# Electroreduction of volatile organic halides on activated silver cathodes

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## Abstract

The electroreduction of polychloromethanes and polychloroethanes has been studied by means of cyclic voltammetry (CV) and preparative electrolysis experiments in acetonitrile (ACN), dimethylformamide (DMF) and their admixtures with water. Silver has been used as cathode material, on account of our extended experience on its well established electrocatalytic activity toward reductive dehalogenation reactions of organic compounds. Polychloromethanes and -ethanes are common chlorinated solvents pertaining to the large family of volatile organic halides (VOH), whose high toxicity, or even carcinogenicity, demands careful treatment of contaminated soils, drinking waters and gaseous emissions. The results confirm the electrocatalytic role of silver and suggest a general route for the development of appropriate degradation processes.

## 1. Introduction

Volatile organic halides represent one of the most challenging categories of organic pollutants, not only for their highly toxic, or even carcinogenic, character, but also because they are, or have until recently been, used as common solvents in many applications. Their presence has been detected in soils, drinking waters and gaseous emissions, at levels that, in water sediments, can be as high as 150 ppb [1]. They may also form during the treatment of effluents containing chlorinated compounds, e.g. in the oxidative mineralization of chlorophenols. Moreover, they are known to withstand total degradation (oxidative as well reductive) and to produce secondary pollutants. Among the several approaches, reductive pathways [2–5] are attractive since the final expected degradation products are dehalogenated low molecular weight hydrocarbons, e.g. methane. In particular, direct electrochemical reduction has been investigated [6–16] on several cathode materials (Pt, Pd, Ag, Cu, Ni, Fe, Pb, glassy carbon, etc.) both in non-aqueous [6–11] and in aqueous [12–16] media, either for synthetic applications or with degradation purposes. In addition to contributions mainly devoted to the development of specific electrolytic processes applicable to selected conditions, the mechanicistic aspects of electron-transfer and bond-breaking successive reactions on glassy carbon in acidic dimethylformamide solutions have been recently presented by Costentin et al. [17]. According to their results, on polychloromethanes the mechanism of the successive reductive elimination of the chloride group involves, as rate-determining step, the concerted transfer of one electron and the cleavage of the C–Cl bond, followed by the immediate second electron transfer to the ensuing radical yielding a carbanion readily protonated by any trace of proton donors in solution. The protonation step seems to be less favoured on α, β-polychloroalkanes, which react according to the same mechanism, save for the fact that the carbanion eliminates a second Cl⁻ and generates the corresponding olefin. In line with these predictions, olefin production has been observed [10] during the electrochemical reduction of CFCs on Ag, Cu, Au, Pt and Ni, which gave $CF_2=CF_2$ as one of the main products.

It is evident that the successful degradation process must ensure, not only complete dehalogenation, but also limited product distribution, stability of the cathode material, and reasonable power consumption.

In this context, our research [18–27] on electroreduction of organic halocompounds on silver cathodes,

oriented toward both synthetic [22–24] and environmental [25, 26] applications, has been extended to the hydrodehalogenation of VOH. In particular, in a recent investigation [27] the electrochemical behaviour of dichloro- and trichloromethane was studied in acetonitrile and acetonitrile-water mixtures, and, as expected, the usual electrocatalytic effect of silver over other electrode materials including Ag–Bi and Ag–Sn alloys has been observed (e.g. on glassy carbon the gain in voltammetric peak potential ranges from 600 to 1000 mV). Interestingly, the reduction pathway for trichloromethane seems to lead to methane, without accumulation of other intermediate compounds. In the present work, further work has been done to confirm the previous preliminary results and to acquire a better understanding of the role of silver in the reduction mechanism. Preparative electrolysis experiments have been paralleled by cyclic voltammetry for qualitative and quantitative analysis of the reaction mixtures and for extending the electrocatalytic "scale" of organic halides on Ag to some possible "transient" reduction compounds, like polychloroethanes.

## 2. Experimental

All substrates ($CCl_4$, $CHCl_3$, $CH_2Cl_2$, $CCl_3$–$CH_2Cl$, $CHCl_2$–$CHCl_2$, $CCl_3$–$CH_3$, $CHCl_2$–$CH_2Cl$, $CHCl_2$–$CH_3$, $CH_2Cl$–$CH_2Cl$), being of analytical grade, were used as received from the producers (Aldrich and Merck).

### 2.1. Cyclic voltammetry (CV) experiments

Voltammetric investigations on polychloro-methanes and -ethanes (Table 1) were carried out by an AMEL 5000 potentiostat/galvanostat driven by Corrware Scribner Associates Inc., in the 100–1000 mV s$^{-1}$ range of sweep rates; the solvents were HPLC grade acetonitrile (ACN), and highly deionized water (MilliQ® Millipore System), either pure or in admixture, with 0.1 M tetraethylammonium tetrafluoborate (TEABF$_4$), tetraethylammonium hexafluophosphate (TEAPF$_6$), potassium hexafluophosphate (KPF$_6$), or potassium perchlorate (KClO$_4$) as supporting electrolytes, and with an aqueous saturated calomel electrode (SCE) as a reference electrode. Ag working electrodes consisted of platinum wires (0.5 mm diameter, 1 cm length), covered with silver by cathodic deposition against a silver anode from a 10 g dm$^{-3}$ KAg(CN)$_2$ bath, at 0.5 mA cm$^{-2}$ deposition current density. The normal cleaning procedure involved sonication in the operating solvent for 5 min [24, 28].

### 2.2. Preparative electrolysis experiments

Preparative electrolyses were carried out in a two-compartment cell, divided by a Nafion® 120 cation-exchange membrane. The catholyte and anolyte volumes were 200–300 cm$^3$. The gas output of the cathodic compartment was equipped with a condenser operated at −45 °C with a mixture of solid $CO_2$ and acetone, to guarantee the total reflux of all the volatile products, with the only exception of $CH_4$ and $CH_3Cl$, and of some stripped solvent. The operating conditions for each substrate are summarized in Table 2. The cathode consisted of a rectangular silver plate (5 cm$^2$), chemically etched prior to use. As anode, a Pt foil in aqueous electrolyte (1 M Na$_2$SO$_4$) was used.

An AMEL 555B potentiostat/galvanostat was used to run electrolyses in potentiostatic mode, a Luggin capillary allowing safe control of the silver cathode potential vs. a SCE.

The electrolyses were carried out in HPLC grade acetonitrile (ACN), in 50% vol admixture with highly

*Table 1.* Reduction peak potentials of polycloro-methanes and –ethanes, on Ag in ACN and DMF from CV investigations at 100 mVs$^{-1}$ scanning rate

| Substrate | Supporting electrolyte | $E_{p1}$/V | $E_{p2}$/V | $E_{p3}$/V |
|---|---|---|---|---|
| Dichloromethane | 0.1 M TEABF$_4$ in ACN | −2.18 | – | – |
| Dichloromethane | 0.1 M TEAPF$_6$ in ACN | −2.43 | – | – |
| Dichloromethane | 0.1 M TEABF$_4$ in DMF | −2.12 | – | – |
| Trichloromethane | 0.1 M TEABF$_4$ in ACN | −1.41 | −1.99 | – |
| Trichloromethane | 0.1 M TEAPF$_6$ in ACN | −1.68 | −2.13 | – |
| Trichloromethane | 0.1 M TEABF$_4$ in DMF | −1.57 | −1.9 | – |
| Tetrachloromethane | 0.1 M TEABF$_4$ in ACN | −1.27 | −1.74 | −2.1 |
| Tetrachloromethane | 0.1 M TEAPF$_6$ in ACN | −1.22 | −1.51 | −2.11 |
| 1,2-Dichloroethane | 0.1 M TEABF$_4$ in ACN | −2.45 | – | – |
| 1,2-Dichloroethane | 0.1 M TEAPF$_6$ in ACN | −2.43 | – | – |
| 1,1,1-Trichloroethane | 0.1 M TEABF$_4$ in ACN | −1.5 | −2.15 | – |
| 1,1,1-Trichloroethane | 0.1 M TEAPF$_6$ in ACN | −1.74 | −2.02 | – |
| 1,1,2-Trichloroethane | 0.1 M TEABF$_4$ in ACN | −1.6 | – | – |
| 1,1,1,2-Tetrachloroethane | 0.1 M TEABF$_4$ in ACN | −1.1 | −1.48 | −1.8 |
| 1,1,1,2-Tetrachloroethane | 0.1 M TEAPF$_6$ in ACN | −1.52 | −1.66 | −1.83 |
| 1,1,2,2-Tetrachloroethane | 0.1 M TEABF$_4$ in ACN | −1.3 | −1.82 | – |
| 1,1,2,2-Tetrachloroethane | 0.1 M TEAPF$_6$ in ACN | −1.22 | −1.83 | – |

*Table 2.* Synopsis of preparative electrolyses for the electroreduction of trichloro- and dichloro-methane on Ag cathodes

| No. | Substrate | Cathodic compartment | Anodic compartment | Working potential/V | Products | Comments |
|---|---|---|---|---|---|---|
| 1 | trichloromethane 0.01 M | Ag foil TEABF$_4$ 0.1 M in 1:1 ACN/water | Pt foil 1 M Sodium sulphate in H$_2$O | −1.26 | methane | $c_f^a = 0.002$ M, $Q^b = 215$, $F$/mol$^c = 1.5$ |
| 2 | trichloromethane 0.01 M | Ag foil TEABF$_4$ 0.1 M in ACN | 1 M Sodium sulphate Pt foil | −1.4 | methane chloromethane polychloroethane | $c_f = 0.009$, $Q = 224$, $F$/mol $= 0.2$ |
| 3 | trichloromethane 0.05 M | Ag foil TEABF$_4$ 0.1 M in ACN | 1 M Sodium sulphate Pt foil | −1.4 | methane chloromethane polychloroethane | $c_f = 0.026$, $Q = 1100$, $F$/mol $= 1.4$ |
| 4 | trichloromethane 0.1 M | Ag foil TEABF$_4$ 0.1 M in ACN + 2% water | 1 M Sodium sulphate Pt foil | −1.2 | methane chloromethane polychloroethane | $c_f = 0.031$, $Q = 457$, $F$/mol $= 0.5$ |
| 5 | trichloromethane 0.1 M | Ag foil TEABF$_4$ 0.1 M in DMF | 1 M Sodium sulphate Pt foil | −1.4 | methane dichloromethane | $c_f = 0.069$, $Q = 541$, $F$/mol $= 1$ |
| 6 | dichloromethane 0.1 M | Ag foil TEABF$_4$ 0.1 M in DMF | 1 M Sodium sulphate Pt foil | −2.2 | methane | $c_f = 0.08$, $Q = 2100$, $F$/mol $= 5$ |

[a] Final substrate concentration, $c_f$/M.
[b] Total quantity of charge, $Q$/C.
[c] Moles of electrons per mol of substance, $F$/mol.

deionized water (MilliQ® Millipore System), or in dimethylformamide (DMF) with 0.1 M TEABF$_4$ as supporting electrolyte. The progress of the electrolytic process was monitored by gas chromatography using a HP 5890 gas chromatograph, equipped with a capillary column (HP-5; crosslinked 5% PH ME siloxane, 30 m) a FID detector connected with a computer. The signal analysis was carried out using the software provided by Azur® (DATALYS – San Martin D'Heres). The products were identified by comparison with commercial standards (Aldrich) either in gas chromatographic analysis or in CV. The analysis of volatile reaction products was also performed by mass spectroscopy (PPT Residual Gas Analyzer).

## 3. Results and discussion

In a recent investigation [27] we reported the formation of methane during the electroreduction of trichloromethane on Ag cathodes in 1:1 ACN/water mixture under controlled potential conditions at −1.26 V vs. SCE (see Table 2, No. 1), which roughly corresponds to the CV peak potential in similar conditions. At the same time no appreciable formation of dichloromethane was detected. Although the working potential was not sufficiently negative to produce the concomitant evolution of hydrogen, we decided to repeat the experiment in pure ACN to avoid any possible contribution of indirect reduction by atomic or molecular hydrogen. Run 2 and 3 were then performed at −1.4 V (about the peak value

in CV) at two different initial concentrations of trichloromethane (namely, 0.01 and 0.05 M). The low concentration of the substrate was chosen in order to limit the resulting current density and avoid oligomerization products, which readily form [27] at more negative potentials ($E_w \geq -2$ V). In both cases methane was observed, together with the transient formation of chloromethane and traces of polychloroethanes. In particular in run 3 it was the main product, thus confirming the preliminary results obtained in mixed ACN/water medium. Unlike run 1, however, during the electrolyses the catholyte became progressively turbid, until a precipitate separated, which was later recognized as a mixture of AgCl and NaCl. While the presence of sodium chloride, poorly soluble in ACN, was understood as combination between the chloride released by the reactant(s) and the sodium ion transferring through the cationic membrane from the anolyte; the presence of silver chloride required further investigation. At the same time, the meaningful determination of dichloromethane by gas-chromatography was prevented by the large, almost overlapping, peak of ACN which could not be totally prevented by the cold trap. These results were confirmed in run 4, which was performed in the presence of 0.1 M (initial concentration) trichloromethane and of water (2% vol) to avoid NaCl precipitation. Interestingly, the presence of water also greatly reduced the formation of AgCl. To be able to check for the absence of dichloromethane, the solvent was changed from ACN to DMF whose retention time in the selected gas-chromatographic conditions is much higher than that of the majority of the possible reduction products. In run 5 trichloromethane was then electrolyzed at

−1.4 V and the main product was methane with a small and almost constant amount of dichloromethane. Finally, run 6 was performed on dichloromethane 0.1 M in DMF to demonstrate that $CH_2Cl_2$ is effectively reducible in the chosen conditions. However, in this case the applied potential had to be increased to −2.2 V to obtain an appreciable current. Again methane was obtained, together with traces of polychloroethanes. Due to the lower conversion degree of the substrates and to its higher solubility in DMF, no sodium chloride precipitation was observed in run 5 and 6.

In summary, it is confirmed that trichloromethane can be electrolytically reduced to methane on silver cathodes in 1:1 ACN/water, ACN and DMF at potentials at which dichloromethane, if formed, could not undergo appreciable reaction. At the same time silver seems to corrode, especially in the absence of added water.

To further investigate this last aspect, CV experiments were performed on electrodeposited silver electrodes in ACN, using different supporting electrolytes.

Recently Dubova et al. [29] have shown that silver can be oxidized in ACN in the −0.5/0 V potential range to give both oxides and dissolution products. They have also demonstrated that the dissolution of silver is enhanced by the use of $KPF_6$ as supporting electrolyte, while it is depressed and shifted to more positive potentials by the addition of water, which favours the passivation of the metal. Therefore in addition to $TEABF_4$, the supporting electrolyte used in the electrolyses, we selected $TEAPF_6$, $KBF_6$, and $KClO_4$ as background salts. Figures 1a and b show the background current recorded on Ag in ACN with the four different electrolytes, in the −0.2 to −1.8 V potential range. From comparison of the 4 curves (see enlargment in Figure 1b), it is evident that the tetraethylammonium cations play a key role in preserving silver from dissolution at $E > −0.4$ V, as observed in $KPF_6$. Moreover, the use of $TEABF_4$ or $TEAPF_6$ greatly reduces the background current in the −0.5/−1.5 V range, also with respect to $KClO_4$. This effect is in line with previous capacitance determinations [30] performed on mono- and polycrystalline silver to investigate the adsorption behaviour of halide ions in ACN, as preliminary characterization of the electrode-solution interphase prior to the addition of organic halides.

When dichloro- or trichloro-methane are added (see Figure 2), it is evident that the two substrates show one and two main reduction peaks, respectively, in the −0.5/−2.8 V interval, as reported in [27], and that in dichloromethane a redox couple is also present between −0.5 and −0.8 V, which closely resembles that recorded in $KPF_6$ at more positive potentials. To better elucidate this behaviour, the CVs presented in Figures 3 and 4 were recorded in ACN + $TEABF_4$, using progressively larger potential intervals, while keeping the starting value fixed at −0.2 V. There is no significant change in the characteristics until the conditions of direct reduction of the organic chloride (namely, $\approx$−1.6 V for $CH_2Cl_2$ and $\approx$−0.9 V for $CHCl_3$) are reached. However,
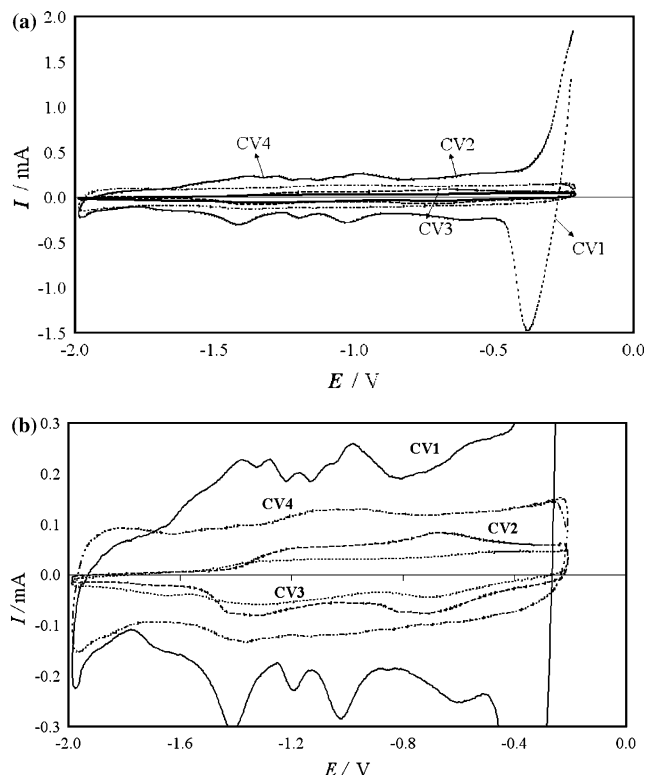


Fig. 1. (a) Cyclic voltammetry on Ag in ACN containing different supporting electrolytes (0.1 M) and in the potential range between −0.2 V and −2.0 V at 1000 mV s$^{-1}$ : CV1(KPF$_6$); CV2 (TEABF$_4$); CV3 (TEAPF$_6$); CV4 (KClO$_4$). (b) Enlargment of Figure 1a; CV1(KPF$_6$); CV2 (TEABF$_4$); CV3 (TEAPF$_6$); CV4 (KClO$_4$).
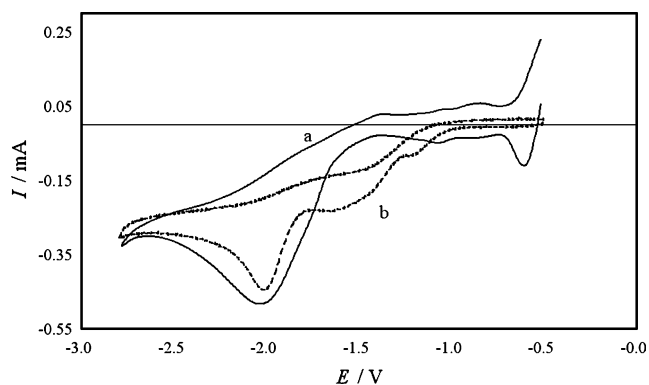


Fig. 2. Cyclic voltammetry on Ag in ACN 0.1 M TEABF$_4$ at 100 mV/s, (a) CH$_2$Cl$_2$, (b) CHCl$_3$.

when the threshold is overcome the quasi-reversible peak becomes more evident the more negative the end point of the forward scan. Moreover, in the presence of $CH_2Cl_2$ this redox pattern is located at far more negative values than in the presence of $CHCl_3$. While it is evident that the dissolution of silver is enhanced by the chloride ions eventually formed during the reduction of the substrates, the different role played by dichloro- and trichloro-methane has still to be fully understood. Although further work is required (and is in progress in this laboratory) to elucidate the reaction pathways,
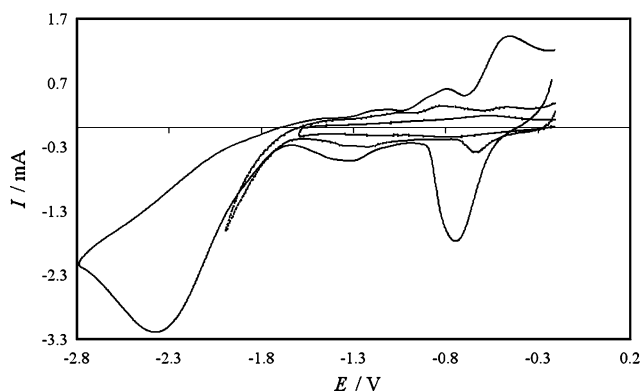
*Fig. 3.* Cyclic voltammetry on Ag in ACN 0.1 M TEABF$_4$ in presence of CH$_2$Cl$_2$ 0.5 M, carried out from −0.2 V to different final potential: −1.4, −1.6, −1.8, −2.0 and −2.8 V.
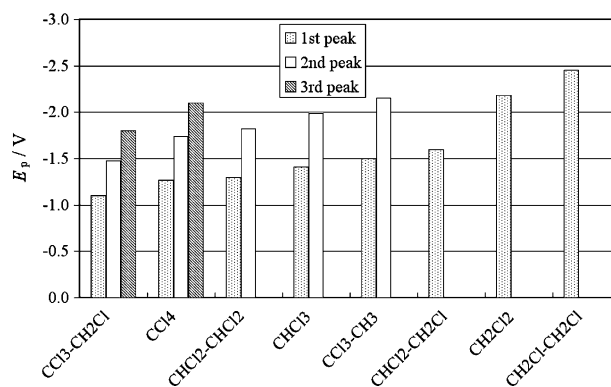


*Fig. 5.* CV peak potentials, $E_p$/V, of polychloro-methanes and -ethanes determined on Ag in ACN 0.1 M TEABF$_4$ at 100 mV s$^{-1}$.

some preliminary remarks can be made by comparison between the CV characteristics of a selection of poly-chloro-methanes and ethanes. Table 1 summarises the reduction peak potentials observed on Ag in ACN + TEABF$_4$ or TEAFP$_6$ as supporting electrolytes, and in two instances in DMF + TEABF$_4$, at 100 mV s$^{-1}$. The reduction sequence CCl$_4$ ≈ CHCl$_3$CH$_2$Cl ≈ CHCl$_2$CHCl$_2$ > CHCl$_3$ > CCl$_3$CH$_3$ > CHCl$_2$CH$_2$Cl > > CH$_2$Cl$_2$ > CH$_2$ClCH$_2$Cl is in agreement with the reactivity of the C centres, which increases with the number of Cl atoms and is finely tuned by the Cl multiplicity on the same C atom. It is intersting to note that, unlike glassy carbon [17] for which the successive reductive expulsion of chloride ions has been shown to follow a 2-electron pathway with a slow first electron transfer, there is no exact match between the peak values of the same series of substrates, as shown in Figure 5. For example, the second peak of carbon tetrachloride does not match with the first peak of trichloromethane, and the sole peak of dichlorome-thane is slightly more negative than the second peak of trichloromethane, which, in turn, is different from the third peak of tetrachloromethane. Moreover, if we plot the potentials of the first peak as a function of the energies [17] required to break the first C–Cl bond,
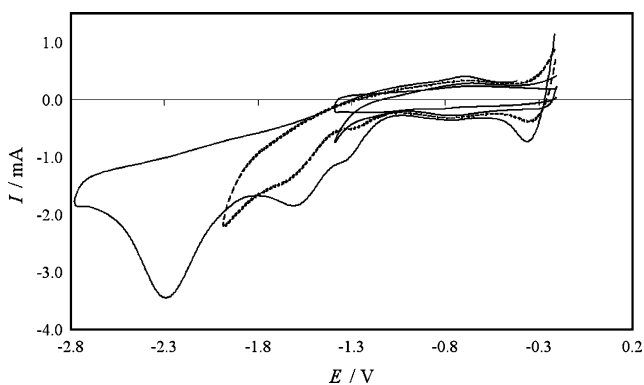
as shown in Figure 6, we can immediately appreciate how straightforward is the correlation between the two quantities in the case of glassy carbon, which confirms its inertness toward the reduction process. On the contrary, the data collected on silver do not align together, to highlight the role of the metal surface in the reaction mechanism. The regular sequence: RC–Cl + e$^-$ → [RC·Cl$^-$]; [RC·Cl$^-$] ⇌ RC· + Cl$^-$; RC· + e$^-$ → RC$^-$; RC$^-$ + HA → RCH + A$^-$; valid for glassy carbon, seems to be partially altered by a Ag-substrate complex which contributes to the observed "shortcuts" to methane.

## 4. Conclusions

The electroreduction of trichloro- and dichloro-methane on silver in ACN yields methane as main product, together with traces of transient polychloroethanes. The energy consumption of the process is surprisingly low, since the reduction potentials are at least 500 mV lower than that needed on glassy carbon and other more popular metals. The reaction mechanism seems to involve partially soluble silver species, which readily form in the presence of released chloride ions and



*Fig. 4.* Cyclic voltammetry on Ag in ACN 0.1 M TEABF$_4$ in presence of CHCl$_3$ 0.5 M, carried out from −0.2 V to different potential: −1.4, −1.6, −1.8, −2.0 and −2.8 V.
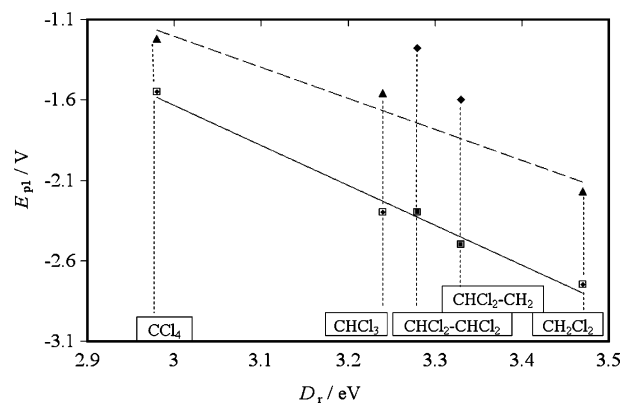


*Fig. 6.* CV potentials of the first peak, $E_{p1}$/V, as a function of the C–Cl bond energies, $D_r$/eV. Full and empty squares: data on glassy carbon from ref. 16; Full triangles and diamonds: data on Ag, this work. The different compounds are labeled directly on the plot.

possibly of some reaction intermediates, as evidenced by the corrosion of silver detected both during some electrolyses and during the CV anodic scans, especially when extended toward the positive region. The presence of a small amount of water is beneficial since it improves the stability of silver, without significantly affecting the reaction pathway.

## Acknowledgments

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