



HAL
open science

The one-electron cleavage and reductive homo-coupling of alkyl bromides at silver-palladium cathodes

Philippe Poizot, Lydia Laffont, Jacques Simonet

► To cite this version:

Philippe Poizot, Lydia Laffont, Jacques Simonet. The one-electron cleavage and reductive homo-coupling of alkyl bromides at silver-palladium cathodes. *Journal of electroanalytical chemistry and interfacial electrochemistry*, 2008, 624, pp.52. hal-00346060

HAL Id: hal-00346060

<https://hal.science/hal-00346060>

Submitted on 2 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID : 2330

To link to this article :

URL : <http://dx.doi.org/10.1016/j.jelechem.2008.07.021>

To cite this version : Poizot, Philippe and Laffont-Dantras, Lydia and Simonet, Jacques (2008) [*The one-electron cleavage and reductive homo-coupling of alkyl bromides at silver-palladium cathodes.*](#) Journal of Electroanalytical Chemistry, vol. 624 (n° 1 - 2). pp. 52-58. ISSN 0022-0728

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr

The one-electron cleavage and reductive homo-coupling of alkyl bromides at silver–palladium cathodes

Philippe Poizot^a, Lydia Laffont-Dantras^a, Jacques Simonet^{b,*}

^aLaboratoire de Réactivité et Chimie des Solides, UMR 6007, Université de Picardie Jules Verne, 80039 Amiens Cedex, France

^bLaboratoire MaSCE, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

A B S T R A C T

We have previously demonstrated that “palladized” silver electrodes obtained by displacement reaction, thanks to an immersion in acidic Pd^{II}-based solutions, display quite interesting capabilities in the cleavage of alkyl halides. Such chemically modified surfaces by an Ag–Pd alloy lead to large potential shifts compared to the use of glassy carbon or smooth silver cathodes as well. The present article now gives preliminary results focused on the particular electrochemical activity of primary and secondary alkyl bromides. Experimental data show that such electrodes may behave quite differently from smooth silver, especially, when acetonitrile and dimethylformamide are used as solvent. While smooth silver cathodes generally entail two-electron cleavage reactions, palladized silver interfaces always yield catalytic cleavages of C–Br bonds according to single one-electron reactions. The homo-coupling processes may generally occur with a rather high efficiency.

Keywords:

Palladium–silver alloy
Silver electrodes
Cleavage reactions
Carbon–bromine bonds

1. Introduction

The use of new metallic electrodes in the field of organic electrochemistry remains nowadays an important task to achieve selective reactions [1]. Since the use of mercury and lead is banned from laboratories for environmental reasons [2,3], electrochemists generally choose as cathode material different carbon surfaces such as glassy carbon, which today seems to provide a sort of universal solid working electrode [4]. However, the reactivity of carbons toward ion insertion (e.g. lamellar compounds like graphite) or/and their tendency to graft some electro-generated species like free radicals, are often mentioned [5,6]. Alternatively, at least within conducting media presenting a certain level of moisture [7], platinum could be used although both cost and weak hydrogen over-voltage make its use beyond -1.5 V vs. Saturated Calomel Electrode (SCE) difficult [8]. The use of other metallic cathodes like copper [7], palladium [8], tin [9], nickel [10] or stainless steel [11] was also put forward during the last decade. However, some specific interfacial reactions, which constitute a major drawback, can occur. Lastly, a huge development of chemically modified interfaces, in particular solid-conducting surfaces, has been performed since the 1980s. For instance, carbons or metals like gold [14] or silicon [15] have been chemically modified either by grafting of groups or with functionalized conductive polymers. Such modified surfaces may have found some interest in interfacial synthesis (with electron transfer).

* Corresponding author. Tel.: +33 23236292; fax: +33 23236732.
E-mail address: jacques.simonet@univ-rennes1.fr (J. Simonet).

Very recently, the interest in using smooth silver [16], smooth palladium and palladized surfaces [17,18] was developed to improve the ease of carbon–halogen bond scission. In the same way, palladium associated with other transition metals in well-defined alloys has been successfully put forward specifically with copper and silver [19–21]. In particular, the Ag–Pd interface was successfully used to strongly speed up scission of carbon–iodine bonds [21]. In the case of carbon–heteroatom bonds, known to be more difficult to split under electron transfer, alkyl bromides are certainly interesting to study especially with the aim to improve the ease of the overall scission (destruction of wastes in industry) as well as form free radical transients useful in radical chemistry (addition to organic radicalophiles and synthesis of homo-dimers). The addition of such radicals may also present some interest in the chemical transformation of surfaces too.

Concerning the σ bond of alkyl bromides, it has been reported that their reductive scission requires high activation energy at glassy carbon surfaces [22–27]. Therefore, the cleavage occurs in most cases under a dissociative electron transfer at potential lower than -2 V vs. SCE. In order to efficiently speed up the cleavage of such carbon–halogen bonds at much higher potentials, palladized smooth silver cathodes have been tested toward the electrochemical activity of alkyl bromides. Here are gathered the first results on the cleavage of a large series of primary, secondary and tertiary alkyl bromides RBr. Reactions are compared to those currently observed at glassy carbon electrodes and at smooth silver using several dipolar solvents like acetonitrile (AN), dimethylformamide (DMF), and propylene carbonate (PC). The advantages of these Ag–Pd surfaces in terms of catalytic character and chemical stability

are developed for the first time. The first results of this investigation using palladized silver substrates are also compared to the recent data obtained on smooth silver electrodes mainly in AN [28–33]. Finally, the aim of this work is also to stress the conditions of obtaining one-electron cleavages with C–Br bonds and to check the formation of homo-dimers in high yields.

2. Experimental

2.1. Chemical doping of smooth silver by palladium and characterization

The general approach to modify silver at the nanometric scale using palladium has been previously detailed [8]. Briefly, the procedure is based on the contact of metallic silver substrates with a fresh aqueous solution of palladium sulphate in sulphuric acid. More specifically, one gram of $\text{Pd}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (Alfa Aesar) dissolved in 100 mL of 0.1 N H_2SO_4 solution is put in the presence of silver. After a few tens of seconds, a shiny layer progressively covers the silver surface. The quasi-instantaneous deposition process onto the smooth silver surface is provoked by the displacement of silver by palladium ($E^\circ(\text{Pd}^{2+}/\text{Pd}) = 0.92 \text{ V/NHE}$ and $E^\circ(\text{Ag}^+/\text{Ag}) = 0.799 \text{ V/NHE}$) concomitantly with an unexpected alloying reaction leading to a specific Ag–Pd interface. Note that palladium nitrate and chloride could be used as well.

It also appeared of interest to test silver electrodes elaborated by *silverization* of solid surfaces. Such electrodes were obtained by galvanostatic deposits of silver from a solution of AgNO_3 (i.e. 10 g L^{-1} in a 0.1 N HNO_3 solution). These deposits, preliminarily elaborated onto gold, nickel or platinum were achieved, thanks to fixed current electrolyses of 0.5 mA mm^{-2} for a passed charge ranging from 10^{-3} to $4 \times 10^{-3} \text{ C mm}^{-2}$ corresponding to average thickness of the order of 1–5 μm . Then, the formation of the Ag–Pd alloy layer was simply obtained by dipping the silvered metallic substrates into Pd^{2+} -based acidic solutions as previously explained. It is expected that the thickness of the layer is not deeply altered by the displacement process.

Characterization of the as-produced layers was carried out by a combined SEM, HRTEM, EDS study. Morphology of the layer formed onto the electrode was first investigated by SEM using a FEI QUANTA F200P coupled with an Oxford Link ISIS instrument for Energy Dispersive Spectroscopy analysis (EDS). The TEM and HRTEM imaging were performed using a FEI TECNAI F20 S-TWIN, whereas the elemental composition was also determined by energy dispersive spectroscopy (EDS) at nanometer resolution. The layer thickness looks strongly dependent on the time of contact with the palladium solution, but cannot be precisely measured owing to the displacement reaction and the fact that silver is slowly attacked by acid. SEM characterizations of the new surface lead to assess that the average thickness of the layer (depending on the contact time) is generally of the order of 1 μm . Note that the layer is efficiently attached to silver and is not easily removed by sonication.

2.2. Electrochemical procedure, salts and solvents

The electrochemical instrumentation has been described in previous publications [17–18]. Typically, all potentials are given against SCE, whereas each electrode used in voltammetry had an apparent surface area of 0.78 mm^2 . The supporting salt concentration was fixed at 0.1 M using either tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) or tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆); these two salts being purchased from Aldrich. Used solvents were dimethylformamide, acetonitrile (quality for analyses) both purchased from SDS and propylene carbonate (qual-

ity for syntheses) purchased from Merck. Experiments performed with platinum and palladium electrodes as substrate did not require especially dry solutions since the explored potential ranges were not lower than -2 V vs. SCE . Finally, each electrochemical experiment was performed under inert atmosphere using dry argon.

Silver, glassy carbon, pure palladium, gold, nickel, and platinum were carefully polished with silicon carbide paper (Struer) or with Norton polishing paper (type O2 and O3). Before use, the electrodes were twice rinsed with water then alcohol and finally, acetone. Lastly, each electrode was dried with a hot air flow for about 30 s. Under such conditions, electrodes could be re-used leading to coherent data. In the present study, electrolysis products were found to be long-chain dimers often insoluble leading to their deposition onto the electrode surfaces. So, a rinsing step with acetone or ether could be necessary to renew the interface efficiency.

2.3. Coulometry and electrolyses

Coulometric measurements and electrolyses of alkyl bromides were carried out using three-electrode system cells with a total catholyte volume of about 5–10 mL. The anodic compartment was separated by a fritted glass of weak porosity. The experiments were completed on small substrate amounts (typically 0.1 mM). In order to avoid the disturbance resulting from the possible presence of silver oxide, which could depend on the history of solid substrate, a pre-electrolysis of the solution was systematically achieved prior to adding the RX compound to the cell.

Macroelectrolysis products (monomeric and dimeric forms from RBr) were analyzed by GC/MS after extraction by a large amount of ether. Analyses were made on the extracts after rinsing by water and drying on MgSO_4 .

3. Results and discussion

3.1. Primary alkyl bromides

Basically, it is known that almost all alkyl bromides give a two-electron irreversible step at glassy carbon electrodes at quite reducing potentials in DMF containing tetraalkylammonium salts (i.e. $E < -2.4 \text{ V vs. SCE}$) [34–38]. Under the same conditions, the use of smooth silver as a cathode induces significant potential shifts toward less cathodic potentials. However, two steps are typically observed (denoted (I) and (II)) with the specificity that the first one, located at a rather less negative potential (i.e. $E_{p/2} \sim -1.3 \text{ V}$), is usually small. The curve B in Fig. 1 shows this particular behaviour with 1-bromooctane in DMF/TBAPF₆. Additionally, it is worth noting that the results are quite similar in AN compared to DMF. As shown in Table 1 when using DMF/TBABF₄ as electrolyte, the sum of currents of peaks (I) and (II) is roughly equal to the current of the two-electron step usually obtained at glassy carbon. Peak (I) is apparently consistent with an activation process by silver involving a preliminary reaction between Ag and the alkyl bromide similar to what was previously described with RI [8] compounds, but the reaction is much slower. The existence of a reaction at silver could also be checked by SEM analysis (see Fig. 2 with 1-bromooctane). Electrochemical reduction in DMF of the modified silver layer at step (I) level gave crystal deposits identified as those of the dimer in C₁₆ (image b).

Generally speaking, secondary bromides exhibit similar results. This electrochemical behaviour, frequently met in DMF with primary and secondary alkyl bromides, strongly suggests that RBr compounds are reduced according to two very different processes at the silver interface: (i) a reduction step of RBr limited by the kinetic of a surface reaction and (ii) a reduction step at much more

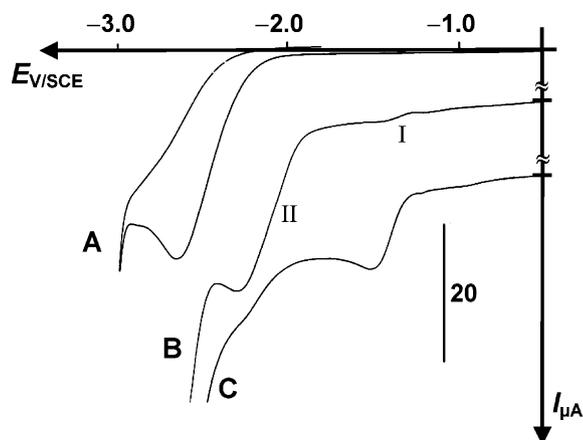


Fig. 1. Voltammograms obtained at different working electrodes using 1-bromooctane (concentration: 10 mM) in 0.1 M TBAPF₆/DMF. Apparent surface areas, $S = 0.78 \text{ mm}^2$. Scan rate: 100 mV s^{-1} : (A) Glassy carbon, (B) Smooth silver with the separation of two steps: I and II, (C) Ag-Pd electrode.

negative potential involving no specific effect of the metal surface. For the latter, the electron uptake is much less dependent on the cathode material, hence, carbon and silver electrodes give comparable results. This proposal is supported by two experimental facts observed with all primary and secondary alkyl bromides. Thus, the first step may exhibit an almost pure kinetic character (i.e. no variation of current upon the scan rate in voltammetry for $10 \leq v \leq 1 \text{ V s}^{-1}$). The variation of the limit current with changes in the RBr concentration is approximately zero beyond a threshold value. The second step progressively increases as the scan rate increases because it is under diffusion control. It is therefore quite possible to expect peak (II) to represent the RBr reduction at silver without any catalytic implication. Regarding the reduction of primary and secondary bromides at smooth silver in AN one notices also a complex reduction process involving again two different steps as shown in Fig. 3 (curves A1 and A2 with 1-bromooctane and 2-bromopentane, respectively).

If keeping in mind that the cathodic reduction of RBr compounds at solid interfaces (such as platinum or glassy carbon) is much less easy than the one observed with the corresponding iodides, the catalytic effect by silver depends on several parameters: the activation process specific to RBr compounds and its kinetics at the metal surface, the choice of the electrolyte anion, the adsorption of the electrolyte at silver as well as the treatment

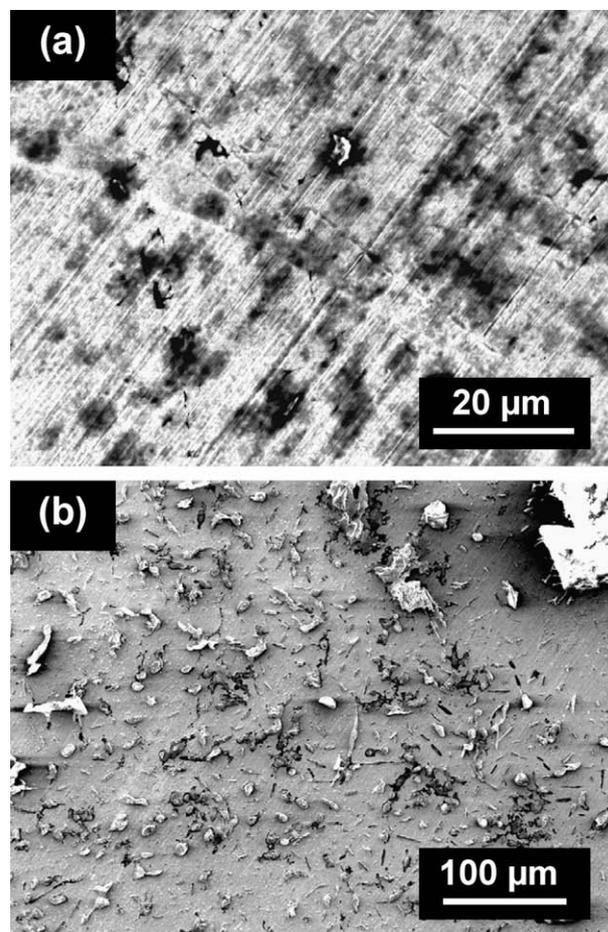


Fig. 2. SEM images showing the reaction of the pristine silver with pure 1-bromooctane in 0.1 M TBAPF₆/DMF: (a) After immersion during 30 min and a rinsing step with alcohol and then acetone. (b) The former surface (without rinsing and in contact with air) maintained at a potential of -2.0 V vs. SCE until nil current.

of the surface. There are some experimental evidences to support the reduction scheme below:

As a matter of fact, the reduction of RBr entails a two-electron process onto smooth silver at least in DMF (see Table 1). Rather negative potentials are necessary to get a reasonable current density (fixed $E_{\text{Red}} < -1.6 \text{ V}$) apparently because the activation by silver is too slow. Therefore, it appears difficult to discriminate

Table 1
Voltammetric data for some bromo-alkanes in 0.1 M TBAPF₄ in DMF

Entry	RBr (concentration)	Glassy carbon el.		Smooth silver el.		Palladized silver el.		Coulometric measurements ^b			
								Ag-Pd el. ^c		Smooth Ag el.	
		$E_{p/2}$ (V)	I_{lim} (μA)	$E_{p/2}$ (V)	Total reduction current (μA) ^a	$E_{p/2}$ (V) ^b	I_{lim} (μA)	E (V)	Q (F mol ⁻¹)	E (V)	Q (F mol ⁻¹)
1	2-Bromopropane (8.5 mM)	-2.25	25	-2.10	24	-1.30	11	-	-	-	-
2	1-Bromopentane (5 mM)	-2.36	15	-1.20	11	-1.24	8	-1.5	1.2	-1.5	1.8
3	2-Bromopentane (6 mM)	-2.25	17	-1.36	15	-1.32	8	-1.5	1.3	-1.6	2.2
4	1-Bromohexane (11 mM)	-2.42	27	-1.48	24	-1.48	13	-1.5	1.3	-	-
5	1-Bromoheptane (10 mM)	-2.56	25	-1.30	25	-1.33	10	-	-	-1.5	2.0
6	1-Bromooctane (10 mM)	-2.54	25	-2.14	25	-1.40	14	-1.5	1.4	-1.6	2.0
7	1-Bromodecane (9 mM)	-2.42	22	-1.36	22	-1.30	13	-1.5	1.2	-1.9	2.0
8	1-Bromododecane (6 mM)	-2.47	20	-1.80	17	-1.26	7	-	-	-1.8	1.9

Scan rate: 0.1 V s^{-1} .

Potentials are referred to aqueous SCE.

All electrodes used in voltammetry had an apparent area of 0.8 mm^2 .

^a Existence of two peaks neatly separated, the first one being, in most of the cases, the minor one.

^b Coulometries were completed until nil current.

^c Silver plates were activated in palladium sulfate during 2 min (see Section 2).

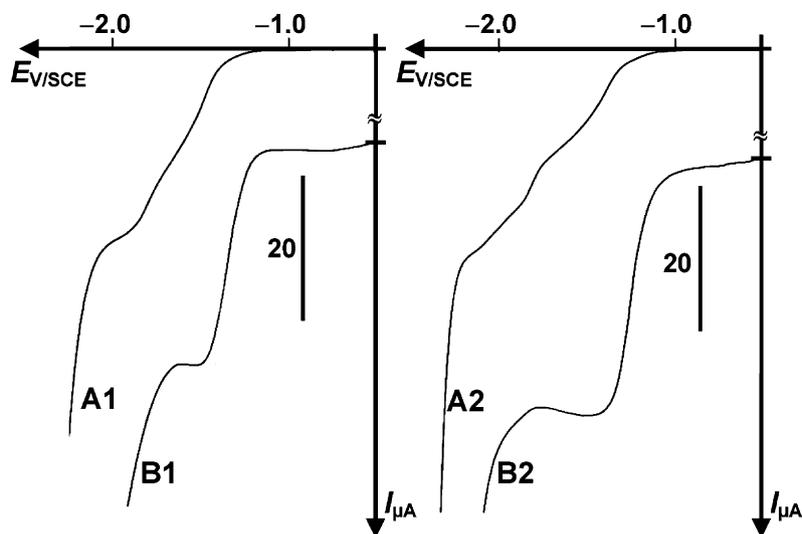


Fig. 3. Voltammetric responses of bromo-alkanes at smooth silver and palladized silver in 0.1 M TBABF₄/AN. Apparent surface areas, $S = 0.78 \text{ mm}^2$. Scan rate: 50 mV s^{-1} . (a) 1-Bromooctane (concentration: 9 mM) at A1, smooth silver and B1, Ag-Pd electrodes; (b) 2-bromopentane (concentration: 9.5 mM) at A2, smooth silver and B2, Ag-Pd electrodes.

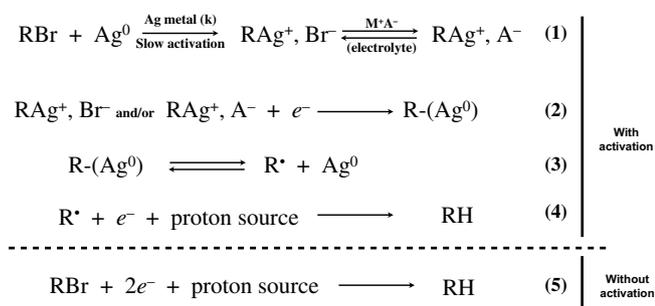
between the two processes suggested in Scheme 1. Thus, free alkyl radicals are readily reduced taking into account that the standard potentials for the transition R/R^- given by Lund [39] are generally higher than -1.4 V vs. SCE . Note that macro-electrolyses achieved at -1.6 V vs. SCE with silver cathodes are mainly oriented to the obtaining of two-electron processes with major formation of the corresponding alkane.

3.2. Reduction of alkyl bromides at Ag-Pd surfaces

If now the silver surface is efficiently palladized by means of the displacement reaction, dramatic changes could be observed in voltammetries: appearance of a large step replacing step (I) observed at smooth silver (see Table 1, Fig. 1, curve C in DMF and Fig. 3, curves B1, B2 in AN) with a concomitant potential shift to less cathodic potentials with a magnitude ranging from 0.1 to 0.2 V. Interestingly, the alkyl bromides reduction then occurred following a one-electron step as demonstrated by coulometry measurements achieved in DMF (see Table 1). It has been shown that the current of this main peak at Ag-Pd interface may keep a certain kinetic character since a weak variation of the peak current upon scan rate is observed (especially with $[\text{RBr}] > 10 \text{ mM}$ and $\nu > 100 \text{ mV s}^{-1}$). It is expected that the doping of the silver surface by palladium specifically leads to faster catalytic process than pure silver interface, but in many cases, observed kinetics remain quite close that of diffusion. Additionally, it could be underlined that long immersion times of the silver substrate in a Pd^{II}-based solution (efficient coverage of silver surface) led to the loss of the kinetic character of the

main one-electron step. The thickness of the modified layer would then contribute to influence the global rate of the surface catalysis.

We also achieved some preliminary experiments with galvanostatic deposits of silver onto gold, platinum, palladium, and nickel. Such silvered interfaces give systematically very reproducible results, which are somewhat better in terms of catalysis than conventional smooth silver. Similarly, the activation of silver deposits by palladization was achieved. For example, the activation of a silver layer on platinum or gold was achieved and these electrodes showed comparable results to the ones described above with massive Ag-Pd electrodes. In other words, very thin galvanostatic deposits of silver (average thickness $\sim 1 \mu\text{m}$) at many solid-conducting surfaces may transform solid-conducting interfaces into efficient and sometime cheap Ag-Pd supported electrodes. Many other solid substrates can also be considered.



Scheme 1.

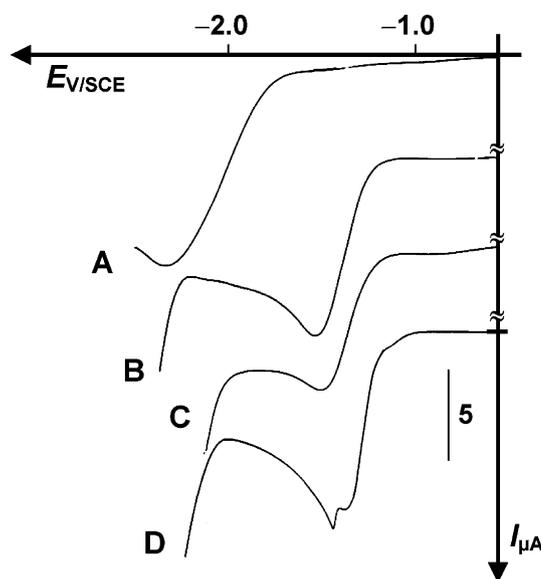


Fig. 4. Comparison, under very similar experimental conditions, between voltammetric responses of 1-iodobutane (concentration: 9 mM) and 1-bromobutane (concentration: 11 mM) in 0.1 M TBAPF₆/PC. Apparent surface areas, $S = 0.78 \text{ mm}^2$. Scan rate: 50 mV s^{-1} : (A) 1-iodobutane at a glassy carbon electrode, (B) 1-bromobutane at a smooth silver electrode, (C) Same than (B) using an Ag-Pd electrode, (D) 1-iodobutane at a smooth silver electrode.

Lastly, let us stress that the reactivity of free radicals on solid surfaces is now considered as quite general and effective especially on transition metals and carbons [6]. Using the same experimental conditions as those linked to Fig. 1 (curves C, case of 1-bromooctane), palladized silver surfaces clearly exhibit a second step equal in current to the first one. In most cases (for the whole series of RBr), the threshold potential of these peaks ranges between -1.5 and -1.8 V vs. SCE. It is likely that these second steps correspond to the reduction of free alkyl radicals: the reduction can probably be disturbed by the specific chemisorption of these radicals onto the Ag-Pd surface, which may lead to a slowing down of the second electron exchange. Anyhow, the use of Ag-Pd interface would enable to efficiently separate the first step involving the formation of the free alkyl radical from the second one corresponding to its cathodic reduction. This electrochemical behaviour makes the use of pure silver electrodes very interesting (see coulometric data in Table 1 with Ag and Ag-Pd working electrodes). Addition-

Table 2
Macro-electrolyses performed with a U-shaped cell with two compartments at Ag-Pd electrodes

Substrate	Solvent	R(-H)%	R(H)%	R-R%	n ($F \text{ mol}^{-1}$)
1-Bromoheptane	DMF	–	–	>99	1.05
1-Bromooctane	DMF	–	–	>99	1.1
1-Bromodecane	DMF	5.9	4.4	90.7	1.1
1-Bromododecane	DMF	55.3	27.7	17.1	1.2
1-Bromododecane	PC	16.6	4.8	78.6	1.1
1-Bromotetradecane	DMF	68	28	3	1.3
1-Bromooctadecane	DMF	39.4	58.9	2.5	1.7
12-Bromododecanoic acid	DMF	–	–	>99	1.1

Separator: fritted glass. Working electrode surface area about 3.5 cm^2 . Solvents: DMF or PC containing 0.1 M TBABF_4 . Applied potential: $E_{\text{Red}} = -1.3 \text{ V}$ vs. SCE.

ally, it is worth noting that separation of the two steps is quite unusual for alkyl halides: it was first mentioned with *tert*-butyl iodide and bromide in non-aqueous media by Savéant [22,25]. Previous data on the use of pure palladium showed that primary alkyl iodides were similarly reduced stepwise [10].

3.3. Use of propylene carbonate as solvent

Surprisingly, the use of propylene carbonate containing tetraalkylammonium salts enables to obtain with smooth silver electrodes very similar results to those observed at Ag-Pd electrodes with DMF and AN. Such results are shown with butylbromide in Fig. 4, curve B. In general, it was found with all the RBr studied that electrochemical responses at silver and Ag-Pd electrodes are strictly identical when using PC as solvent. It can be suggested that the high dielectric constant of PC ($\epsilon_r = 65.1$) activates the dissociation of the C-Br σ bond and speeds up the reaction with silver. It is therefore remarkable that RBr in PC exhibit a very close threshold potential to those of parent iodides in any solvent. This point is clearly evidenced in Fig. 4 where curve B (RBr) is quite similar to curve D (RI). This reinforced the proposal of a transient with RBr of the form: $\text{R-Ag}^+, \text{A}^-$ (Scheme 1, reaction 2) in which the electrolyte anion A^- plays the major role. Unfortunately, macro-electrolyses achieved with RBr in PC at smooth silver turned to be fast self-inhibited by the adsorption of free alkyl radicals on silver or coverage of the surface by insoluble R-R dimers.

3.4. Voltammetries of tertiary alkyl bromides

Tert-Butyl bromide exhibits almost identical data at smooth silver and Ag-Pd electrode whatever the solvent. The unique

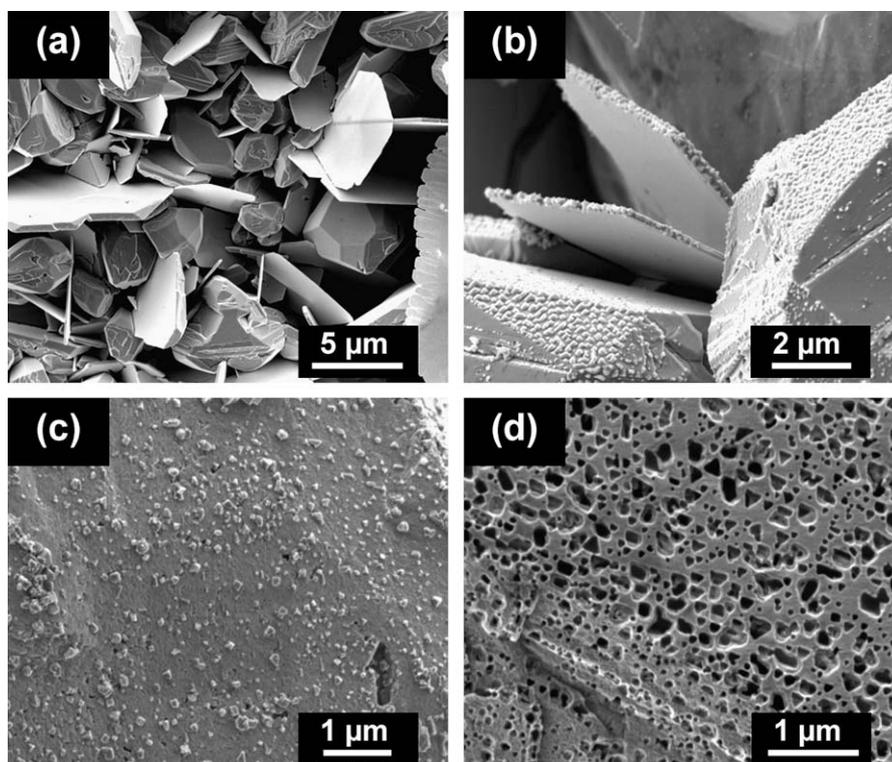
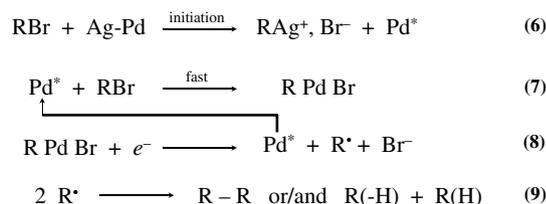


Fig. 5. SEM images of silver deposits by galvanostatic means onto smooth nickel (electricity amount: 0.3 C cm^{-2} , image A) and glassy carbon (electricity amount: 0.6 C cm^{-2} , image C), where the silver deposit was transformed into an Ag-Pd layer. These two kinds of surface were used as catalysts for the reductive coupling of RBr in different solvents containing 0.1 M TBABF_4 at -1.3 V vs. SCE. Reduction of 1-bromodecane in PC at Ni-Ag (image B) and 1-bromooctane in DMF at Ag-Pd supported by glassy carbon (image D). The electricity amounts were 0.6 C cm^{-2} in both experiments.

observed step located at $E_p = -1.24$ V at smooth silver and -1.22 V at Ag–Pd electrodes (both in 0.1 M TBABF₄/PC) is always one-electron. Within a similar potential range, 1-bromoadamantane does not exhibit any visible reduction step at smooth silver in DMF. On the contrary, at an Ag–Pd electrode, it is curious to see the clear presence of an adsorption type reduction peak at -1.10 V. This could be explained by the compact coverage of the silver surface by adamantly-Ag⁺ ions slowly formed, and their further reduction into adamantyl radicals. However, 1-bromoadamantane recently reported needs further investigations. Very weak currents with RBr enabled to repeat data on the homo-coupling of 1-iodoadamantyl recently reported at silver electrodes [32].

3.5. Reduction products at macro Ag–Pd cathodes

Macro-reductions of several primary alkyl bromides were achieved using large Ag–Pd electrodes (surface areas of about 3–4 cm²). In particular, results in DMF containing TBABF₄ do confirm the one-electron character of the global cathodic process. Most reductions achieved at quite moderate potentials ranging from -1.2 V to -1.4 V vs. SCE are somewhat similar to the data already reported [10–13] at palladium cathodes (case of primary alkyl iodides) and at copper–palladium electrodes (case of primary alkyl bromides) [20]. They underline the peculiar role of palladium in the cleavage of carbon–halogen bonds. As seen in Table 2, preliminary macro-electrolyses achieved with RBr in C₇, C₈, C₁₀, and C₁₂ are in agreement with the transient formation of a free radical R. able to dimerize with a good efficiency. Additionally, a minor disproportionation of radicals leads to corresponding alkane and alkene. With short alkyl chains, the dimeric forms are formed almost quantitatively. Quite successfully, reduction of 12-bromododecanoic acid gave homo-dimer (tetracosanedioic acid) in high yield. On the contrary, long alkyl chains RBr with R > C₁₂ displayed in the course of electrolyses a fast decay of currents after a few coulombs have passed through the cell. This behaviour can be explained by involving the precipitation of dimer crystals onto the surface, which could progressively poison its catalytic activity. This is displayed by the coverage of Ag crystals first electrodeposited onto nickel (Fig. 5, image B) in the course of the reduction of 1-bromodecane in PC with the formation of fine dimers crystals on the nanometric scale. Those crystals are surprisingly equally distributed onto the silver surface. Under these conditions, the capability of Ag to catalyze in PC the one-electron process is clearly evidenced. On the other hand, surfaces covered by an Ag–Pd layer are displayed in Fig. 5, image C. After electrolysis of a RBr compound, the surface state is dramatically changed (image D) with formation of channels through the surface with apparently loss of palladium. This fact strongly supports the chemical implication of palladium in the one-electron reduction of RBr. It is then believed that reaction of RBr with cathode material would lead to efficiently activate palladium Pd^{*} by dissociation of Ag–Pd (initiation reaction (6), followed by a chain (reactions (7) and (8)) according to Scheme 2.



Scheme 2.

4. Conclusions

The aim of the present work was to describe a new cathodic material capable to achieve, at moderate potentials, one-electron reduction processes with primary alkyl bromides taken here as target substrates. Thus, for the first time, a Ag–Pd alloy considered as modifier of smooth silver surfaces was used to reduce non-activated C–Br bonds. The energy gain is large, often larger than 1 V, when referred to the data obtained at quite common electrode material such as glassy carbon. These preliminary results are extremely encouraging because this new cathodic material combines two important properties: (i) the specific catalysis of silver toward primary and secondary alkyl bromides and (ii) the role of palladium metal in directing such cleavages to one-electron reduction whatever the solvent. Therefore, these preliminary results have pointed out that the use of such Ag–Pd electrodes could be considered as a source of free alkyl radicals as shown by means of voltammetric analysis, coulometries and fixed potential electrolyses. The reduction step was found to be generally diffusion-controlled and electrolyses could be achieved stepwise. The stability of the surface appeared to be good and macro-electrolyses (current densities up to 50 mA cm⁻²) allowed several runs by using the same electrode. However, until now, the intrinsic reason to obtain electro-catalysis at such electrodes is not totally understood, and the unexpected synergy [Ag + Pd] needs additional studies even if the presence of Pd nanoparticles close to the cathode surface should play a crucial. A general scope with other kinds of organic substrates, which also possessing a chemical bond capable to cleave under electron transfer, will be undertaken.

Acknowledgements

The authors are deeply thankful to Professor V. Jouikov, Université de Rennes1, for his efficient collaboration (GC/MS analysis), as well as Michèle Nelson for helpful assistance.

References

- [1] H. Lund, O. Hammerich (Eds.), Organic Electrochemistry, M.M. Dekker, New York, Basel, 2001.
- [2] O.R. Brown, in: A.K. Covington (Ed.), Phys. Chem. Org. Solvent Syst., Plenum Press, London, 1973, pp. 747–781.
- [3] J.R. Ochoa, A. De Deigo, J. Santa-Alalla, J. Appl. Electrochem. 23 (1993) 905.
- [4] C. Ji, D.G. Peters, J. Electroanal. Chem. 445 (1998) 147.
- [5] E. Coulon, J. Pinson, Langmuir 17 (2001) 7102.
- [6] J. Pinson, F. Podvorica, Chem. Soc. Rev. 34 (2005) 429.
- [7] C. Cougnon, J. Simonet, Platinum Met. Rev. 46 (2002) 94.
- [8] P. Poizot, L. Laffont-Dantras, J. Simonet, J. Electroanal. Chem., in press.
- [9] A.P. Tomilov, V.V. Turygin, A.V. Khudenko, Zhur. Prilad. Khim. 72 (1999) 329.
- [10] J. Simonet, J. Electroanal. Chem. 583 (2005) 34.
- [11] V. Svetlicic, P.B. Lawin, E. Kariv-Miller, J. Electroanal. Chem. 284 (1990) 185.
- [12] C. Laza, E. Dunach, Adv. Synth. Catal. 345 (2003) 580.
- [13] F. Kanoufi, C. Combellas, H. Hazimeh, J.-M. Mattalia, C. Marchi-Delapierre, M. Chanon, J. Phys. Org. Chem. 19 (2006) 847.
- [14] A. Ulman, Chem. Rev. 96 (1996) 1533.
- [15] J.M. Buriak, Chem. Rev. 102 (2002) 1271.
- [16] S.B. Rondinini, P.R. Mussini, F. Crippa, G. Sello, Electrochem. Commun. 2 (2000) 491.
- [17] J. Simonet, Electrochem. Commun. 7 (2005) 74.
- [18] J. Simonet, Electrochem. Commun. 7 (2005) 619.
- [19] J. Simonet, P. Poizot, L. Laffont, J. Electroanal. Chem. 591 (2006) 19.
- [20] P. Poizot, L. Laffont-Dantras, J. Simonet, Platinum Met. Rev. 52 (2008) 84.
- [21] P. Poizot, L. Laffont-Dantras, J. Simonet, Electrochem. Commun. 10 (2008) 864.
- [22] J.M. Savéant, J. Am. Chem. Soc. 109 (1987) 6788.
- [23] C. Andrieux, I. Gallardo, J.M. Savéant, K.B. Su, J. Am. Chem. Soc. 108 (1986) 638.
- [24] J.M. Savéant, J. Am. Chem. Soc. 114 (1992) 10595.
- [25] J. Grimshaw, J.R. Langan, G.A. Salmon, J. Chem. Soc. Faraday Trans. 90 (1994) 75.
- [26] C. Andrieux, I. Gallardo, J.M. Savéant, J. Am. Chem. Soc. 111 (1986) 1620.
- [27] J.M. Savéant, in: T.T. Tidwell (Ed.), Advances in Physical Organic Chemistry, vol. 35, Academic Press, New York, 2000, p. 177 (and references therein).
- [28] P.R. Mussini, S. Ardizzone, G. Gappelletti, M. Longhi, S. Rondinini, L.M. Doubova, J. Electroanal. Chem. 552 (2003) 213.

- [29] S. Ardizzone, G. Cappelletti, M. Lioudmila, P.R. Mussini, S.M. Passeri, S. Rondinini, *Electrochim. Acta* 48 (2003) 3789.
- [30] S. Rondinini, A. Vertova, *Electrochim. Acta* 49 (2005) 4035.
- [31] G. Fiori, S. Rondinini, G. Sello, C. Alberto, M. Cirja, L. Conti, *J. Appl. Chem.* 35 (2005) 363.
- [32] C.A. Paddon, F.A. Bhatti, T.J. Donohoe, R.G. Compton, *J. Phys. Org. Chem.* 20 (2007) 115.
- [33] A.A. Isse, A. De Giusti, A. Gennero, *Tetrahedron Lett.* 47 (2006) 7735.
- [34] M. Ferdurco, L. Coppex, J. Augustynski, *J. Phys. Chem.* 106 (2002) 2625.
- [35] C. Ji, D.G. Peters, *J. Electroanal. Chem.* 516 (2001) 36.
- [36] M.S. Mubarak, D.G. Peters, *J. Org. Chem.* 60 (1995) 681.
- [37] M.S. Mubarak, D.G. Peters, *J. Electrochem. Soc.* 143 (1996) 3833.
- [38] D.G. Peters, in: H. Lund, O. Hammerich (Eds.), *Organic Electrochemistry*, M.M. Dekker, New York, Basel, 2001, p. 341 (Chapter 8).
- [39] D. Occhialini, K. Daasberg, H. Lund, *Acta Chem. Scand.* 47 (1993) 1100.