



## Why a cathodic activation by silver interface? Facile reductive homocoupling of 1-iodoalkanes

Philippe Poizot<sup>a</sup>, Lydia Laffont-Dantras<sup>a</sup>, Jacques Simonet<sup>b,\*</sup>

<sup>a</sup>Laboratoire de Réactivité et de Chimie des Solides, UMR 6007, Université de Picardie Jules Verne, 80039 Amiens Cedex, France

<sup>b</sup>Laboratoire MaSCE, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

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### ABSTRACT

Smooth silver electrodes were used for the cathodic one-electron cleavage of primary alkyl iodides, RI. It has been shown that the catalytic process making possible the reduction of RI species is based on pre-reacting alkyl iodides with silver. It is then proposed that the transient species formed (via electron transfer?) at the silver interface could be written as  $R-Ag^+$ ,  $I^-$ . Arguments to support this proposal are presented. Such chemically modified interfaces showed a specific electrochemical behaviour in propylene carbonate (PC) in the presence of tetraalkylammonium ammonium salts. Experimental conditions for yielding specifically a one-electron step for RI species are discussed and the resulting homocoupling is evidenced.

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### 1. Introduction

Basically, it seems uncertain that totally inert electrodes exist at least within the cathodic range. For instance, mercury is well known to react with electrogenerated radicals from the cathodic reduction of benzyl and allylic halides [1] whereas palladium leads to oxidative insertions with many activated aryl-heteroatom bonds (at least at the stage of electrogenerated  $Pd^0$ ) [2]. This property was used in the cathodic activation of carbon–iodine bonds at smooth palladium electrodes [3]. Even glassy carbon was very recently shown to attract free radicals, and this method was applied to the building of new modified surfaces by organic functional groups [4,5]. Moreover, in superdry conditions, platinum may cathodically react with electrolytes to give iono-metallic structures possessing reducing properties [6]. Pure copper, free of oxide, can also react chemically with organic iodides and bromides [7] leading to specific cathodic reactions [8]. Last but not least, silver was reported to be an interesting cathodic material to activate the reduction of organic halides [9–11]. In particular, the reductive coupling [10,12] of benzyl and adamantyl halides has been recently achieved at silver electrodes with a large gain of energy if compared with the potential necessary to reduce those organic species using more conventional material like glassy carbon. However, benzyl halides and tertiary alkyl iodides and bromides were already reported to produce reduction in two steps and the transient

formation of corresponding free radicals (benzyl and *tert*-butyl) mentioned at regular cathode materials like glassy carbon [13,14].

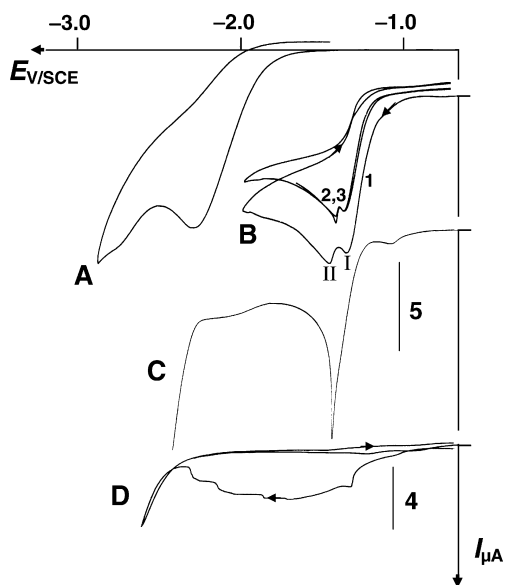
The aim of the present article is to report that silver reacts onto alkyl halides (in particular iodides) to form electroactive organo-silver intermediates, which lead to the strong activation observed with this metal. Beyond the interest presented by reduction processes achievable at quite moderate potentials (range:  $-1.2$  to  $-1.5$  V vs. SCE), experimental conditions necessary to get one-electron reductions were probed using a large palette of primary alkyl iodides RI (*R* varying from *n*-propyl to *n*-octadecyl). Several tetraalkylammonium salts and polar solvents were tested. We will first report the data obtained when using tetrabutylammonium salts (TBABF<sub>4</sub> and TBAPF<sub>6</sub>) dissolved in propylene carbonate (PC). Beyond displaying a large dielectric constant ( $\epsilon_r = 65.1$ ), this solvent possesses an environmental interest and is able to separate the two-electron transfers relative to RIs at silver cathodes. It is shown hereafter that these conditions enable reductive homo-couplings in high yield.

### 2. Results

The cathodic behaviour of primary alkyl iodides RI can be summarized in Fig. 1. While a two-electron step is observed in non-aqueous solvents (curve A, step  $<-2$  V at glassy carbon), the electron transfer is strongly favoured when smooth silver is used as cathode material. With DMF as solvent (curve C) a very sharp peak is observed, whereas two steps (curve B) are obtained with PC. By comparison with DMF, the reduction process is shifted to less negative potentials in PC (curve B). The main peak in PC and

\* Corresponding author. Tel.: +33 23236292; fax: +33 23236732.

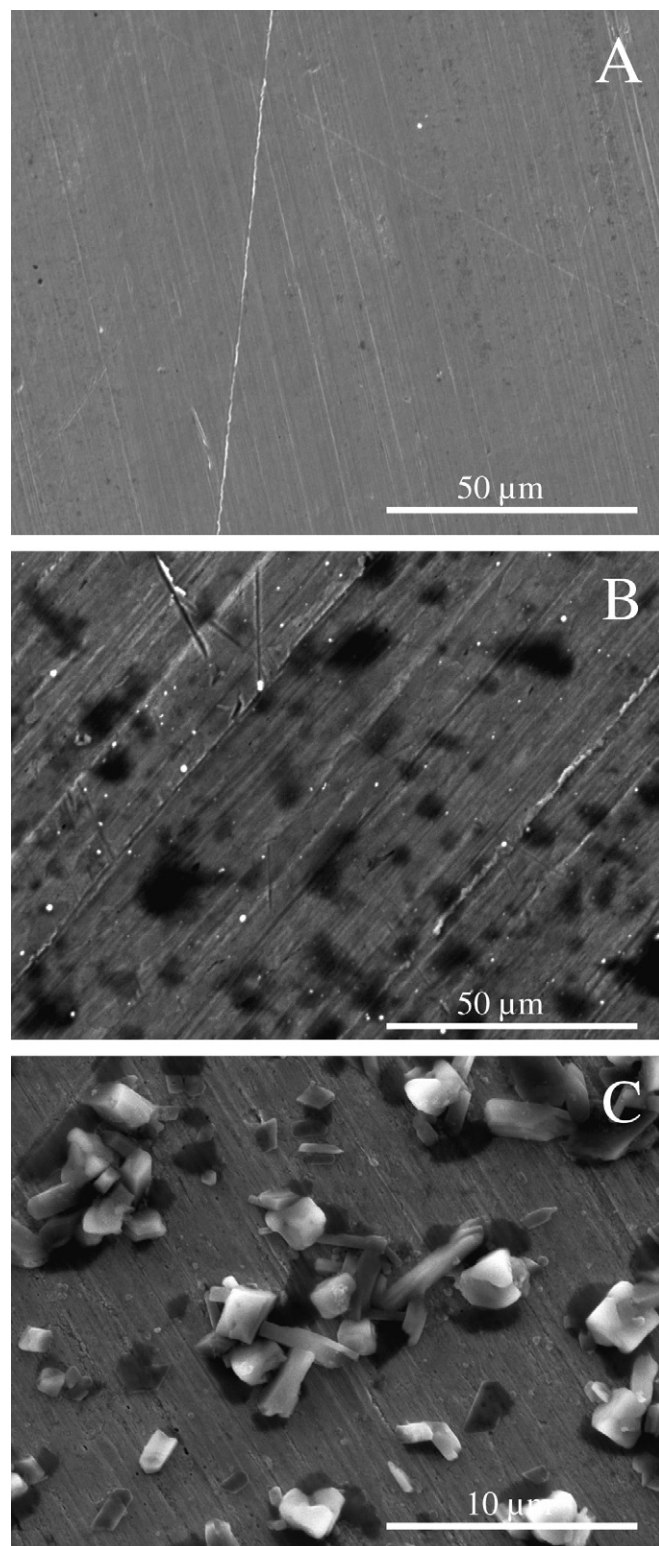
E-mail address: [jacques.simonet@univ-rennes1.fr](mailto:jacques.simonet@univ-rennes1.fr) (J. Simonet).



**Fig. 1.** Electrochemical behaviour of primary alkyl iodides at a micro cathode (surface area:  $0.8 \text{ mm}^2$ ) in  $0.1 \text{ M TBABF}_4$ . Reference electrode: aqueous saturated calomel electrode (SCE). Scan rate:  $50 \text{ mV s}^{-1}$ . (A) 1-Iodo-hexane (concentration:  $11 \text{ mM}$ ) at glassy carbon using propylene carbonate as solvent. (B) Response of the solution above at a smooth silver electrode. First scan and then, second and third (juxtaposed) scans. (C) 1-Iodooctane (concentration:  $5 \text{ mM}$ ) at a smooth silver electrode. Solvent: DMF. (D) Cathodic response of a silver electrode after a contact of a solution of 1-iodooctane ( $10\%$ ) in DMF during  $30 \text{ min}$ . Thorough rinsing in acetone (three times) and then in DMF before the scan. First and second scans.

the sharp peak in DMF are both diffusion controlled. If the silver electrode is dipped for a few minutes in a RI-based solution using DMF or PC as solvent, then thoroughly rinsed in acetone and DMF, it obviously remains some traces of (reacted) RI compound when cycled in a solution free of RI Fig. 1, curve D). Integration of the cathodic signal between  $-1 \text{ V}$  and  $-2.2 \text{ V}$  yields to relatively high amounts of electricity per surface units, and then suggests that an electroactive species was formed at the interface. The amount of electricity was found to depend on the contact time between Ag and RI. The electrochemical response of the silver electrode in the course of the second scan totally disappears. One may deduce that silver chemically reacts with RI, and the electroreduction of the intermediate is irreversible leading to the inactivation of the silver interface.

So, what is specifically the reaction at the silver surface? Elements can be found thanks to a SEM analysis of silver samples after contact with pure RI compounds (Fig. 2). It seems clear that the silver surface is corroded (image B) and covered with an organic compound (the EDS analysis revealed the presence of carbon beside silver). If such samples of modified surfaces are reduced until nil current at a fixed potential of  $-1.2 \text{ V}$  vs. SCE corresponding to the first step in PC (see Fig. 1, curve B), another huge change in the surface structure is then observed. Fig. 2, image C, displays the growth of crystals assigned to insoluble dimer onto the interface. Such experiments show that silver and RI are both involved in the interface structural change (reaction 1). Quite similarly, if a RI compound such as 1-iodooctane dissolved in PC is first mixed, then reacted in the presence of silver powder (particle size  $<250 \mu\text{m}$ ), and then the solution is electrolyzed using a glassy carbon plate at  $-1.2 \text{ V}$  (after addition of a TBA salt), a noticeable current is observed at a potential where RI is *not electroactive* at this material. Quite unexpectedly, silver is electrodeposited onto the carbon surface after total current completion obtained at less than  $1.2 \text{ F mol}^{-1}$  of RI. Moreover, in anodic voltammetry of RIs at silver, the specific oxidation steps of iodide can be observed. Conse-



**Fig. 2.** SEM images of silver plates before and after contact with RI compounds. (A) SEM image of a commercial (clean) silver surface. (B) SEM image of an Ag sample dipped into pure *n*-butyl iodide during  $30 \text{ min}$ . Rinsing three times with acetone and then pure DMF. (C) The samples according to (B) after reduction in  $\text{TBABF}_4/\text{DMF}$  at  $-1.2 \text{ V}$  vs. SCE.

quently, it is proposed that primary RIs lead to a kind of oxidative insertion of Ag (through a one-electron transfer?) into the C–I  $\sigma$  bond affording an organo-silver salt according to reaction 1. This assumption is finally equivalent to the well-established reaction

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