1} for Ag. The characteristics of the observed band can be rationalized by the existence of several different adsorbed species. Among them, acetylides in which the metal is σ -bonded to a carbon atom are the most simple compounds, and copper acetylides show the largest frequency downshifts for coinage metals. Besides, acetylides tend on these metals to associate and to form a $\sigma\pi$ bond with one or two other metal atoms [38]. Finally, another possible assignment of this band should be mentioned. It has been reported [39] that the electrocatalytic dehydrochlorination of 1,1,2-trichloroethane at a Ni electrode leads to the formation of a carbene analogue, as indicated by a broad band at 1960 cm^{-1} assigned to the carbon-carbon stretching mode of *sp*-bonded carbons [40]. Therefore, we tentatively assign the band centered at 1900 cm^{-1} to an acetylide-Cu species. The potential dependence of the SER spectra might also be expected to yield insight into the adsorbate structure but the large bandwidths tend to obscure any clear-cut trends. However, the intensities of the bands

are markedly potential dependent and this would suggest that an electrochemical reaction (more likely hydrogenation) of the adsorbate may have taken place in the system.

Finally, our experimental results show that the broad feature appearing between 1100 and 1600 cm^{-1} develops with increasingly negative potentials, resulting in two bands at 1330 and 1590 cm^{-1} , respectively. These bands are common for all forms of polycrystalline graphite or amorphous carbon (G and D bands) with a broad distribution of sp^2 and sp^3 bonded carbon atoms, and indicate the formation of graphitic reaction products on the electrode surface. In view of these results, XPS analyses were carried out for the copper working electrode after and before the preparative electrolysis at -1V, the latter serving as a control experiment. The results show the presence of C1s peaks in the spectrum obtained, with an increase of C in the surface electrode, confirming that the two bands at 1330 and 1590 cm^{-1} arise from the final carbonaceous reduction products at this electrode potential.

With all the previous information, a plausible explanation can be given for the voltametric behavior shown in Figure 3 at potentials more positive than -0.36 V where, in static conditions, higher anodic current densities are recorded in presence of PCE than those obtained in its absence in opposite to Figure 3B, where a enhanced mass-transport conditions increases the cathodic contribution in the potential range. Keeping in mind the decreasing of the oxidation of copper electrode in presence of Cl^- , at potential higher than -0.36 V (figure 5A), and that the oxidation of chlorinated compounds is not a favored process [16], it means that enhancement of the copper oxidation in figure 3A is not due to the Cl-Cu interactions but likely to the Cu-PCE byproducts, which seems to improve the

copper oxidation. Stable copper acetylide complex has been detected in the Pd/Cu catalyzed coupling reactions of acetylenic derivatives [41], in the dimerization and hydration of acetylene in water with a copper(I) catalyst, as activated catalyst, $[H\cdots Cl-Cu-C_2H]$, formed in the reaction mixture, with acetylene or water [42] and as thermal products of copper acetylenedicarboxylate system [43]. The band at 1900 cm^{-1} assigned to an acetylide-Cu species would support the role of the Cu-PCE byproducts in the improvement of the Cu oxidation at potential higher than -0.36 V . SER spectra also show that, in this potential window, several processes take place, at least, oxidation of copper and adsorption-reduction of PCE. Due to the low solubility of PCE, the electroreduction of PCE is not favored under static conditions and so, an increase of the mass-transport conditions can favor the process related to the PCE interaction with the surface.

Bulk electrolysis of the system aqueous PCE- Na_2SO_4 -Cu electrode

As preliminary results about the electrochemical reduction of PCE, more qualitative information about the process was obtained through the comparison between preparative electrolysis experiments and the direct chemical reduction with copper in analogous experimental conditions. In this way, three conical glass flasks were provided with (i) PCE- Na_2SO_4 solutions without copper, (ii) PCE- Na_2SO_4 solutions with equivalent copper powder to have the same surface area as the copper electrode used in bulk electrolysis and (iii) PCE- Na_2SO_4 solutions with a huge excess of powder copper (2000 times higher than test (ii)). In any case, no PCE reduction products were obtained so we can exclude direct chemical reduction under our experimental conditions.

For bulk electrolysis, three different electrode potentials were chosen: at -0.3 V where, upon an increase in the mass-transport conditions, the net anodic current becomes cathodic current; at -0.55 V, where tentatively simultaneous copper oxide and PCE electroreduction take place; and at -1 V, just prior to the massive hydrogen evolution potential range. No incipient hydrogen evolution was observed at -1V but TCE was clearly detected along with DCE in the catholyte by HPLC, with a DCE/TCE molar ratio lower than one. In addition, Cl^- was detected in the catholyte by potentiometric titration, establishing the electroreduction of PCE at this potential. In the gas phase, a similar molar ratio was detected. The results obtained at -0.55 V and -0.3 V are similar, but different from those obtained at -1.V. HPLC was not able to detect TCE or DCE in solution at any charge, so a poor efficiency must be attributed to the electroreduction at these experimental conditions. However, the most sensitive gas chromatography detected a peak of DCE from the catholyte (but not TCE). Cl^- anions were again detected in the catholyte, in agreement with PCE electroreduction.

Finally, a reasonable explanation for the potential dependence of the presence or absence for DCE and TCE can be directly related to the adsorbed $-\text{C}\equiv\text{C}-$ structure. The presence of this structure on the surface would imply that a multi-electron reduction can be favored, giving DCE rather than TCE as reduction product. The low level of DCE detected suggests that the process takes place at the surface. The detection of TCE and DCE at potentials more negative than -1 V in the preparative electrolysis and the disappearance of the band at 1900 cm^{-1} at these potentials could imply that another pathway is being favored, a stepwise C-Cl cleavage.

Conclusions

The potential-dependent formation of perchloroethylene derivatives on a copper surface in neutral noncomplexing aqueous media reveals that perchloroethylene undergoes reduction at $E \leq -0.3$ V, this process taking place simultaneously with copper oxidation. This is confirmed by the emergence of intense Cu-Cl stretching (band at 290 cm^{-1}), C-H stretching (contribution to the band at 2920 cm^{-1} as shown by the appearance of a band at 2130 cm^{-1} in D_2O solvent) and the presence of Cl^- and DCE in the catholyte during electrolysis at -0.3V .

A band centered at 1900 cm^{-1} has been detected in the 0 to -0.9 V potential region, and it has been assigned to $-\text{C}\equiv\text{C}-$ structures, supported by the existence, according to the literature, of stable $\text{Cu}-\text{C}\equiv\text{CH}$ complexes. This fact together with the presence of DCE and absence of TCE detected during the preparative electrolysis (at potentials -0.55V and -0.3 V) is correlated to a C-Cl multi-bond cleavage process, favouring the direct generation of dichloroethylene in front of a step process via trichloroethylene.

The presence of carbon on the surface of the copper electrode is supported by the appearance of two bands at 1330 and 1590 cm^{-1} at potentials lower than -1 V, and by the XPS analysis of the electrode surface after preparative electrolysis carried out at -1.0 V.

Finally, the band centered at 2920 cm^{-1} , which appears when Cl^- is present and that does not shift upon changing from H_2O to D_2O as solvent, can be tentatively assigned to surface molecular complexes composed of chloride ions and copper (ad)atoms. The occurrence of this band should be taken into account when C-H stretching is being contemplated. Experiments using D_2O as solvent and with PCE present in the solution evidence the existence of species containing C-D bonds on the electrode surface.

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References

1. J. Simonet, J. F. Pilard in: H. Lund, O. Hammerich (Eds.), *Organic Electrochemistry*, M. M. Dekker, New York, 2001. Chapter 29.
2. J. M. Savéant, in: T. T. Tidwell (Ed.) *Advances in Physical Organics*, Vol. 35, Academic Press, New York, 2000.
3. M. D. Hawley, in *Encyclopedia of Electrochemistry of the Elements*, ed A. J. Bard and H. Lund, Marcel Dekker, New York, 1980, Vol. XIV, p.1.
4. D. G. Peters, in *Organic Electrochemistry: An introduction and a guide*, eds. H. Lund and M. M. Baizer, Marcel Dekker, New York 3rd edn., 1990, p361-394.
5. S. Rondinini, P. Mussini, P. Muttini and G. Sello *Electrochim. Acta*, 46 (2001) 3245.
6. F. L. Lambert and G. B. Ingall *Tetrahedron Lett.* (1974) 3231.
7. J. Simonet, P. Poizot, L. Laffont, *J. Electroanal. Chem.* 591 (2006) 19
8. J. Simonet and D. G. Peters *J. Electrochem. Soc.*, 151 (2004) D7
9. C. P. Andrieux, I. Gallardo, J.-M. Savéant and K.G. Su, *J. Am. Chem. Soc.*, 108 (1986) 638
10. C. P. Andrieux, J.-M. Savéant and K. B. Su *J. Phys. Chem.*, 90 (1986) 3815.
11. W. A. Arnold and A. L. Roberts *Environ. Sci. Technol.*, 34 (2000) 1794
12. T. Li and J. Farrel *Environ. Sci. Technol.* 34 (2000) 173
13. J. Rohrs, G. Ludwig and D. Rahner, *Electrochim. Acta* 47 (2002) 1405

14. N. Sonoyama, K. Ezaki and T. Sakata *Adv. Environ. Res.*, 6 (2001) 1
15. L. J. Weathers, G. F. Parkin and P. J. Alvarez *Environ. Sci. Technol.*, 31 (1997) 880
16. K. Rajeshwar and J. Ibañez, in *Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement*, Academic Press, London, 1997 Chp. 3.
17. G. Horányi and K. Torkos *J. Electroanal. Chem.* 140 (1982) 329
18. N. Sonoyama, K. Hara and T. Sakata, *Chem. Lett.* 2 (1997) 131
19. C. S. Criddle and P. L. McCarty, *Environ. Sci. Technol.* 25 (1991) 973
20. D. P. Pursell, M. L. Bocquet, J. M. Vohs and H.-L. Dai, *Surf. Sci.* 522 (2003) 90.
21. S. C. Larote, S. Haq, R. Raval, Y. Jugnet and J. Bertolini *Surf. Sci.*, 435 (1999) 193.
22. M. X. Yang, P. W. Kash, D.-H. Sun, G. W. Flynn, B. E. Bent, M. T. Holbrook, S. R. Bare, D. A. Fischer and J. L. Gland *Surf. Sci.* 380 (1997) 151.
23. L. H. Bloxham, S. Haq, C. Mitchell and R. Raval *Surf. Sci.* 489 (2001) 1.
24. V. H. Grassian, G. C. Pimentel *J. Phys. Chem.*, 88 (1988) 4478.
25. Z. Liu, E. A. Betterton and R. G. Arnold, *Environ. Sci. Technol.* 34 (2000) 804.
26. J. Farrell, N. Melitas, M. Kason, T. Li, *Environ. Sci. Technol.* 34 (2000) 2549.
27. M. Graff, J. Bukowska and K. Zawada, *J. Electroanal. Chem.* 567 (2004) 297.
28. H. Y. H. Chan, Ch. G. Takoudis, M. J. Weaver, *J. Phys. Chem. B* 103 (1999) 357.
29. S. Haq, S. C. Laroze, C. Mitchell, N. Winterton and R. Raval, *Surf. Sci.*, 531 (2003) 145.
30. B. Pettinger, M. R. Philport and J. G. Gordon, *J. Phys. Chem.*, 85 (1981) 2746.
31. K. N. El'tsov, G. Ya Zueva, A. N. Klimov, V. V. Martynov, A. M. Prokhorov, *Chem Phys Lett.*, 158 (1989) 271.
32. Y. Jugnet, N. S. Prakash, J. C. Bertolini, S. C. Laroze and R. Raval, *Catal. Lett.*, 56 (1998) 17.

33. J. M. E. Storey, R. D. Shelton, T. E. Barber and E. A. Watcher *Applied Spectroscopy*, 48 (1994) 1265
34. G. M. Brown and G. A. Hope, *J. Electroanal. Chem.*, 405 (1996) 211.
35. K. Mullen and K. Carron, *Anal. Chem.*, 66 (1994) 478
36. L. M. Abrantes, M. Fleischmann, I. R. Hill and L. M. Peter, *J. Electroanal. Chem.*, 164 (1984) 177.
37. H. Feilchenfeld and M. J. Weaver, *J. Phys. Chem.* 93 (1989) 4276.
38. J. Chatt, R. G. Guy and L. A. Ducanson, *J. Chem soc.* (1961) 827.
39. X. Wang, G. Shi and Y. Liang, *J. Electroanal. Chem.*, 470 (1999) 95.
40. M. Kijima, T. Toyabe and H. Shirakawa, *Chem. Commun.* (1996) 2273.
41. P. Bertus, F. Fecourt, C. Bauder and P. Pale, *New J. Chem.*, 28 (2004) 12
42. Y. Tokita, A. Okamoto, K. Nishiwaki, M. Kobayashi and E. Nakamura, *Bull. of the Chem. Soc. of Japan* 77 (2004) 1395
43. B. J. McCormick, C. Siemer, F. Afroz, J. R. Wasson, D. M. Eichorn, B. Scott, S. Shah, K. Noffsinger and P. K. Kahol, *Synth. Metals* 120 (2001) 969

Figures

Figure 1.- Spectroelectrochemical PTFE cell.

Figure 2A.- Linear voltammogram for a SERS-active copper electrode (treatment 2) in 0.05M Na₂SO₄, scan rate 50 mV s⁻¹. Electrode area 0.07 cm². a) -0.1V, b) -0.3V and c) -1V.

Figure 2B.- Surface-enhanced Raman spectra at SERS-active copper electrode (treatment 2) from 0.05M Na₂SO₄ at different potentials showed in the figure 2A. * copper oxide band, **sulphate band.

Figure 3A.- Linear voltammogram for a SERS-active copper electrode (treatment 2) in I) 0.05M Na₂SO₄ and II) 50 ppm perchloroethylene + 0.05M Na₂SO₄, scan rate 50 mV s⁻¹. Electrode area 0.07 cm². E_i = 0 V Inlet graph: Linear voltammogram for a polished copper electrode (treatment 1) in I) 0.05M Na₂SO₄ and II) 50 ppm perchloroethylene + 0.05M Na₂SO₄, scan rate 50 mV s⁻¹. Electrode area 0.07 cm². E_i = -0.3V.

Figure 3B.- Linear voltammogram for a polished copper RDE (treatment 1) in 0.05M Na₂SO₄ + 50 ppm perchloroethylene, scan rate 10 mV/s. Electrode area 0.196 cm². I) 500 and II) 5000 rpm. Inlet graph: Linear voltammogram for a polished copper RDE (treatment 1) in I) 0.05M Na₂SO₄ and II) 50 ppm perchloroethylene + 0.05M Na₂SO₄, scan rate 10 mV s⁻¹. Electrode area 0.196 cm². 5000 rpm.

Figure 4.- Surface-enhanced Raman spectra of (a) bared copper, (b) 0.05 M Na₂SO₄ and (c-m) 10 ppm perchloroethylene + 0.05 M Na₂SO₄ adsorbed on SERS-active copper electrode at different potentials showed in the figure.

Figure 5A.- Linear voltammogram for a SERS-active copper electrode in I) 0.05M Na₂SO₄ and II) 1mM NaCl + 0.05M Na₂SO₄, scan rate 50 mV s⁻¹. Electrode area 0.07 cm². a) 0V, b) -0.1 V, c) -0.3 V and d) -1.0 V.

Figure 5B.- Surface-enhanced Raman spectra at SERS-active copper electrode from 1mM NaCl + 0.05M Na₂SO₄ at different potentials showed in the figure 5A.

Figure 6.- Surface-enhanced Raman spectra at SERS-active copper electrode from (a) 1mM NaCl in D₂O, (b-e) 10 ppm perchloroethylene + 0.05 M Na₂SO₄ in D₂O at different potentials showed in the figure.