

## The Electrocatalytic Reductive Dehalogenation of Aromatic Halides on Silver

Sandra Rondinini\*, Patrizia Mussini, Alberto Vertova

Department of Physical Chemistry and Electrochemistry,  
University of Milano,  
Via Golgi 19, 20133 Milano, Italy  
phone +39 02 26603217; fax +39 02 26603203;  
emails: sandra.rondinini@unimi.it,  
patrizia.mussini@unimi.it, alberto.vertova@unimi.it

The increasing concern about environment prompted in the last years an increasing number of research groups to focus on the major problem of setting up innovative technologies for the detoxification and disposal of organohalides in industrial effluents. Most of the proposed methodologies are based on either chemical or electrochemical oxidation, often achieving complete mineralization, but suffering from the intrinsic severe drawback of possible formation of compounds more dangerous than the starting ones even if present in traces, e.g. dioxines or volatile halocompounds, the latter escaping from the cell together with the anodic gases. *Vice versa*, dehalogenation processes based on either chemical or electrochemical reduction, although unable to afford complete mineralization, easily afford complete dehalogenation, which allows easy disposal together with non-halogenated effluents. In this context some researchers have aimed to mostly indirect electrochemical dehalogenation<sup>1,2,3</sup>, operating under background current conditions on carbon electrodes, often enhancing their activity for hydrogen reduction by loading them with noble metal particles. Direct electrochemical dehalogenation, alone or in competition with the former indirect one, was achieved employing cathode materials having more electrocatalytic activity for halogen displacement, such as mercury and lead<sup>4</sup>; however, both these popular cathode materials suffer from the drawback of possible formation of traces of dangerous organometallic compounds.

In the present work the remarkable electrocatalytic properties of silver, recently evidenced by our research group<sup>5-12</sup> for organic halide reduction have been advantageously applied to obtain quantitative direct dehalogenation of mono- and polyhalophenols.

The process, environmentally friendly as based on a non-toxic electrocatalytic material, also appears highly competitive on account of its mildness of operating conditions, selectivity and current efficiency. Peculiar care was devoted to the analysis of the reaction mixtures, never finding any product but those of hydrogenation of the halogen position(s). Another interesting feature is the absence of filming effect allowing the reaction to proceed with fairly high current density.

Structure effects on the reaction pathways (clearly recognizable from the electrolysis monitoring, as in the case in the Figure aside) are discussed with the support of systematic cyclic voltammetric experiments on silver, mercury, and glassy carbon. The role of the solvent is also discussed on the basis of experiments carried out in acetonitrile (the solvent chosen for preliminary investigation), in acetonitrile/water 1:1 mixed solvent, and in water (the most interesting solvent from the applicative point of view) especially focusing on current yield and energy consumption parameters.

Finally, a preliminary reactivity investigation points to the

possibility of generalizing the same advantageous process to all aromatic halides.

ACKNOWLEDGMENTS. The financial support (COFIN99) of the Italian Ministry of University and Scientific and Technological Research (MURST) is gratefully acknowledged

<sup>1</sup> A. I. Tsiganok, I. Yamanaka and K. Otsuka, *J. Electrochem. Soc.*, **145** 3844 (1998).

<sup>2</sup> A. I. Tsyganok and K. Otsuka, *Appl. Catalysis B. Environ.*, **22** 15 (1999)

<sup>3</sup> I. F. Cheng, Q. Fernando and K. Norte, *Environ. Sci. Technol.*, **31**, 1074 (1997)

<sup>4</sup> N. C. Ross, R. A. Spackman, M. L. Hitchman and P. C. White, *J. Appl. Electrochem.*, **27**, 51 (1997)

<sup>5</sup> M. Benedetto, G. Miglierini, P. R. Mussini, F. Pelizzoni, S. Rondinini and G. Sello, *Carbohydr. Letters*, **1**, 321 (1995)

<sup>6</sup> S. Rondinini, P.R. Mussini, G. Sello and E. Vismara, *J. Electrochem. Soc.*, **145**, 1108 (1998)

<sup>7</sup> M. Guerrini, P. Mussini, S. Rondinini, G. Torri, E. Vismara, *Chem. Comm.*, 1617 (1998).

<sup>8</sup> S. Rondinini, P. R. Mussini, G. Cantù, G. Sello, *Phys. Chem. Chem. Phys.*, **1** 2989 (1999).

<sup>9</sup> S. Rondinini, P. R. Mussini, F. Crippa, M. Petrone, G. Sello, *Coll. Czech. Chem. Comm.*, 881 (2000).

<sup>10</sup> S. B. Rondinini, P. R. Mussini, F. Crippa, G. Sello, *Electrochem. Comm.*, **2** 491 (2000).

<sup>11</sup> G. Fiori, P. R. Mussini, S. Rondinini, A. Vertova, *Annal. Chim.*, **91**, 151 (2001)

<sup>12</sup> S. Rondinini, P. R. Mussini, M. Specchia, A. Vertova, *J. Electrochem. Soc.*, in press (2001)

