



THE SOLVENT EFFECT IN THE ELECTROCHEMICAL REDUCTION OF ORGANIC BROMIDES ON SILVER

UNIVERSITÀ DEGLI STUDI
DI MILANO

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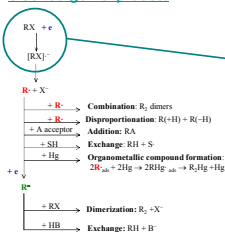
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1. A model process in organic electrocatalysis studies: the electrocatalytic reductive cleavage of the carbon-halogen bond

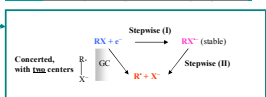
Recently, the **electrocatalytic reductive cleavage of the C-X bond in organic halides** has been chosen as the **most convenient model process in organic electrocatalysis** on account of its **fundamental and applicative interest** and of the circumstance that both **specific adsorption of halide anions onto metal electrodes** and **non-electrocatalytic reduction of organic halides** have been thoroughly investigated by authoritative research groups

The generalized, complete electroorganic process

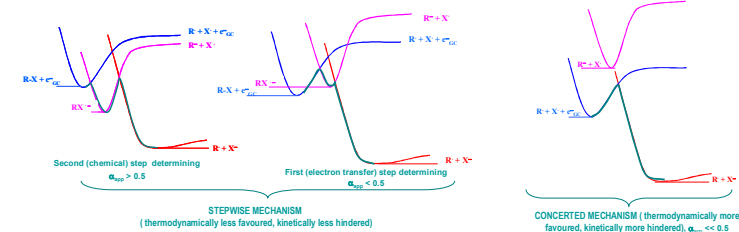


Focusing on the dissociative electron transfer (DET) step in non-catalytic conditions following the Marcus-Savéant theory

The two alternative pathways in the outer sphere (non-catalytic) case:



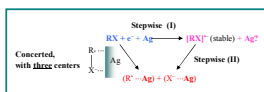
Representation in terms of Morse-curve diagrams (energy vs reaction coordinate)



2. Our extension to the inner sphere (catalytic) DET case on Ag cathodes

A.A. Isse, L. Falciola, P.R. Mussini, A. Gennaro, Chem. Comm. (2006), 344-346

A. Gennaro, A.A. Isse, L. Falciola, P.R. Mussini Silver electrocatalysis and dissociative electron transfer mechanisms (This Meeting, Poster S8-P-23)



- We are taking into account the **modification of the Morse curves** associated with the **presence of a "third body"** (the catalytic Ag surface)
- The presence of **catalytic effects** always appear associated with a **concerted reaction mechanism**; intrinsically stepwise mechanisms become (or tend to) concerted, intrinsically concerted mechanisms remain concerted

- The catalytic effects in the process are **modulated by many parameters...**

molecular structure of RX

- Intrinsic DET mechanism**
- nature of the halide leaving group X:
- π -network delocalization of the radical anion charge
- substituents with inductive effects
- adsorption auxiliary groups

- surface**
- nature (Ag vs other cathode materials)
- morphology
- state (re)action procedures, cfr. SERs

- medium**
- solvent**
- supporting electrolyte

...each of them requiring a specific, systematic investigation

4. A reliable standard for intersolvental normalization of the CV characteristics: the decamethylferrocene/decamethylferrocene couple

E. Castello, L. Falciola, P.R. Mussini, T. Mussini, M. Rossi, A comparative investigation of reference redox couples for intersolvental comparison of electrode potential scales (This Meeting, Poster S8-P-23)

Voltammetric studies in nonaqueous solvents are currently referred to the ferrocene/ferrocene redox couple, following the 1986 IUPAC document [1], assuming the above redox process to take place at an invariant potential in all solvents. However, the above assumption of intersolvental invariance of the Fc^+/Fc redox potential has been recently questioned [2, 3], suggesting that **only permethylated ferrocene derivatives** ("electron-reservoir sandwich complexes") **could be considered as unaffected by solvent coordination and therefore to be reliable intersolvental references**.

In this context, we have carried out along a careful protocol an exhaustive voltammetric reactivity study on ferrocene, either as such or functionalized on the cyclopentadienyl rings, together with other reversible redox couples, on both stationary and rotating electrodes, in a series of model organic solvents with constant supporting electrolyte.

Me_10Fc^+/Me_10Fc emerges as the best intersolvental reference because:

- it shows the **best electrochemical and chemical reversibility features**;
- it shows **no anomalies with respect to water**, the aqueous redox potential being aligned with the organic solvent ones (unlike the Fc^+/Fc case);
- its diffusion coefficients give the **best agreement with Stokes' law** (purely viscous motion with no specific interactions with the surrounding solvent);
- it shows **constant potential differences with its analogous permethylated cobaltocene** in the tested solvents, notwithstanding their remarkable distance.

These evidences point to the interactions between this molecule and the investigated solvents being very little if any.

An additional bonus is that the Me_10Fc redox potentials of this couple are very near the SCE ones; therefore the potentials normalized vs this couple fall in a more familiar range than those normalized vs Fc .

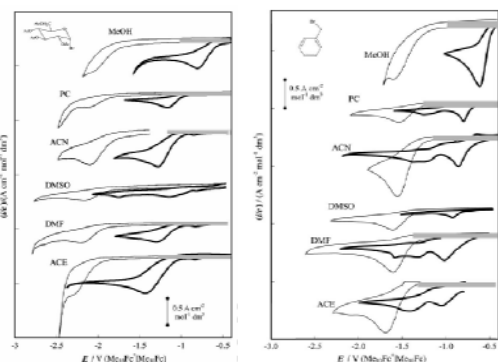
Accordingly, in the present study all potentials have been compared after normalization vs the decamethylferrocene ones in the same solvents

[1] G. Zlotnik, J. Kuta, Pure Appl. Chem. 56 (1984) 461.

[2] J. Ruiz, D. Astruc, Comptes Rendus de l'Académie des Sciences Series IB Mechanics Physics Chemistry Astronomy 1(1) (1999) 21.

[3] I. Novak, K.N. Brown, D.S. Fleming, P.T. Goulet, P.A. Lay, A.F. Masters, L. Phillips, J. Phys. Chem. B 103 (1999) 6713

6. The solvent effect on the reduction of two model bromides in six model organic solvents on catalytic Ag electrode and on the non-catalytic glassy carbon one



- The catalytic effects of silver (peak potential anticipation) are **huge in all cases considered**
- In all cases the DET mechanism is **concerted** (both on GC and Ag), as predicted by Savéant for most aliphatic halides (which can hardly give a stable radical anion)

- When, as a consequence of the catalytic effect, the reduction takes place **within the potential range of bromide adsorption** (shaded areas), the CV patterns become more complex in multiplicity and shape (peaks of mixed diffusive and adsorptive character)
- Neatly diffusive peak currents **satisfactorily comply with Stokes' law** (i.e. the diffusion coefficients of the reacting molecule, obtained from limiting currents (after peak convolution, linearly decrease with increasing viscosity), pointing to a viscous motion of the reactant molecule with negligible solvent interactions

Fig. 2. A synopsis of the normalized CV characteristics of MBR on GC (—) and potential after Ag (---) electrodes, in MeOH, in different solvents, with constant 0.1 M TEA/TB supporting electrolyte, at 0.2 V s⁻¹. The shaded areas mark the potential range in which specific adsorption of bromide anions can be assumed to take place.

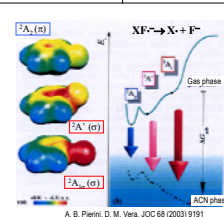
Fig. 3. A synopsis of the normalized CV characteristics of MBR' on GC (—) and potential after Ag (---) electrodes, in MeOH, in different solvents, with constant 0.1 M TEA/TB supporting electrolyte, at 0.2 V s⁻¹. The shaded areas mark the potential range in which specific adsorption of bromide anions can be assumed to take place.

3. Focusing on the solvent effect

L. Falciola, A. Gennaro, A.A. Isse, P.R. Mussini, M. Rossi, J. Electroanal. Chem., 593 (1-2), (2006) 47-56

Solvation modifies the free energy profile along the whole reaction coordinate. Such a modification may be huge and, above all, **asymmetric**. For instance, a polar solvent such as ACN will result in preferential stabilization of the species having the highest charge density, i.e., in the current case, the reaction products including halide anions that bear a net negative charge

The solvent modifies the **thermodynamics** of the process, modifying the free energies of both reagents and products through their solvation



Solvation modifies the process **kinetics**, also modifying the energy of the reaction intermediates. It also affects, through its viscosity, the **rate of mass transfer** to the electrode and hence the peak currents will show a strong solvent dependency.

Last, dealing with an heterogeneous catalytic process, the extent and mode of **solvent (co)adsorption** on the working electrode can strongly influence the inner-sphere electron transfer to/from the reacting molecule

Studying the solvent effects required two preliminary investigations:

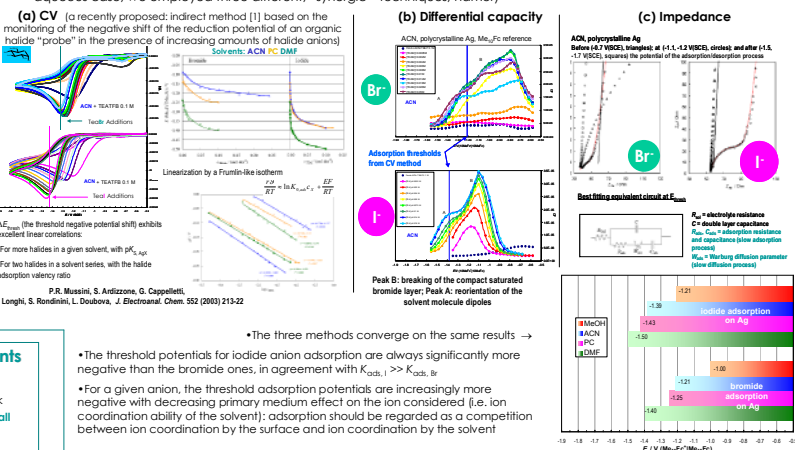
(a) Identification of a reliable standard redox couple for intersolvental normalization of the CV characteristics

(b) Determination of the threshold potential for the specific adsorption of X⁻ on Ag in each solvent studied

5. Determining the threshold potential for the specific adsorption of X⁻ on Ag in the working organic solvents

L. Falciola, P.R. Mussini, S. Trasatti, L. M. Drouba, J. Electroanal. Chem., 593 (1-2), (2006), 185-193; L. Falciola, Oral presentation, This Symposium, Tuesday 29th, 17.50

A parallel research project had to be devoted to the investigation of the potential range for specific halide anion adsorption on silver in each tested solvent. Since the task was a much more critical one with respect to the thoroughly investigated aqueous case, we employed three different, "synergic" techniques, namely



• The three methods converge on the same results →

- The threshold potentials for iodide anion adsorption are always significantly more negative than the bromide ones, in agreement with $K_{ads, I} \gg K_{ads, Br}$
- For a given anion, the threshold adsorption potentials are increasingly more negative with decreasing primary medium effect on the ion considered (i.e. ion coordination ability of the solvent); adsorption should be regarded as a competition between ion coordination by the surface and ion coordination by the solvent

7. The solvent modulation on the catalytic effects of the Ag electrode

The solvent modulation on the peak potentials on the non-catalytic and the catalytic electrode

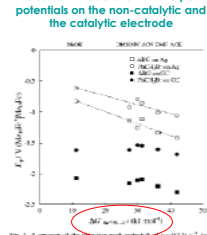


Fig. 4. A synopsis of the normalized CV characteristics of MBR on GC (—) and potential after Ag (---) electrodes, in MeOH, in different solvents, with constant 0.1 M TEA/TB supporting electrolyte, at 0.2 V s⁻¹. The shaded areas mark the potential range in which specific adsorption of bromide anions can be assumed to take place.

The solvent modulation on the catalytic effects, accounted for by the reduction potential differences between the catalytic electrode and the non-catalytic one, ($E_p, Ag - E_p, GC$)

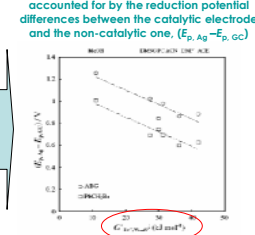


Fig. 5. Solvent modulation on the catalytic effects, accounted for by the reduction potential differences between the catalytic electrode and the non-catalytic one, ($E_p, Ag - E_p, GC$)

The sequences of both the normalized reduction peak potentials and the catalytic effects in the six solvents point to a **key role of the solvation of the Br⁻ ion** produced in the process, resulting in flat characteristics on the non-catalytic GC, and on steeply linear, parallel characteristics on highly catalytic Ag.

Stronger Br⁻ solvation results in more positive reduction peaks and higher catalytic effects (the prolic and highly Br⁻-coordinating MeOH resulting in huge catalytic effects). This might be accounted for by the solvent assistance in the turnover of the catalytic cycles.

Both the peak potentials on the catalytic electrode and the catalytic effects exhibit a linear dependence on the primary medium effects on the Br⁻ ion (decreasing with increasingly stronger halide solvation)