



Review Article

Dissociative electron transfer mechanism and application in the electrocatalytic activation of organic halides

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Abstract

The electrochemical dehalogenation of organic halides has been a widely investigated topic *in primis* for fundamental investigations of dissociative electron transfer (DET) and as a green way for the electrosynthesis of organic compounds and environmental remediation. The main drawback associated with the electrochemical activation of C-X is the very negative potentials required, and this is particularly true in the case of organic chlorides, which represent the most investigated ensemble among organic molecules containing a leaving group. This has boosted over the last decades the research of electrode materials that are active toward C-X bond breaking, and without any doubt, Ag possesses extraordinary electrocatalytic properties, so far unsurpassed by any other electrode material. In this paper, we will attempt to brush up on important concepts related to DET in organic halides, while also evaluating recent developments in terms of electrode materials used in electrosynthesis based on organic halides and R-X degradation processes.

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Keywords

Silver, Organic halides, Dissociative electron transfer, Electrocarboxylation, Dehalogenation.

Introduction

The transformation of chemicals to added-value or less harmful products is a trending topic in electrocatalysis.

In particular, the reductive dehalogenation of carbon-halogen (C-X; X = Cl, Br, I) bonds is of enormous interest because of its fundamental role in waste degradation, organic electrosynthesis, and mechanistic investigations associated with electron transfer [1–3]. Indeed, halogenated compounds, especially chlorinated and polychlorinated alkanes, alkenes, and aromatic derivatives, are well-known environmental pollutants for soil and underground waters, and their contaminant action is particularly dangerous due to their toxic and carcinogenic character, which is worsened by their relatively high solubility in water and hence their great mobility in soil. Furthermore, the utilization of several halogenated volatile organic compounds (HVOCs) as reagents, solvents, or additives in industrial processes is nowadays banned. For example, bromine and chlorine compounds are widely used as flame retardants in the electronic industry, and it is impossible to get rid of them when recycling electronic components. That is why in 2019, the European Commission banned their use in electronic displays, including televisions, monitors, and digital signage displays [4]. Other examples are halogenated pesticides, such as p,p'-dichlorodiphenyltrichloroethane (DDT) or β -hexachlorocyclohexane (β -HCH), which, however, are still used in several developing countries. Carbon tetrachloride and CFC-11 are banned substances under the Montreal Protocol, with the 2010 phase-out for developing countries, but production and consumption for non-dispersive use as a chemical feedstock and as a process agent are still allowed [5]. Despite the environmental concerns, organic halides are precursors or intermediates for many industrial productions as X^- is a good leaving group, and the formation of R^\bullet or R^- opens routes to a plethora of organic reactions. The electrochemical activation of R-X is an important method to generate reactive intermediates by simply using electrons as a green reductant, which significantly reduces the reliance on sacrificial chemicals and the potential risk of secondary polluting products. One example is the abatement of volatile polychlorinated organic compounds or carboxylation to produce chemicals of synthetic interest [6–8]. In this sense, the electrochemical activation of carbon-halogen bonds is as sustainable as photocatalytic activation and even more effective in the case of chlorides. A

case apart is photoelectrocatalytic processes, which will not be considered in this paper to focus more on the purely electrocatalytic activation of R-X under various aspects. We will first recall the fundamental and mechanistic aspects of the dehalogenation reaction and then report the most recent developments in terms of electrode materials and applications in the field of electro-synthesis and environmental electrochemistry.

Dissociative electron transfer in organic halides

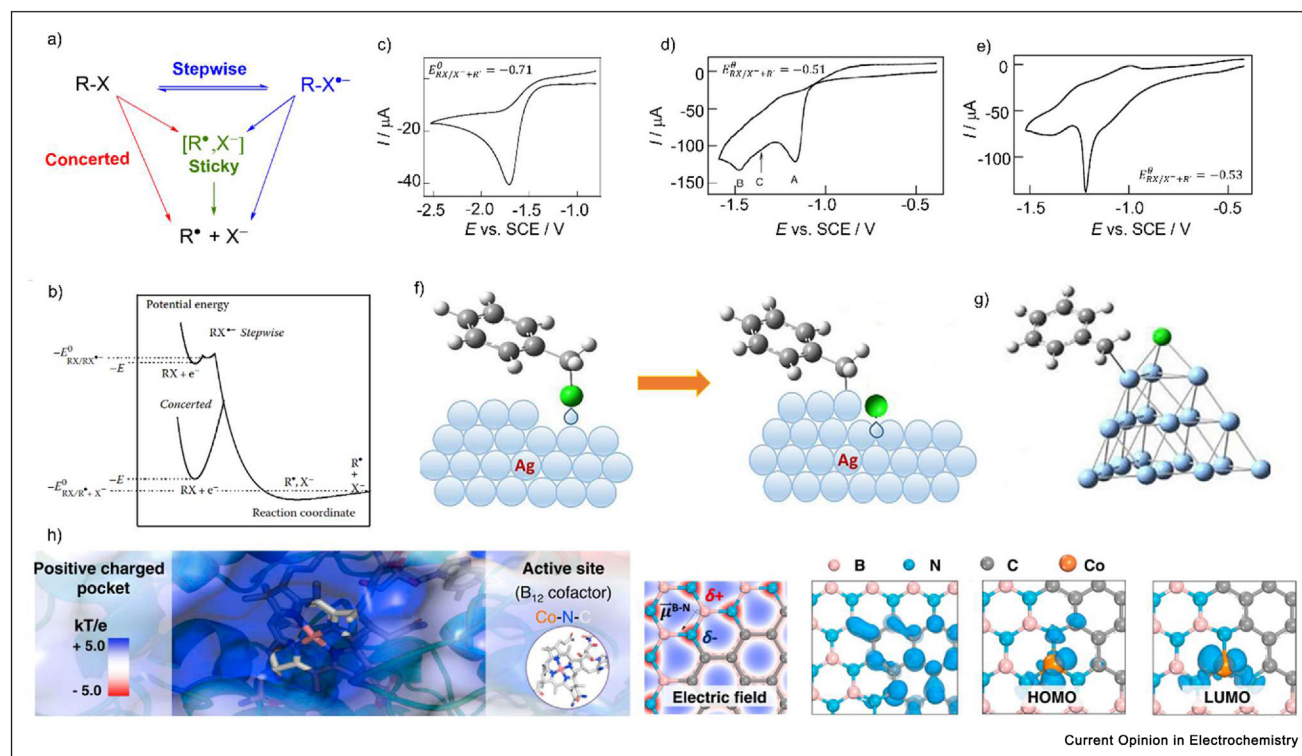
In organic halides, the C-X σ bond can be broken upon the injection of one electron donated by a chemical reagent or an electrode, and the process is generally named as dissociative electron transfer (DET). There are two possible DET pathways: a concerted route that proceeds in a single step and a two-step one in which a radical anion intermediate is formed. The first is known as concerted DET (CDET) (Figure 1a), and the second as stepwise (or sequential) DET (SDET) [9]. A “sticky” DET (STDET) model was also proposed by Savéant and co-workers as a third possible mechanism, where the R-X bond is broken, but the

two fragments give weak interactions in the solvent cage [9].

From a thermodynamic point of view, CDET has the advantage of avoiding the formation of high energy intermediates, yielding directly the final products (Figure 1b), but suffers from a kinetic hindrance due to the large intrinsic activation barrier deriving from bond cleavage. In the SDET, the first step is the formation of a radical anion ($RX^{\bullet-}$), which then breaks to yield the same products of CDET. The radical generated in either mechanism may be further reduced to R^- (Figure 1a). Before the formation of separated R^\bullet and X^- , an ion-radical adduct that, may or may not survive, in a polar solvent may be formed (minimum in Figure 1b) for both mechanisms; in that case, the dynamics of the DET process are better fit by the STDET model [10,11]. This adduct was observed when the radical fragment could form a dipole thanks to the presence of a strong electron-withdrawing substituent [12].

The competition between the CDET and SDET pathways depends upon intramolecular (structural and electronic) and environmental (solvent and energy of

Figure 1



(a) DET mechanisms. (b) Energy profiles for the reductive cleavage of R-X. (c–e) Cyclic voltammetry of $PhCH_2X$ in $CH_3CN + 0.1$ M TEAP at Ag cathode: (c) 1.0 mM $PhCH_2Cl$ at 0.2 V s^{-1} ; (d) 3.0 mM $PhCH_2Br$ at 1 V s^{-1} ; (e) 3.0 mM $PhCH_2I$ at 1 V s^{-1} . (f) schematic representation of $PhCH_2Cl$ adsorption, followed by a DET and (g) adsorption of DET fragments on Ag. (h) Electrostatic surface representation for the reductive dehalogenases mimic system based on Co–N–C and boron nitride; electron density plots of carbon-doped boron nitride (BCN) with the electric field around B–N bond; the isosurface contours reveal discontinuity in electron density between the N (negatively charged) and B (positively charged) atoms. Orbital density images of C atoms in BCN and of the HOMO and LUMO of isolated Co atom supported on BCN. Figure b–g reproduced from Refs. [12,15–18] with permission.

the incoming electron) factors. Three aspects could be considered to influence the type of mechanism, namely the bond dissociation energy (D_{RX}), the standard reduction potential of RX ($E_{RX/RX^{\bullet-}}^{\circ}$), and the standard oxidation potential of the leaving group X^{-} ($E_{X^{\bullet}/X^{-}}^{\circ}$); in addition, it is possible to predict that a weak bond, a negative value of $E_{RX/RX^{\bullet-}}^{\circ}$, and a positive value of $E_{X^{\bullet}/X^{-}}^{\circ}$ will favor the concerted mechanism and *vice versa*. A general distinction can be made between aryl and alkyl halides. The direct attachment of the halogen to the aromatic system in aryl halides allows accommodation of the incoming electron on a low energy π^* orbital. Thus, aryl halides usually follow a stepwise mechanism. Instead, in an alkyl halide, the first available orbital is σ^* , where the rupture of the C–X bond is energetically favored over the formation of a species with one electron in a σ^* orbital. Few examples of borderline cases with mechanism transition between SDET and CDETs have been reported [13,14].

Outer-sphere ET to RX, especially alkyl halides, requires quite negative potentials. This mechanism is observed on non-interacting (inert) electrodes like glassy carbon (GC), while an inner-sphere ET could be seen at electrodes that give some interaction, like Hg, lowering the overpotential. Therefore, much effort has been devoted to the research on catalytic electrodes able to lower the activation barrier, and among various materials, Ag showed the highest activity, regardless of the type of halogen [19,20]. Figure 1c–e reports the electrochemical behavior of benzyl halides at a silver cathode. The process follows a CDET mechanism, and Ag shows a remarkable catalytic effect. Indeed, the reduction of PhCH₂-X at Ag is positively shifted by 0.45, 0.72, and 0.48 V for X = Cl, Br, and I, respectively, as compared to the process at a non-catalytic electrode, such as GC.

Pd and Cu were also studied, and among the other transition metals, they manage to some extent to produce activities approaching those of Ag [21,22]. Simonet was a pioneer in proposing palladium as cathode material for dehalogenation in the form of a thin film obtained by displacement deposition on silver and copper supports [23,24], and his papers paved the way for more recent studies, *vide infra*, on the treatment of halogenated compounds in an aqueous media.

Silver was found to be one of the best electrocatalytic materials both in aqueous and non-aqueous solutions [21,25,26]. One important feature of the process, common to all catalytic materials, is that no catalysis is observed when the DET to R-X occurs according to a stepwise mechanism. The catalytic surfaces affect the reaction scheme, offering a more favorable route possibly through the formation of strongly adsorbed activated complexes

(Figure 1f). The crucial role of adsorption in electrocatalytic DET to R-X was demonstrated by Amatore and co-workers by surface-enhanced Raman spectroscopy (SERS) coupled with density functional theory (DFT) [27], and more recently by DFT calculations, adopting benzyl chloride as a probe molecule and silver electrodes as electrocatalytic surfaces [17]. DFT studies were refined in the last ten years, and the most recent study indicated that PhCH₂Cl adsorption is rather weak and can be essentially described as a physical adsorption rather than chemisorption, so that no Raman response is expected. Conversely, according to the DFT analysis, the concerted dissociative pathway evolves through the strong chemisorption of the two fragments, PhCH₂[•] and Cl⁻, which are partially charged, on the silver surface [17]. The chemisorption of the benzyl radical through the formation of a bond between the methylene carbon and a silver atom (C–Ag bond) was confirmed by the presence of a very intense and broad Raman band at 350 cm⁻¹, whereas the interaction of the halide fragment with Ag resulted in a weak Raman signal because of the preferential adsorption at three-fold hollow sites (Figure 1g).

Other metals, such as Au, Mg, Mn, Zn, Pb, Ti, Fe, and Ni, have been tested as cathodes for the reductive dehalogenation of organic compounds, but none of them showed the capability to compete with Ag or Cu in terms of activity and stability. From early studies on two-dimensional bulk electrodes, research on R-X electrocatalysis advanced to the use of nanostructured materials with low metal content, ultimately opening the way to metal-free carbon-based catalysts [28]. For example, Ag, in the form of nanoparticles (NPs), core–shell structures, or nanowires, was proposed for RX dehalogenation in both organic and aqueous electrolytes and ionic liquids (ILs) as well [29–32]. Ag NPs confirmed a remarkable electrocatalytic activity which is comparable to that of the bulk metal or even higher. Furthermore, Pandit *et al.* [32] reported the DET of CCl₄ at a nanostructured Pd-graphene electrode. According to the authors, the dehalogenation process follows a modified STDET mechanism with the adsorption energy of chlorinated species contributing to the kinetics of the overall process. What is even more unexpected is that the same process observed at Ag-graphene and nanostructured PdAg-graphene electrodes follows a modified SDET with a net increment of the catalytic activity, especially at the PdAg-graphene electrode. As previously reported for DET of organic halides in organic electrolytes, catalysis is relevant only when ET is concerted with R-X breaking. In this case, a controversial result was reported. In fact, a stepwise mechanism was proposed, and according to the authors, the observed catalytic activity is due to the adsorptive stabilization of the electrogenerated radical anion intermediate, which decreases the intrinsic barrier of the DET process [32].

Foam electrodes decorated by ultrafine palladium NPs were also proposed in the literature for electrocatalytic dechlorination of chlorinated antibiotics, such as florfenicol [33]. Furthermore, biomimetic or bioinspired electrocatalysts are commonly designed taking natural systems as an example. Some bacteria use organohalides for respiring [34], and the active center that can be regarded as a binding pocket is composed of cobalt in a porphyrin-like structure [35]. Inspired by this process, Min et al. [18] produced a single-atomic-site Co catalyst supported on carbon-doped boron nitride (BCN) with locally polarized B–N bonds to simulate the reductive dehalogenases binding pocket, as shown in Figure 1h. The locally polarized B–N, which is similar to a charged pocket in native enzyme bonds, plays a key role for binding organochlorides. Upon the adsorption of chloramphenicol on Co SAs/BCN, a strong interaction was observed resulting from the transfer of electrons from the Co-3d orbital to the Cl-2p orbital giving rise to the Cl–Co bond, as shown in Figure 3h. This work suggests that single-atom catalysts might open new opportunities for the design of high-performance enzyme-like catalysts. Another example of non-conventional metal electrode comes from Dauda et al. [36], who proposed Co–MoS₂, a non-noble metal electrocatalyst, loaded on a graphite felt for the reductive degradation of CHBr₂Cl, C₃H₅Br₂Cl, CHBr₃, CHCl₃, and CCl₄. Authors do not provide any insights about the possible direct reduction of halogenated compounds at Co–MoS₂, but they consider the mediating role of adsorbed hydrogen *H as necessary for the halo-organics reduction. *H is produced by the synergic action of CoS and MoS₂ in the hydrogen evolution reaction [36]. This novel electrode material displayed a current efficiency of ~13% and the degradation efficiency of more than 90% for each of the analyzed compounds after 60 min of electrolysis in an aqueous electrolyte [36].

Besides the type of electrode materials, also technological aspects related to the cell and electrode design, are becoming more and more important in the perspective of a feasible employment of dehalogenation at an industrial scale. For example, Vertova and co-workers demonstrated the feasibility of applying a silver gas diffusion electrode (GDE) to the dehalogenation process of CHCl₃ [6]. They proved that the main dehalogenated product is methane, with small amounts of mono- and dichloromethane. In this configuration, the process can reach a current efficiency higher than 70%, when a properly wetted electrode is used.

Carbon-halogen bond activation for electrosynthesis

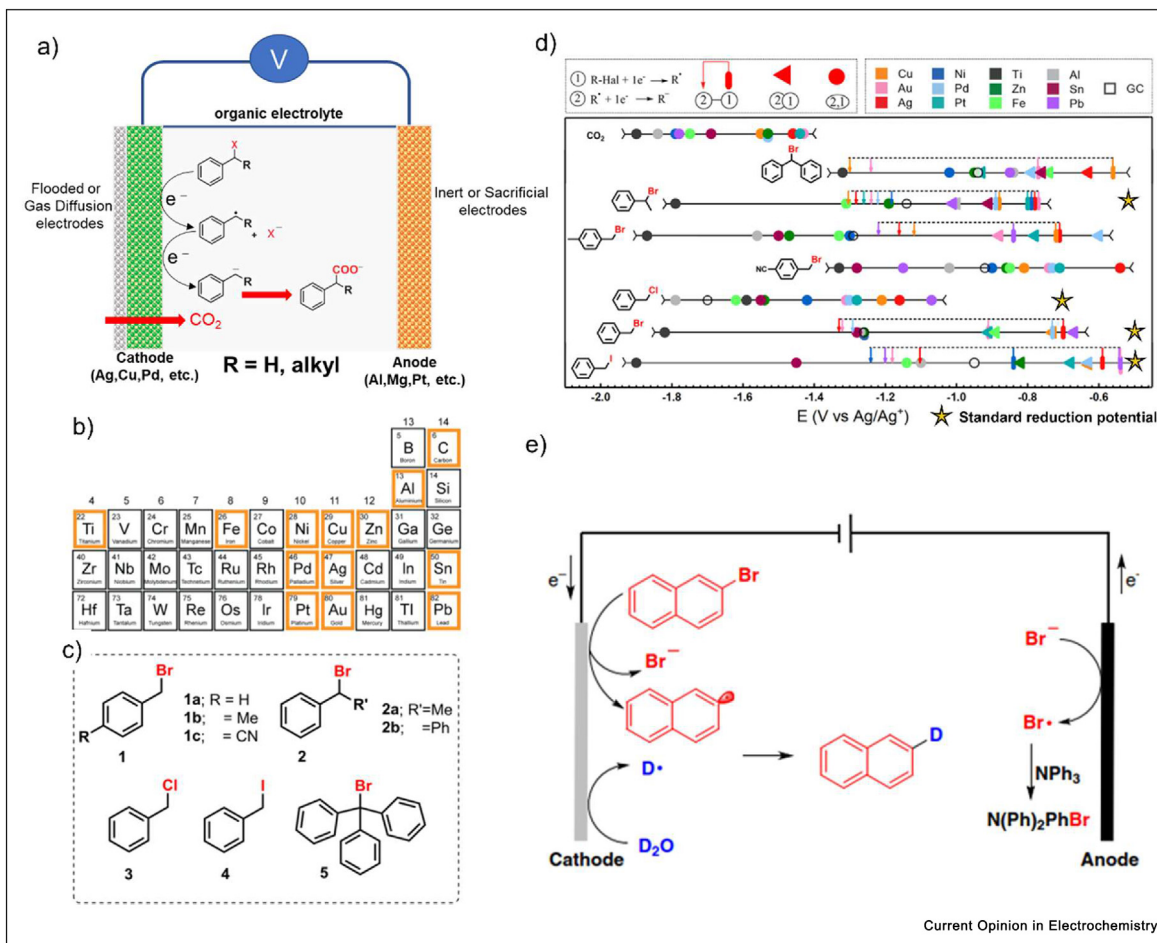
Besides the general fundamental interest for DET process, the electrochemical activation of R–X finds application in two main research fields: electrosynthesis [8,37,38] and environmental remediation [39–41]. The

production of chemical precursors for industrial processes had been always a challenge since mass production requires easy and cheap steps. Recently, the research has moved toward processes that not only allow us to obtain useful chemicals but also look at environmental aspects. On this regard, electrocarboxylation is the most widely studied electrocatalytic process combined with the dehalogenation process. The use of non-toxic aprotic solvents and CO₂ as a raw material makes the electrocarboxylation reaction a green and sustainable process. Dehalogenation coupled with carboxylation was a very hot topic in the early 2000s, and the pioneering works of Isse and Gennaro on CO₂ reduction in organic solvents are milestones for this field. These authors published several papers on the electrocatalytic carboxylation of carbon-halogen precursors at metal cathodes in polar aprotic solvents, such as acetonitrile [42–45] and dimethylformamide [45,46]. The electrocarboxylation reaction consists in the addition of CO₂ onto organic substrates with different functional groups, for example, organohalides or pseudo halides, conjugated alkenes, fluorosubstituted alkenes, ketones, etc. [8]. In the case of organohalides, the dehalogenation process, prompted either by the direct electroreduction at the electrode surface or mediated by a redox probe, produces a carbanion (R[−]) capable of nucleophilic attack on CO₂. As a result, the corresponding carboxylate (R–COO[−]) is obtained (Figure 2a). Just to give an example, already in 2008, Scialdone et al. [47] proposed the synthesis of cyanoacetic acid from chloroacetonitrile and CO₂ in organic media at a silver cathode. The electrochemical method offers advantages over the classical industrial process based on the reaction between chloroacetic acid and alkali metal cyanides. In dry CO₂-saturated acetonitrile, selectivities and Faradaic efficiencies (FEs) higher than 80% were achieved by working both under galvanostatic and potentiostatic conditions.

Although many experimental conditions have been already studied for RX electrocarboxylation and the process has been well rationalized, this topic has regained attention in the last five years also pointing the attention to improve the scalability.

Recently, Medvedev et al. [48] studied the activity of a wide range of metals toward the electro-organic coupling of CO₂ with benzyl halides (Figure 2b–d). The reduction of PhCH₂X on Fe, Al, Sn, Zn, and Ti required high energy input to form PhCH₂[−] species. Other metals, such as Ag, Au, Cu, Pt, Pd, and in some cases, Ni and Pb showed noticeable catalytic activity toward the reduction of PhCH₂Br. Cyclic voltammetry on these metals showed two distinct peaks corresponding to PhCH₂[•] generation and its reduction to PhCH₂[−] (see e.g. Figure 1d). The potentiostatic electrolysis of PhCH₂Br in the presence of CO₂ at catalytic metals (Au, Cu, Pb, and Ag) proceeded without any

Figure 2



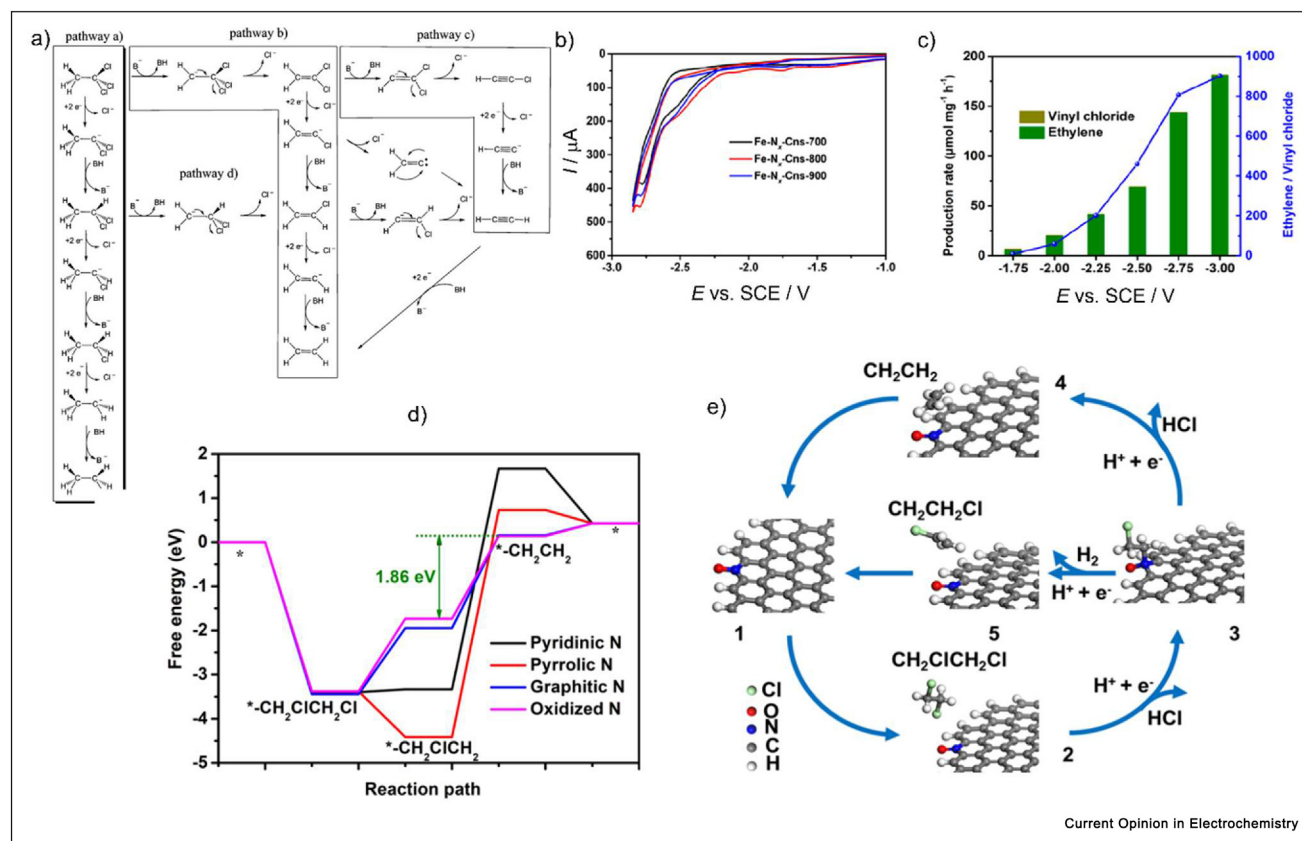
(a) Schematic representation of electrocarboxylation of organic halides in the presence of CO_2 , (b) types of metal electrodes tested for electrocarboxylation; (c) example of molecular structures of benzylic halides investigated in Ref. [48]. (d) Reduction potentials of organic halides and CO_2 at different bulk metal cathodes in CH_3CN (see the legend on the top). The empty circles correspond to the potentials at 5 mA cm^{-2} for the two-electron reduction of RX to $\text{R}^- + \text{X}^-$ at GC. The filled bars correspond to the potentials at 5 mA cm^{-2} for the one-electron reduction of RX to $\text{R}^{\bullet} + \text{X}^-$ for the cases when two separate reduction waves are observed in CV; the downward arrows correspond to the onset potentials of the second reduction wave, $\text{R}^{\bullet} + 1e^- \rightarrow \text{R}^-$. The triangles correspond to the potentials at 5 mA cm^{-2} for the one-electron reduction of RX for the cases when two reduction waves are overlapped. The filled circles correspond to the potentials at 5 mA cm^{-2} for the two-electron reduction of RX to $\text{R}^- + \text{X}^-$ for the cases when a single peak is observed. In the case of CO_2 RR, the circles correspond to the onset potentials of the reduction of CO_2 to $\text{CO}_2^{\bullet -}$. (e) Setup for deuteration used by Lu *et al.* [55]. Reproduced with permission from Refs. [48,55].

contribution of competing CO_2 reduction reaction (CO_2 RR), giving rise to the target product with FEs up to 81%.

A further step is to engineer the metal surface by dispersing the metal NPs on a support (metal or carbon). A recent example was presented by Shan *et al.* who reported for the first time the electrocarboxylation of benzyl bromide by using mesoporous silver under galvanostatic conditions [49]. The mesoporous silver had a regular structure and showed high electrocatalytic performance because of optimized pore network. The best-performing catalyst showed about a FE approaching 70% for the production of phenylacetate.

The electrochemical cell configuration is also extremely important for industrial applications. It has been shown that the electrocatalysis of organohalides with different cathodes in undivided cells with sacrificial Mg or Al anodes generally results in the formation of the corresponding carboxylic acids in the form of metal salts at moderate to high yields [50]. For example, Zhang *et al.* proposed the electrocarboxylation of bromopyridines on a silver electrode, using Mg as a sacrificial anode. Depending on the position of the C-Br bond on the pyridine ring, yields of 59.0–65.8% were achieved in DMF/TBABr with a current density of 9 mA cm^{-2} , para-bromopyridine giving the highest performance. Although the formation of these salts simplifies the

Figure 3



(a) Different pathways for 1,1,1-trichloroethane electroreduction at Ag [59]. (b) Cyclic voltammetry of DCE at different Fe–Nx–C functionalized electrodes in DMF/TPABF₄ [64]. (c) Production rate and selectivity of Fe–Nx–Cns–800 under different potentials [64]. (d) Calculated energy profile for the dechlorination of DCE into CH₂CH₂ [68]. (e) Illustration of the DCE dechlorination mechanism on the oxidized N site. All images were reproduced under the right permission of original works.

work-up procedure, it negatively affects the reaction atom economy due to the anode consumption during the reaction. To avoid this, Medvedev et al. recently showed an electrochemical route for CO₂ fixation to α -methylbenzyl bromide in a two-compartment cell with a membrane separator [51]. The type of membrane is critical, and the authors showed that anion exchange membrane has a superior performance with higher electrochemical selectivity and lower cathode passivation than either cation exchange membrane or bipolar membrane.

Reche et al. proposed an environmentally friendly synthesis of phthalate derivatives by electrocarboxylation of halobenzonitriles. The presence of an electron-withdrawing group, such as CN, helps to decrease the energy required for the reduction process [52]. The synthesis of dicarboxylated compounds using this strategy is of interest for making plastic polymers in a foreseeable future. In detail, the electrolysis of 4-halobenzonitrile in CO₂-saturated solutions was carried out on graphite or

silver cathodes, but Ag allowed the application of a less negative potential. Mono- and di-substituted products were obtained and tuned with reaction conditions. With fluorine, the di-substituted compound is the only carboxylated product at a low yield, whereas the dicarboxylated product was obtained at a yield of 90% from 4-bromobenzonitrile in the presence of CH₃CH₂Br as an alkylating agent.

Mena et al. proposed electrochemical synthesis for ibuprofen from 1-chloro-(4-isobutylphenyl)ethane and CO₂ in ILs, using a silver cathode [53]. EMIM TFSI, PP13 TFSI, DMF, and a mixture of DMF and PP13 TFSI were used as solvents. Dried PP13 TFSI gave the best results with full reagent conversion and 83% yield of acid. Indeed, although the price of a single experiment in IL doubles that of DMF + 0.1 M of TBABF₄, the IL can be recovered and reused at almost 80% at the end of the experiment, making this methodology highly viable and attractive. Controlled-potential electrolysis of 1-chloro-(4-isobutylphenyl)ethane under CO₂ atmosphere allows

ibuprofen to be obtained in good yields and excellent conversion rates. The same authors accomplished the synthesis of 4-cyanobenzoic acid by electrocarboxylation of 4-iodobenzonitrile in ILs, adopting similar conditions as in the case of ibuprofen [54]. The use of silver cathodes enabled the production of 4-cyanobenzoic acid under mild experimental conditions with moderate yields and conversion rates.

A different family of products that can be obtained from dehalogenation is deuterated compounds. Deuterium is a relatively inexpensive and nonradioactive isotope of hydrogen. Moreover, the cleavage of the C–D bond is more difficult than the C–H bond. Because of the above characteristics, deuterated compounds are widely used in many fields, such as mechanistic study (kinetic isotope effect), quantitative analysis, and pharmaceutical research [55]. Lu *et al.* deuterated several aromatic halides using D₂O in DMF. Different electrode materials and additives were tested. Using Pb and Pt as cathode and anode, respectively, and NPh₃ as additive, a yield of 99% was obtained for the deuteration of bromonaphthalene. The role of NPh₃ is to trap Br[•] generated at the anode (Figure 2e). Although the use of certain materials might be a drawback, the work is of inspiration for electrochemical synthesis of deuterated compounds, which is not very common in the literature.

Carbon-halogen bond activation for environmental purpose

Thermal decomposition, catalytic oxidation, UV oxidation, procedures using thermal plasma, ozonization, photochemical degradation on TiO₂, and electrochemical oxidation are the most common chemical or physical treatments of pollutants. A drawback of several of these methodologies applied to organic halides is the uncontrollable formation of by-products, which might be more harmful or recalcitrant than their precursors. The dehalogenation of pollutants is of special interest as it can decrease toxicity, enhance pollutant biodegradability, and possibly produce useful materials. This is particularly true for organic chlorides, such as alkyl and aryl chlorides, which are widely used as solvents, chemicals, or raw materials in many processes (e.g. pesticides, refrigerants, pharmaceuticals, adhesives, etc.). The electrochemical dehalogenation on catalytic electrodes represents a more sustainable alternative to chemical or photochemical processes, especially for organic chlorides. Some reviews on the topic are present in the literature [56]; here, the most recent and representative examples are reported.

The dehalogenation of common halogenated solvents and HVOCs was deeply studied by Gennaro and co-workers on Ag [1,25,57] and Cu [58,59]. Although Cu is less active than Ag, it is cheaper than Ag and is thus more attractive in large-scale applications. The catalytic activity of Cu or Ag is enhanced by the presence of a

proton source, like acetic acid, which helps the protonation of the intermediate carbanion. Cu also allows the exhaustive electrochemical degradation of highly toxic polychloroethanes to ethane and ethylene. Depending on the presence or the absence of a proton source, different reaction pathways for the two products were proposed (Figure 3a) [26]. Furthermore, the electrocatalytic activity was also found to be affected by the structure of the polychloroethane: it increases with an increasing number of Cl atoms bound to the same carbon center. Instead, the number of Cl atoms bound to the second C atom has two opposite effects: favorable polarity effect contrasted by steric hindrance effects on the transition state. Brudzisz *et al.* prepared silver nanowires to reduce chloroform [31]. The catalytic effect demonstrated by silver in aqueous KClO₄ was attributed to the ability of water to favor the desorption processes and, consequently, enhance the turnover frequency of the catalytic sites. Previously, Rondinini and co-workers proposed the employment of GDEs functionalized with Ag NPs for the conversion of gaseous trichloromethane to less chlorinated compounds in aqueous 0.1 M KClO₄ [60].

Peters and co-workers have for long time investigated the electrochemical reduction of organohalides, and recently, they studied the electrochemical degradation of acetochlor, a widely diffused herbicide [61]. As common to many organochlorides, the voltammetric response of acetochlor in DMF containing 0.05 M TMBF₄ at GC and Ag exhibits a single, irreversible cathodic peak with a sensitive anticipation (0.40 V) at Ag. The presence of a proton source, such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), induces further anodic potential shift, and computational models suggest that HFIP can interact with the intermediate carbanion by hydrogen bonding, facilitating the reduction process.

Still on the subject of metallic catalysts, Zhou *et al.* [62] prepared palladium/granular activated carbon (Pd/GAC) functionalized with cetyltrimethylammonium bromide (CTAB) and tested its activity for 2,4-dichlorobenzoic acid (2,4-DCBA). The catalyst showed strong and selective adsorption of the pollutant, which helped dechlorination. This study suggested that the idea of functionalizing the catalyst to improve its adsorption performance could open a new strategy for electrocatalytic reductive dechlorination technology. Qin *et al.* [39] prepared a three-atom alloy using the best-performing metals, such as Cu, Ag, and Pd. The introduction of Cu and Ag on palladium NPs allows creating vacancies (v-PdCuAg), which are the key for the efficiency of this catalyst. Direct electrocatalytic dehalogenation was observed under aqueous conditions because of promoted electron transfer on the catalyst surface. Experimental and theoretical investigations showed that indirect electrocatalytic hydrodehalogenation was greatly enhanced over the v-

PdCuAg electrocatalyst because of the strong generation and storage capacity of *H species with high adsorption energies (3.78–3.93 eV).

Like many other electrocatalytic processes, the tendency is to reduce the use of metal-based catalysts, generally for the cost, by eliminating the metal or reducing its content. Carbon-based materials, for example, doped carbons (heteroatom functionalized carbons) and single-atom catalysts supported on carbon, are commonly studied for this purpose. Lou et al. prepared single-atom Fe–N catalysts supported on carbon and FeCo NPs [63]. The particular electronic structure, as confirmed by DFT calculations, had electron-rich properties on the Fe–N₄ sites due to the transfer of electrons from FeCo NPs to Fe–N₄ sites, which increasingly decreased the intrinsic barrier of C–Cl bond breaking. Gan et al. [64] used a common Fe–N₄ prepared from dopamine and FeCl₃ to produce active single-atom catalysts for the selective electrochemical dechlorination of 1,2-dichloroethane (DCE) to ethylene with higher selectivity than a commercial 20% Pt–C catalyst [64]. The electrochemical activity of Fe–N_x–C was confirmed by cyclic voltammetry in an organic electrolyte (DMF/TPABF₄), where DCE reduction is visible as a two-step reduction process with the intermediate formation of vinyl chloride at the first step (Figure 3b). Electrolysis performed at different applied potentials confirmed an increased conversion of DCE to ethylene by moving toward more negative potentials where also vinyl chloride can be fully dehalogenated (Figure 3c). Experiments and theoretical calculations indicated a significant influence of the coordination pattern of Fe on the electrochemical performance of DCE dechlorination. The atomically dispersed Fe center in the Fe–N₄ structure was identified as the dominating catalytic site for DCE reduction to ethylene with an energy barrier of 0.44 eV. This study highlighted the employment of single-site catalysts as promising materials for electrochemical dehalogenation and possibly hydrogenation of organohalides. Additionally, this approach can take advantage of the long experience on the synthesis and characterization of Fe–N–C catalysts, which are widely employed as electrocatalysts for O₂ and CO₂ reductions. Indeed, a very similar approach was adopted for the carboxylation of styrene on copper single-atom catalysts [65].

Li et al. studied the dechlorination of trichloroethylene to acetylene by green rust/N-doped graphene [66]. Green rust is a generic name for various green crystalline chemical compounds containing iron(II) and iron(III) cations, the hydroxide (OH[−]) anion, and another anion, such as chloride (Cl[−]). They showed that the synergy between green rust and nitrogen-doped graphene enhances conversion and, among various tested anions, carbonate increases process performance.

Metal-free catalysts could be attractive, especially for the easy disposal and recycling of exhausted catalysts, and carbon-based materials represent a very valid choice. It is known that carbon catalysts could catalyze dehalogenation, and, as for other reactions, the role of functionalities and the actual active site are not trivial to elucidate. In particular, fundamental studies are needed for heteroatom-doped carbon (N, O, and S). Recently, Gan et al. reported the use of reduced graphene oxide (RGO) as a catalyst [67]. A series of RGOs with different contents of oxygen was prepared by hydrothermal reduction. The best-performing one showed to be active for the dechlorination of DCE with a selectivity approaching 94% for ethylene. Combining experimental and theoretical calculations indicated that C=O functionality is the main contributor to the catalytic performance, and the C atom neighbored to C=O at armchair edge is the best candidate as active site. The same authors also studied nitrogen-doped carbons for the dechlorination of DCE to CH₂CH₂ [68]. Comparing the DCE electroreduction on Fe–N–C [64] and N–C [68], it is worth stressing that a difference in catalytic activity, as deducible from the voltammetric behavior, is not perceivable. Authors also reported first-principle calculations of energy profiles for the dechlorination of CH₂ClCH₂Cl into CH₂CH₂ on the four possible nitrogen functional groups: pyridinic N, pyrrolic N, graphitic N, and oxidized N (Figure 3d). According to the energy profiles, the rate-determining step is second dechlorination step of DCE into CHClCH₂, and the most active center for the dechlorination is the oxidized N site. A sketch of DCE dechlorination mechanism on the oxidized N site is reported in Figure 3e.

Conclusion and future perspective

The electrochemical reduction of organic halides is still nowadays a hot topic, especially for applications in electrosynthesis and environmental remediation. In electrocatalysis, the most important aspect is the role of the electrode material. Despite important developments of the past two decades, there have been few efforts to improve electrode materials in recent years, with silver always being the unsurpassed material, closely matched only by copper on a cost-benefit basis. Some new efforts have been made considering functionalized carbons, but, at the moment, the results are a long way from the catalytic capabilities of silver and copper. As for the rest, little has been done to engineer the structure, composition, and morphology of nanostructured metallic materials, even in terms of ligand, strain effect, or support effect, with a few sporadic exceptions [69]. Furthermore, there are only few examples of in-operando tracking of the dehalogenation processes, so there is plenty of room for research.

Electrocarboxylation is for sure the most attractive way in which the electrocatalytic activation of the C–X bond

might be exploited for the synthesis of useful chemicals, especially from brominated and chlorinated derivatives. However, this process still needs further developments. For example, no study on metal-free alternatives is present in the literature. Other electrochemical processes involving R-X and electrophilic species other than CO₂ have been less investigated. Therefore, exploiting the electrocatalytic activation of C-X bonds will predictably open new fields of research for the time to come.

In the field of dehalogenation, most research is oriented toward chlorinated derivatives, especially for their recalcitrant behavior, and, for sure, the electrochemical process can play a pivotal role, provided that also a technological development in terms of cell geometry, electrodes, and device/plant structure goes hand in hand with the study of degradation phenomena. Some timid examples of technological development are present in the recent literature with the introduction of GDE, membrane electrodes, and foam electrodes, but the research is still very explorative, and solid evidence of further improvements is missing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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