Electrocatalytical Reduction of Organic Halides on Silver: the Modulating Effects of the Molecular Structure, of the Surface State, and of the Supporting Electrolyte

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We have recently shown [1–9] the remarkable electrocatalytic properties of silver for organic halide reductions in acetonitrile, consisting in both a dramatic anticipation of the reduction potentials for all compounds tested and a tendency to promote monoelectronic intermolecular reactions (except for aryl halides such as halophenols [8,9]), with respect to more popular cathode materials such as the glassy carbon and the mercury electrode.
Considering the strong halide tendency to specifically adsorb onto silver surfaces even at surprisingly negative potentials[10,11] we have explained both effects on the basis of an "attenuated radical intermediate" R··· X··· Ag [6–8], accounting for both a lowering of the activation energy for the process and a "cage effect" promoting coupling reactions between coadsorbed species [2–8].
It is therefore evident that in order to throw further light on this electrocatalytic process it is necessary to carefully consider the interactions of the silver surface with the RX substrate, as a function of the *molecular structure*, of the *surface state* and of *other possibly coadsorbed species* (e.g. ions from the *supporting electrolyte*).
<u>*Effect of molecular structure*</u> An extensive, systematic program of cyclovoltammetric investigations will be presented, carried out on alkyl-, glycosyl-, benzyl- and aryl halides on polycrystalline silver electrodes of constant controlled surface in constant medium (acetonitrile with 0.1 M TeaP as the supporting electrolyte). Under these "normalising" conditions we can consider the relevant reduction potentials as determined by three main contributions, either independent or coupled:
(a) the intrinsic R···X reactivity (XR) which should mostly account for the reduction potential scale in the case of a nearly inert electrode, such as glassy carbon, i.e. in the absence of electrocatalytic effects;
(b) the metal···halogen interaction (XM), a contribution regularly increasing with the known sequence Cl, Br, I consistently with the adsorption studies mentioned above;
(c) the effect of the molecular structure on the R··· X··· Me intermediate (RM), a combination of many aspects such as the surface accessibility to the leaving group and the possible presence of adsorption auxiliary groups (i.e. groups having themselves specific affinity for the metal).
XM and RM effects can be evidenced by normalizing the reduction potentials on silver with respect to those on glassy carbon, which account for the XR term. The same scheme has been extended to mercury, also having specific affinity for halides, but a lower one than silver.
<u>*Effect of active surface.*</u> Working in the above constant medium with model molecule acetobromoglucose and polycrystalline electrodes of increasing active surface resulted in a regular positive shift of reduction potential [7], while surface filming *e.g.* by reaction products resulted in a corresponding remarkable negative shift (but it is possible to *in-situ* regenerate the free surface).
<u>*Effect of the supporting electrolyte*</u> Systematic experiments, carried out on constant surface electrodes and model molecule acetobromoglucose with a large set of alkylammonium salts, show that while on mercury and glassy carbon the main factor determining both reduction potentials and current intensities appeared to be the length of the cation alkyl chains, on silver this is true only in the case of inert, non-halide anions such as tetrafluoborate and perchlorate, while halide anions resulted both current and potential determining, an important clue on the interphase structure in the operating conditions.

ACKNOWLEDGMENTS. The financial support of the National Research Council (CNR) is gratefully acknowledged

[1] S. Rondinini, P. R. Mussini, V. Ferzetti, D. Monti, *Electrochim. Acta*, **36** 1095 (1991)
[2] M. Benedetto, G. Miglierini, P. R. Mussini, F. Pelizzoni, S. Rondinini and G. Sello, *Carbohyd. Letters*, **1**, 321 (1995)
[3] S. Rondinini, P.R. Mussini, G. Sello and E. Vismara, *J. Electrochem. Soc.*, **145**, 1108 (1998)
[4] M. Guerrini, P. Mussini, S. Rondinini, G. Torri, E. Vismara, *Chem. Comm.*, 1617 (1998).
[5] S. Rondinini, P. R. Mussini, G. Cantù, G. Sello, *Phys. Chem. Chem.Phys.*, **1** 2989 (1999).
[6] S. Rondinini, P. R. Mussini, F. Crippa, M. Petrone, G. Sello, *Coll. Czech. Chem. Comm.*, 881 (2000).
[7] S. B. Rondinini, P. R. Mussini, F. Crippa, G. Sello, *Electrochem. Comm.*, **2** 491 (2000).
[8] G. Fiori, P. R. Mussini, S. Rondinini, A. Vertova, *Annal. Chim.*, **91** 151 (2001)
[9] S. Rondinini, P. R. Mussini, M. Specchia, A. Vertova, *J. Electrochem. Soc.*, In press
[10] M. L. Foresti, M. Innocenti, F. Forni, R. Guidelli, *Langmuir*, **14** 7008 (1998)
[11] M. L. Foresti, M. Innocenti, H. Kobayashi, G.Pezzatini, R. Guidelli, *J. Chem. Soc., Far. Trans.*, **92** 3747 (1996)