Relative activity of metal cathodes towards electroorganic coupling of CO₂ with benzylic halides

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Abstract:

Electrochemical reduction of benzylic halides represents a convenient route to generating carbanions for their subsequent coupling with CO₂ to obtain various carboxylic acids. Despite the industrial prospects of this synthetic process, it still lacks systematic studies of the efficient catalysts and reaction media design. In this work, we performed a detailed analysis of the catalytic activity of a series of different metal electrodes towards electroreduction of benzylic halides to corresponding radicals and carbanions using cyclic voltammetry. Specifically, we screened and summarized the performance of 12 bulk metal cathodes (Ag, Au, Cu, Pd, Pt, Ni, Ti, Zn, Fe, Al, Sn, and Pb) and 3 carbon-based materials (glassy carbon, carbon cloth, and carbon paper) towards electrocarboxylation of eight different benzylic halides and compare it to direct CO₂ reduction in acetonitrile. Extensive experimental studies along with a detailed analysis of the results allowed us to map specific electrochemical properties of different metal electrodes, i.e., the potential zones related to the one- and two-electron reduction of organic halides as well
as the potential windows where the electrochemical activation of CO$_2$ does not occur. The reported systematic analysis should facilitate the development of nanostructured electrodes based on group 10 and 11 transition metals to further optimize the efficiency of electrocarboxylation of halides bearing specific substituents and make this technology competitive to current synthetic methods for the synthesis of carboxylic acids.

Keywords: electrocarboxylation, reduction of organic halides, CO$_2$ reduction, catalysis, electroorganic synthesis

1. Introduction

Carbon dioxide emissions into the atmosphere are responsible for continuous climate change driving the development of new technologies for CO$_2$ capture and utilization [1]. Large-scale utilization of CO$_2$ as a chemical feedstock can mitigate climate change and open the door for a carbon-neutral chemical industry [1-3]. About 130 megatones of carbon dioxide are used every year for the industrial synthesis of urea, salicylic acid, cyclic carbonates, and polycarbonates [4]. However, it is still not comparable with the annual CO$_2$ emissions (over 40 billion tones) [5]. Electrochemical fixation of CO$_2$ by different organic compounds (electrocarboxylation, or EC) is a promising strategy for the eco-friendly synthesis of carboxylic acids and their derivatives [6,7], which are widely used in the production of polymers, biopolymers, coatings and pharmaceuticals. EC is well-established as a method of synthesis of carboxylic acids from CO$_2$ and organic halides [8-14], carbonyls [15-19], alkenes [20-22], alkynes [23,24], imines [25-28] and some other compounds [29-31]. Despite a significant progress in the field, this technology is still not competitive to displace existing industrial approaches due to insufficient EC faradic efficiencies, difficulties in reaction scale up, and a lack of studies on the efficient catalysts and reaction media [32-34]. The majority of reported EC rely on the use of sacrificial anodes, which usually ensures the high yields and stability of target
carboxylic acids. However, these systems have several drawbacks, such as a gradual consumption of the electrode material, low atom economy of the overall process, and the passivation of electrodes caused by the precipitation of insoluble products. Even though more sustainable sacrificial anode-free systems are being increasingly suggested [35,36,37], the difficulty in optimizing these approaches is associated with a lack of systematic studies of the performance of different cathodic materials in these systems.

The EC of organic halides (R-Hal) has attracted more attention than the EC of other organic compounds since this reaction leads to the direct substitution of halogen by CO$_2$H function without the formation of other functions in the substrate structure (e.g. OH, NH$_2$ groups) [6]. Moreover, the EC of organohalides has relatively low energy requirements that are associated with high reactivity of C-Hal bond and the presence of specific interactions between the halogens and the metal atoms, which are usually used as cathode material. In particular, EC of benzylic halides can lead to a variety of value-added carboxylic acids and their derivatives: Ibuprofen, Naproxen, Flurbiprofen (non-steroidal anti-inflammatory drugs [39]), Clopidogrel (antithrombotic drug [40]), styrylacetic acid derivatives (synthons of γ-arylbutyrolactones [41-43]).

In general, reaction starts with an electrochemical one-electron reductive cleavage of the carbon-halogen bond yielding radicals R$^\cdot$ (E$_1$) [44], which are inactive towards CO$_2$ capturing and can only undergo free radical transformations, such as radical coupling (Figure 1a) [10,45]. At more negative potentials (E$_2$), R$^\cdot$ undergoes further reduction to R$^-$ species followed by its reaction with CO$_2$ that leads to the corresponding carboxylic acids [6]. The formation of both radical and anion species on the electrode surface in a course of organohalide reduction has been evidenced by surface-enhanced Raman spectroscopy, DFT calculations, and electron spin resonance spectroscopy [44,46,47]. Another mechanism is possible at highly negative potentials (E$_3$), where CO$_2$ can be directly reduced at the cathode surface forming an anion-radical [49], which
can either react with R-Hal [50,51] yielding carboxylic acid or be reduced to CO or oxalate [52,53]. The latter competing direct CO\(_2\) reduction reactions (CO\(_2\)RR) are not desirable as they significantly decrease the Faradaic efficiency of target EC products. Thus, an optimal catalyst for E should have a weak affinity to CO\(_2\) and a low energy requirement for the formation of a carbanion from an organic halide (R\(^+\) + 1e\(^-\) → R\(^-\)). Since the nature of the electrocatalyst affects the energy requirements of the aforementioned processes (EC and CO\(_2\)RR), an appropriate choice of a catalyst can significantly improve the efficiency of EC.

Historically, the electrochemical reduction of organic halides was widely studied at non-catalytic electrodes, such as glassy carbon [54]. In this case, the reduction process can be approximated as an outer-sphere electron transfer and a subsequent formation of anion-radical R-Hal\(^-\), followed by the bond breakage and the formation of R\(^-\) [55]. In contrast, when a metal electrode is used, the reduction usually proceeds through a so called concerted dissociative electron transfer mechanism consisting in the R-Hal bond breaking on the metal surface yielding radical R\(^-\), while an anion-radical is only a transient highly reactive surface-bound species in this case [55]. Besides the difference in the mechanism of the first step, the strong interaction of R-Hal with electrocatalyst surface in the transition state significantly lowers the energy requirements for the reaction on metal electrodes. Consequently, many EC studies were performed with catalytically active metals as cathodes, such as Ag [6,56], Cu [9,11,56], Ni [9,11,56].

Only a few works attempted to compare the activity of different metal surfaces towards electrochemical reduction of R-Hal [57]. In addition, the competing CO\(_2\)RRs were poorly studied. The absence of systematic studies of EC of benzylic halides created a need of systematic mapping of tendencies in catalytic activity of different metals towards EC and competing CO\(_2\)RRs in aprotic media. A systematic analysis along with mechanistic insights can narrow down the list of potential cathode materials to the most promising ones. Further advancements in
nanostructured materials based on the selected metals can significantly improve the efficiency of EC and make this technology competitive to current synthetic methods for the synthesis of carboxylic acids.

In this work, we screened and summarized the performance of 12 bulk metal cathodes and 3 carbon-based materials in EC and CO₂RRs (Figure 1b). Moreover, to elucidate the effect of the organic substrate structure on the catalytic activity of these metals, we performed a detailed study of the electrochemical behavior of a series of benzylic halides 1-5 (Figure 1c) and CO₂ with each cathode material. This study allowed us to map the potential windows for efficient EC on a range of cathodic materials, which is expected to facilitate further development of EC catalysts.

2. Experimental

2.1. Chemicals

Acetonitrile (CH₃CN; anhydrous, 99.8%, Sigma-Aldrich) was kept over molecular sieves prior to use. Tetraethylammonium tetrafluoroborate (TEA-BF₄; 99% Alfa Aesar), benzyl bromide (98%, Sigma-Aldrich), benzyl chloride (99%, Sigma-Aldrich), 4-methylbenzyl bromide (97%, Sigma-Aldrich), (1-bromoethyl)benzene (97%, Sigma-Aldrich), sodium iodide (> 99%, Sigma-Aldrich), 4-(bromomethyl)benzonitrile (99%, Sigma-Aldrich), bromodiphenylmethane (95%, Sigma-Aldrich), and bromotriphenylmethane (98%, Sigma-Aldrich) were used as received without further purification. Benzyl iodide was synthesized form benzyl bromide and sodium iodide according to the reported in the literature procedure [58] and purified by column chromatography (SiO₂, eluent petroleum ether – Et₂O 95:5).

2.2. Pretreatment of electrodes
12 polycrystalline bulk metals were screened as cathodes in this work: Ag, Au, Pt, Pd (>99.9%, Sigma-Aldrich) Cu, Ni, Ti, Zn, Fe, Al, Sn, and Pb (>99%, VWR). With the exception of Ag, Au, Pt, Pd, and Ti foils, all metal surfaces were mechanically cleaned to remove oxide layer and then sequentially polished with 0.3μm and 50nm alumina powders prior to electrochemical measurements. After polishing, the electrodes were washed with Milli-Q water (18.2 MΩ•cm) in an ultrasonic bath and then rinsed with acetonitrile. The cleaning procedure was repeated prior to each measurement to minimize the effect of surface oxides on the electrochemical performance of the cathodes. The carbon-based cathode materials (glassy carbon (SPI Supplies), carbon cloth (AvCarb 1071 HCB, FuelCellStore), and carbon paper (Toray Carbon Paper 060, Wet Proofed, FuelCellStore) were used as received. The surfaces of all the studied materials after the cleaning were characterized by scanning electron microscopy (SEM; Figure S4), illustrating that their surface morphologies were comparable on the nanoscale. In addition, the double layer capacitance of all electrodes was measured (Figure S3).

2.3. Instrumentation

Electrochemical measurements were carried out using a computer-controlled electrochemical workstation (Biologic SP-300). Cyclic voltammetry experiments were carried out in a three electrode H-cell equipped with an AEM (Fumasep FAB-PK-130, FuelCellStore), Pt-mesh anode, and Ag-wire quasi-reference electrode. All potentials are reported as measured (vs Ag/Ag+ quasi-reference electrode that was calibrated with Fc/Fc+ redox couple). A solution of 0.1 M TEA-BF₄ in CH₃CN (13 ml) was used as an electrolyte for both cathodic and anodic compartments in all experiments. Before each experiment the catholyte was saturated with Ar (Praxair, 99.998%) or CO₂ (Praxair, 99.999%) by continuously bubbling the gas at 10 ml min⁻¹ for 15 min, and the solution headspace kept under a positive pressure of a corresponding gas (Ar or CO₂) during the electrochemical measurements to eliminate the presence of oxygen in the
solution. All CVs were recorded within the electrolyte and cathode stability windows to avoid the effects of the electrolyte decomposition or metal oxidation on the CV behavior.

Chronoamperometric experiments were performed in the same electrochemical cell as described above; CO₂ was continuously bubbled through the reaction mixture at the rate of 14 mL min⁻¹. All reactions were stopped after passing 1F mol⁻¹, unless otherwise stated. Identification of reaction products was carried out by gas chromatography and nuclear magnetic resonance (NMR). The gas composition in the headspace of the cell was analyzed using in-line gas chromatography analysis every 20 minutes until the completion of the reaction. Liquid products were analyzed by ¹H NMR (Bruker 300MHz) of crude reaction mixtures combined with an internal standard (1,2,4,5-tetrachlorobenzene) and compared against the previously reported NMR data for R-CO₂R’, and R-R [59,60].

3. Results and discussion

3.1. CO₂RR at different metal cathodes

As generally EC of organohalides via the activation of R-Hal requires a lower energy input than EC via CO₂ activation, we first set to determine the potential window where the CO₂ activation does not occur. To this end, we investigated the electrochemical behavior of CO₂ at different bulk metal cathodes by performing cyclic voltammetry (CV) in a CO₂-saturated CH₃CN containing 0.1M TEABF₄ (Figure 2a,b). The onset potentials for CO₂ ranged from -1.4V to -1.9 V and no peaks were observed for all metals. Ag, Au, and Pt showed the least negative onset potentials (-1.4 to -1.5 V), followed by Cu, Sn, Zn, and Pd (-1.5 to -1.7 V). Ni, Pb, Fe, Ti, and Al showed the highest energy requirements for direct CO₂RR (Eₚ₀ < -1.7 V). A significant difference in CO₂RR current density values was observed for all metals following the same trend (Figure 2c). The highest rates of CO₂RR were observed for Ag, Au, Pt, Pd and Cu (>18 mA cm⁻² at -2 V), while Zn, Sn, Pb and Fe showed moderate to poor CO₂RR activity (7-12 mA cm⁻² at -2
V. Al and Ti electrodes did not show any noticeable CO$_2$RR activity in the studied potential range. It is worth noting that Ag, which is a typical catalyst of choice for EC, had the highest activity towards CO$_2$RR among the studied metals, meaning that a noticeable contribution of competing CO$_2$RR can be expected in EC at this cathode. On the other hand, all screened metals showed a very low to no CO$_2$RR activity at E > -1.5 V, making these potentials optimal for efficient EC via R-Hal activation with a minor contribution of competing CO$_2$RR.

3.2. Electrochemical reduction of benzylic halides

The voltammetric behavior of primary benzylic bromides 1a-c, secondary benzylic bromides 2a,b, benzyl chloride 3, benzyl iodide 4, and tertiary bromide 5 at different electrodes have been investigated by CV of 0.1M solution of the bromide 1-5 in Ar-saturated CH$_3$CN containing 0.1M TEABF$_4$ (Figure 3-5).

3.2.1. Benzyl bromide

The onset potentials of benzyl bromide 1a reduction were highly dependent on the nature of the metal and ranged from -0.6V to -1.6V. The lowest onset potentials were observed for group 11 (Cu, Ag, Au) and group 10 (Pd, Pt) metals, as well as for Pb.

With the exception of Ti, all metal electrodes showed at least one reduction peak (Figure 3). Only in the case of Ag, two distinct peaks were observed in CV scans of bromide 1a, which correspond to two major reduction processes: one-electron reductive cleavage of the C-Br bond with the formation of benzyl radical (PhCH$_2$Br + 1e$^-$ → PhCH$_2^*$ + Br$^-$; $E_p$ = -1.07 V), and subsequent reduction of benzyl radical to the corresponding anion (PhCH$_2^*$ + 1e$^-$ → PhCH$_2^-$; $E_p$ = -1.45 V). For Au, Cu, Pd, Pt and Pb, first reduction peak was observed as a shoulder of the second reduction peak, indicating that the reduction of PhCH$_2^*$ to PhCH$_2^-$ proceeds easier on these metals than on Ag and the two reduction steps are hardly separated from each other. For
Ni, Fe, Zn, Al, and Sn only one reduction peak was observed at $E < -1.5 \text{ V}$, more negative potentials than the reduction potential of PhCH$_2^\cdot$ ($E_{R^\cdot/R^-} = -1.43 \text{ V vs SCE}$ [61], or $\sim -1.25 \text{ V vs Ag/Ag}^+$; for conversion see SI, Figure S1). As benzyl radical has a less negative reduction potential than the parent molecule (PhCH$_2$Br), it is reduced instantly to corresponding anion at these metal electrodes and the overall process represent a stepwise two electron transfer (PhCH$_2$Br + $1e^- \rightarrow$ PhCH$_2^\cdot$ (slow) + $1e^- \rightarrow$ PhCH$_2^-$ (fast)). Based on the position of the most pronounced reduction peak, metals can be ordered in terms of their activity towards 1a reduction as follows: Ag > Cu > Pt, Au, Pd, Fe, Pb, Al > Ni, Sn, Zn > Ti.

3.2.2. 4-Methylbenzyl bromide and 4-(bromomethyl)benzonitrile

To elucidate the effects of substituents on the electrochemical behavior of benzylic bromides at different metal electrodes, we performed a series of CV experiments for bromides with an electron donating (EDG) methyl group 1b and an electron withdrawing (EWG) cyano group 1c in the para position of the aromatic ring (Figure 3) compared to benzyl bromide 1a with $\Delta E_{ons}$ of up to 0.4V and $\Delta E_p$ of up to 0.2V. Bromide 1b bearing EDG showed negatively shifted onset and peak potentials for the majority of metals: Au, Ni, Pt, Ti, Zn, Al, Sn, Pb (Table S2, S3). This shift correlates with a more negative reduction potential of 4-Me-C$_6$H$_4$CH$_2^\cdot$ ($E_{R^\cdot/R^-} = -1.62 \text{ V vs SCE}$ [61], or $\sim -1.44 \text{ V vs Ag/Ag}^+$) compared to PhCH$_2^\cdot$. Similar to the reduction of 1a, a single reduction peak was observed for Ni, Zn, Fe, Sn electrodes, indicating a stepwise two electron transfer. Ti and Sn did not show any reduction peaks. In the CV of Ag, Au, Cu, Pt, Pd, and Pb, two reduction waves were observed, either as two distinct peaks or as a peak and a shoulder. In contrast to all other metals, for Ag, the first reduction wave ($R$-Br + $1e^- \rightarrow R^\cdot$) was more pronounced for both bromides 1a and 1b which indicates the better kinetics of the first electron transfer compared to the subsequent reduction of radical species. In the case of bromide 1c with an EWG cyano group, a single irreversible peak followed by two reversible peaks were observed for almost all studied metals (with the exception of Al and Ti; Figure S2). The first peak position
was highly dependent on the nature of electrode material ranging from -0.96 V (Ag) to -1.63 V (Sn), while the positions of the following two peaks were consistent regardless of the nature of the metal (≈ -1.4 V and -1.7 V, respectively). The first peak potential for all metals (at -1.0 V to -1.6 V) was more negative than the reduction potential of 4-CN-C₆H₄CH₂⁻ (E_R•/R⁻ = -0.77 vs SCE [61], or ≈ -0.6 V vs Ag/Ag⁺), and therefore this reduction wave can be attributed to the irreversible two-electron reduction of R-Br to R⁻. Thus, the electrochemical reduction of benzyl bromides bearing a strong EWG leads to the formation of highly unstable radical species that rapidly undergo reduction to the corresponding anions. As the other two peaks at ≈ -1.4 and ≈ -1.7 V were not observed in the CVs of bromides 1a and 1b, this was a specific case for CN-substituted bromide 1c. The observed reduction waves represent a reversible reduction of CN group in bromide 1c and in electrochemically formed products (e.g., R-R, R-H) to N-centered anion radical [62]. Overall, the introduction of EDG substituent in the para position of the aromatic ring of benzyl bromide leads to negligible and metal-dependent changes in the onset and peak potentials, whereas the introduction of EWG substituent noticeably shifts onset and peak potentials towards less negative values. The reduction of H- and EDG-substituted benzyl bromides showed two noticeable peaks indicating two electron transfers. However, in the case of EWG-substituted benzyl bromide reduction, only single peak that correspond to 2e⁻ transfer was observed.

### 3.2.3. Secondary benzylic bromides: (1-bromoethyl)benzene and bromodiphenylmethane

The onset potentials for bromide 2a were highly dependent on the metal and ranged from -0.55 V to -1.45 V (Figure 4). Two distinct reduction peaks were observed for Cu, Ag, Au, Ni, Pd, and Pt at potentials ranging from -1.05 to -1.2 V (Ph(Me)CH-Br + 1e⁻ → Ph(Me)CH⁻) and -1.45 to -1.6 V (Ph(Me)CH⁻+ 1e⁻ → Ph(Me)CH⁻). A good separation of waves corresponding to the one-
and two-electron reduction processes on these metals is attributed to a higher stability of a secondary radical compared to a primary radical derived from bromide 1a. For Sn, Pb, and Al, an overlapping of the two reduction waves was observed. Fe, Zn and Ti did not show any reduction peaks. The onset potentials for bromide 2b were observed at less negative potentials (-0.3 V to -0.8 V) than that for bromide 2a (Figure 4). In contrast to 2a, only Cu and Au showed two reduction waves for the reduction of 2b (Ph2CH-Br + e⁻ → Ph2CH⁺ at -0.9 V to -1.3 V; and Ph2CH⁺ + e⁻ → Ph2CH⁻ at ~ -1.5 V). With the exception of Ti, other metals showed either peak with a shoulder (Ag, Pd, Pt, Sn, and Fe) or a single reduction peak (Ni, Zn, Al, and Pb). The observed trend indicates that a stepwise two-electron transfer is dominant for these metals, which is associated with lower energy requirements for the reduction of Ph2CH⁺ compared to Ph(Me)CH⁻ (∼0.9 V vs NHE and -1.49 V vs NHE, respectively [63]).

3.2.4. Benzyl chloride and benzyl iodide

To show the effect of the halogen on the electrochemical behavior of benzyl halides, we performed a series of CV experiments for the reduction of benzyl chloride 3 and benzyl iodide 4 at different metal electrodes (Figure 5). The onset potentials for chloride 3 were observed at more negative potentials than for benzylic bromides 1a-c and 2 (from -1.0 V to -1.5 V vs Ag/Ag⁺), which correlates with a higher bond dissociation energy of C-Cl bond compared with C-Br for benzyl halides (∼ 300 kJ mol⁻¹ and 257 kJ mol⁻¹, respectively) [64]. In contrast to benzyl bromide 1a, only single peaks were observed for Ag, Au, Cu, Pd, Pt and Pb (from -1.55 V to -1.8 V vs Ag/Ag⁺) and no peaks were observed for other metals. As the reduction peaks were observed at more negative potentials than the reduction potential of PhCH₂⁺, thus, the overall process can be considered a two-electron reduction leading to PhCH₂⁻. The onset potentials for iodide 4 were observed at less negative potentials (-0.2 V to -1.4 V) than that for benzyl chloride and bromide (Figure 5). The lower energy requirements for the reduction of iodide 4 is associated with relatively low dissociation energy of C-I bond (188 kJ mol⁻¹ [64]).
Two distinct reduction peaks were observed for Ag, Au, and Pb, indicating better separation of first and second reduction processes compared to benzyl bromide. Thus, benzyl iodide is a better organic substrate for the generation of radical species rather than anions. Ag, Ni, Pd, Pt, Pb and Zn showed peak and a shoulder, while Sn, Al, Fe, and Ti did not show any distinct peaks.

3.2.5. Bromotriphenylmethane

Finally, the reduction of tertiary bromide 5 has been studied (Figure 4). In contrast to primary and secondary benzylic halides 1-4, bromide 5 spontaneously dissociates giving a rise to cation Ph₃C⁺ [65], thus, a completely different reduction mechanism is expected in this case. Moreover, the formation of radicals in the presence of metals proceeds spontaneously [65]. Under the applied voltage, the enhanced radical formation peaked for all metals at potentials ranging from -0.24 V to -0.7 V (Ph₃C⁺ → Ph₃C●). With the exception of Ti and Pb, all metals showed a second reduction peak at a voltage between -1.0 V and -1.3 V that corresponds to the anion formation (Ph₃C● → Ph₃C⁻). For Au, Ag, Pd, and Pt the second wave consisted of two overlapping peaks that can be associated with the reduction of coexisting benzyl and aryl forms of Ph₃C● radical. For Pb, only the first reduction peak at -0.8V was observed, while Ti did not show any distinct peaks.

3.3. Electrochemical reduction of benzylic halides at carbon-based electrodes

To elucidate the catalytic activity of metals towards electrochemical reduction of organic halides, we compared the voltammetric behavior of the halides 1-5 at different metal electrodes to that at a glassy carbon electrode (GC) (Figure 6a). The reduction of benzyl bromide 1a at GC was observed at E < -1.2V with a peak at -1.75V. With the exception of Ti, all metals showed less negative onset potentials. The catalytic activity of metal electrodes was quantified by \( \Delta E_p = E_p(M) - E_p(GC) \) [66], where \( E_p(M) \) and \( E_p(GC) \) represent peak potentials for metal electrode and for glassy carbon, respectively (Table S1-S5). The value of \( \Delta E_p \) ranged from 0.68 V to -0.42 V.
Based on $\Delta E_p$ value, metals can be ordered in terms of their catalytic activity towards $1a$ reduction as follows: $\text{Ag} (0.68 \text{ V}) > \text{Cu} (0.42 \text{ V}) > \text{Pt}, \text{Au}, \text{Pb} (0.26 \div 0.3 \text{ V}) > \text{Fe}, \text{Pd}, \text{Al} (0.14 \div 0.21 \text{ V}) > \text{Sn} (0.09 \text{ V}) > \text{Zn}, \text{Ni} (-0.04 \div -0.02 \text{ V}) > \text{Ti} (-0.42 \text{ V})$. A remarkable catalytic activity was observed for Ag as well as for Cu, Pt, Au and Pb. Fe, Pd and Al showed a moderate catalytic activity towards the reduction of $1a$, while Sn, Zn, Ni and Ti did not show any enhanced activity compared to GC. Moreover, the negative $\Delta E_p$ value of -0.42V observed for Ti indicated its poor electrochemical activity. Due to the absence of catalytic activity in case of Sn, Zn, Ni and Ti, one can assume that the reduction of $1a$ on these metals proceeds via the outer sphere electron transfer.

The reduction of benzyl bromide $1b$ with EDG at GC was observed at $E < -1.2 \text{ V}$ with a peak at -1.78 V, i.e., at a more negative potential than unsubstituted benzyl bromide. A significant positive shift of the onset (to -0.72 V) and peak potential (to -1.14 V) with respect to the unsubstituted benzyl bromide was observed in the case of benzylic bromide $1c$ with EWG. A noticeable catalytic activity towards the reduction of $1b$ with $\Delta E_p$ values of $0.23 \div 0.78 \text{ V}$ was observed for Ag, Pb, Pt, Pd, Au and Cu, while the other metals behaved as non-catalytic electrodes. A positive shift of the peak potential for $1c$ reduction was observed only in the case of Ag ($\sim 0.21 \text{ V}$), indicating that the reduction on other metals likely proceeds via the outer sphere electron transfer. Similar to the metal electrodes, additional two peaks at $\sim -1.4 \text{V}$ and $\sim -1.6 \text{V}$ related to the reduction of CN group were observed in the CV of $1c$ at GC. Since the position of these peaks was the same regardless of the electrode nature, this reduction process should also proceed via the outer sphere electron transfer.

The reduction of a secondary bromide $2a$ at GC was observed at $E < -1 \text{ V}$ with a peak at -1.58V. The presence of catalytic activity in this case was observed for group 10 and 11 metals (Cu, Ag, Au, Ni, Pd, Pt) with $\Delta E_p$ values of $0.34 \div 0.51 \text{ V}$. Interestingly, Ni showed an enhanced activity towards the reduction of bromide $2a$ in contrast to the reduction of primary bromides $1a$-
c. A positive shift of both onset and peak potentials was observed for the reduction of secondary bromide 2b at GC (to -0.7V, and to -1.24V, respectively) compared to that for bromide 2a. Noticeable catalytic activity was observed only for Cu and Ag with ∆E_p values of 0.38÷0.12. Interestingly, in the case of tertiary bromide 5, all metals showed high catalytic activity with ∆E_p values of 0.3÷0.9V.

The reduction of benzyl chloride 3 at GC was observed at E < -1.5V with no peak in the studied range of potentials. Ag, Au, Cu, Ni, Pd, Pt and Pb showed less negative onset potentials for the reduction of 3, while other metals did not show a significant difference in the onset potentials compared to GC. The reduction of benzyl iodide 4 at GC was observed at E <0.8 V with a reduction peak at -1.39 V. Ag, Au, and Pb showed highest catalytic activity with ∆E_p values of up to 0.4 V. Other metals showed only moderate to no catalytic activity.

The catalytic activity of metals towards the electrochemical reduction of organic halides is associated with strong interactions of R-Hal molecule with a metal surface that lead to the formation of metal-coordinated R-Hal adducts with a weakened C-Hal bond [44,45,46]. Since the binding of a halogen atom to a metal corresponds to a significant fraction of the overall adsorption energy, the catalytic activity would be proportional to the efficiency of this binding. The catalytic activity of different metal surfaces towards the R-Hal reduction has been previously assessed from the M-Hal bonds energies [67] and the intrinsic affinity of metals to halide anions [68,69]. These studies showed that some transition metals, such as Au, Ag, and Cu, are expected to have a high catalytic activity. However, the reduction process is complex, and other factors such as the molecular structure of the organic substrate, the nature of the supporting electrolyte and the solvent has been shown to play a vital role in electrocatalytic process as well [66,68]. It is worth noting that further studies are required to further elucidate the electrocatalytic activity of metals towards EC; future DFT studies of R-Hal and intermediates adsorption on the
In addition, we performed a series of CV experiments for the reduction of bromide 2a at some other typical carbon support materials (carbon paper and carbon cloth; Figure 7b,c). In the absence of an organic substrate (Ar-saturated 0.1M TEABF₄) carbon paper showed noticeable currents at E < -1.6V, indicating a significant activity of the surface in the aprotic media, while carbon cloth along with glassy carbon were inactive. The electrochemical activity of carbon paper in the absence of any organic substrates can be associated with the presence of hydrophobic additives, such as Teflon, which may participate in electroreductive transformations [70]. In the presence of 2a, both carbon-based supports were active towards the reduction of benzylic bromide 2a at E < -0.8V, with performance comparable to that of GC; we note that no peak was observed in the CV in the case of carbon cloth, likely due to mass transport limitations associated with a high surface area of this material.

3.4. Electrochemical reduction of benzylic bromides in the presence of CO₂

As mentioned above, the reduction of benzylic bromides in the presence of CO₂ yields carboxylate (RBr + CO₂ + 2e⁻ → RCO₂⁻ + Br⁻). EC can proceed either via the activation of R-Hal or via the activation of CO₂ yielding the same product. The mechanism of EC in the potential window of CO₂ stability (E > -1.5V) is well understood and represents a nucleophilic addition of electrogenerated carbanions to CO₂. At more negative potentials, the mechanism becomes more complex due to the formation of CO₂⁻. To elucidate the effect of the presence of CO₂ on EC, we carried out a series of CV experiments for the reduction of bromide 2a in Ar- and CO₂-saturated electrolyte (0.1M TEABF₄) at Ag, Au, and Pd electrodes (Figure 7). The organic substrate and the electrodes were chosen due to a high distance between two reduction
peaks in these systems ($\Delta E = 370\div440\text{mV}$) that makes possible to separately analyze the effect of CO$_2$ on the electrochemical conversion of 2a to the corresponding radical and anion.

The CV curves for the reduction of bromide 2a were almost identical for Ar- and CO$_2$-saturated electrolyte in the radical zone for all three metals, which supports the absence of interactions between R’ species and CO$_2$. Noticeable changes in CV curves were observed at more negative potentials after CO$_2$RR onset potential: the reduction currents were significantly increased in the presence of CO$_2$ (in 1.6, 2.0 and 1.4 times at -1.8 V for Ag, Au, and Pd, respectively). These changes indicate the presence of a new reduction process besides the reduction of bromide 2a, i.e. CO$_2$ + e$^-$ → CO$_2$•−. In our previous studies, we showed that at these potentials, CO was not formed in a course of EC of 2a at Ag electrode when the concentration of an organic substrate was relatively high (0.05 M); however, the formation of CO was observed, when the concentration was low [10]. The higher current densities observed in EC and the absence of CO as a product support the hypothesis that CO$_2$•− reacts with R-Br yielding carboxylate. One of the possible mechanisms is the electron transfer from CO$_2$•− to R-Br [50] leading to R’ and its subsequent coupling with excess of CO$_2$•−. A detailed understanding of the interactions of reactive intermediates of both EC and CO$_2$RR with the catalytic surface is required for a better description of the reaction mechanism at high negative potentials. However, these interactions are rarely considered in the electrochemical reduction of organic halides [44], especially in EC [10].

In all studied combinations of the organic substrates and electrode materials, no to minor influence of CO$_2$ on the electrochemical behavior of bromide 2a was observed in the CO$_2$ electrochemical window. At more negative potentials, the presence of both EC mechanisms, via the activation of R-Hal and via the activation of CO$_2$, is expected due to a limited mass transport of both CO$_2$ and R-Hal species to the electrode surface. The contribution of the latter mechanism for a specific metal electrode should correlate with the rate of CO$_2$RR at that metal (Figure 2).
Thus, based on our experimental data presented in the Section 3.1, at \( E < -1.5V \), the highest rates of EC via \( \text{CO}_2 \) activation is expected for Ag and Au, followed by Cu, Pt and Pd.

In addition to the CV studies, we performed potentiostatic electrolysis of benzyl bromide 1a in the presence of \( \text{CO}_2 \). All reactions were carried out at the initial bromide concentration of 25 mM using different metals and glassy carbon as cathodes. The potentials for electrolysis were selected near the reduction peak in the cathodic sweeps of the CV that correspond to \( 2e^- \) transfer with two exceptions. Specifically, in the case of Al and Fe, the electrolysis was performed at more negative potentials due to the low activity of these electrodes at peak potentials under the electrolysis conditions. All reactions were stopped after passing electric charge of 1 F mol\(^{-1}\). The gas products were analyzed using the in-line GC analysis every 20 minutes that allowed us to estimate \( \text{FE}_{\text{CO}}(t) \) dependence and calculate total FE of \( \text{CO} \). The products of benzyl bromide reduction were analyzed and quantified by NMR of crude reaction mixture with 1,2,4,5-tetrachlorobenzene as an internal standard. The results are summarized on the Figure 8a,b and in Table S10. The major products of all reactions were carboxylate \( \text{RCO}_2^- \) with FEs ranging from 50 to 91\%, dimer \( \text{R-R} \) (0-36\%), and \( \text{CO} \) (0-17\%). Cu, Ag, Au, Pd, Pt, Pb, and GC showed the lowest FEs of \( \text{CO} \), since the carboxylation reactions proceeded at the potentials at the very onset of \( \text{CO}_2 \RR \). The FE of carboxylate was high for all electrodes but Ag. In the case of Ag, the main by-product was \( \text{R-R} \) (36\%) that was formed by a coupling of electrogenerated radicals. From all the aforementioned metal electrodes, Cu and Au showed the highest FE of carboxylate (up to 81\%). Other tested metals (Ni, Zn, Fe, Al, Sn) showed noticeable FEs of \( \text{CO} \) and only moderate FEs of carboxylate. The electrolysis in these cases proceeded at the potentials significantly more negative than \( \text{CO}_2 \RR \) onset (< -1.7 V), which was the reason of high rates of this competing process. Ti was the only exception, and FE of \( \text{CO} \) in this case was only 4.4\% even though the applied potential was very negative (~2.25 V). The FE of carboxylate was also surprisingly high in this case (~ 85\%). Overall, the highest FEs of carboxylate were observed for three catalytic
metals (Cu, Au, and Pb; FE$_{RCO_2}$ ~ 80%) and two non-catalytic electrodes (Ti and GC; FE$_{RCO_2}$ of up to 91%). Even though the highest FE of carboxylate were observed at non-catalytic electrodes, the reaction in these cases proceeded at more negative applied potentials and at significantly lower current densities (2-8 mA cm$^{-2}$) compared to Cu, Au and Pb (15-25 mA cm$^{-2}$).

Finally, to show the effect of the halogen on the competition between EC and CO$_2$RR processes, we performed potentiostatic electrolyses of benzyl bromide, chloride and iodide at Ag electrode at high negative applied potential of -1.9V, where CO$_2$RR and EC have comparable initial current densities. (Figure 8c). In all these cases, almost no CO was produced in the beginning of the electrolysis (Q < 0.5 F mol$^{-1}$). Noticeable FEs of CO (> 2 %) were observed for electrolysis benzyl iodide, bromide and chloride after passing an electrical charge of 0.5, 0.75 and 0.1 F mol$^{-1}$, respectively. FE of CO in the case of the bromide and iodide rose to 80% close to 2F mol$^{-1}$ charge passed, while in the case of the chloride FE of CO was still below 20%. The difference between the halides behavior at high negative potentials can be associated with their different adsorption profiles. For instance, it was shown that binding of benzylic bromides to the Ag surface decreases with a shift of applied potentials to more negative values [10].

3.5 Summary of the results

Figure 9 summarizes the performance of all studied metal electrodes towards the reduction of benzylic halides 1-4 and CO$_2$. Metals in group 11 (Cu, Ag, Au) and group 10 (Pd, Pt; also Ni for halides 2a and 4), as well as Pb in some cases (for halides 1a,b, and 4) showed the highest activities in both electroreduction processes making these metals the most promising materials
for electrochemical reduction of organic halides. Due to the enhanced catalytic activity observed for these metals, it is expected that the atomic and nanoscale surface morphology can significantly affect efficiency and selectivity of EC, as it has been shown for other electrocatalytic processes [71,72]. Systematic studies of nanostructured electrodes comprised of these metals in EC is a promising route to further optimization of the onset potentials and the activity of the electrocatalytically active sites. Zn, Fe, Sn and Al showed moderate to low activity in the majority of studied reduction processes; Ti was found to be inefficient towards EC. Moreover, the latter metals did not show noticeable catalytic activity.

The mechanism of R-Hal reduction was found to be highly dependent on both the nature of the electrocatalyst and the structure of the organic substrate. With the exception of organic halides bearing a strong EWG, the first electron transfer proceeds at relatively low potentials (E < -0.6V); however, the second electron transfer (R’ + 1e− → R−) requires a higher energy input and generally proceeds at E < -1.0V for all studied metal electrodes. The presence of EWG in the structure of a halide significantly lowers the energy requirements for the second electron transfer, which in this case can proceed at E > -1.0V. The EC of organic halides via the activation of R-Hal occurs in a narrow potential window (∆E ~ 0.1÷0.7 V for halides 1a,b, 2a,b, 4 and 3; ~ 0.4÷0.9 V for halide 1c; Tables S2-S9). Among the metals with high catalytic activity towards the reduction of organic halides, Ni and Pb showed the widest gap between EC and CO2RR with ∆E > 0.5 V, while for other catalytic metals ∆E ranged from 0.1 to 0.3 V. At high negative potentials the competing formation of CO2− species is observed. Even though at high concentrations of organic substrate the CO2− species still participate in EC, with a decrease in the organic substrate concentration competing CO2RR starts to dominate, resulting in decreased faradic efficiencies of EC. Subsequently, this factor can lead to difficulties in achieving full conversion without CO as a side product. Metal nanoparticles with optimized catalytic sites can solve the problem with a narrow potential gap between CO2RR and EC by selectively decreasing
the energy requirements for the second electron transfer ($R^\cdot + 1e^- \rightarrow R^-$). Moreover, the absence of the direct correlation between the activity of a metal towards the reduction of an organic halide and CO$_2$ makes possible further EC optimization by favoring the electrocatalyst selectively towards reducing an organohalide in the presence of CO$_2$ in a wide potential range while avoiding CO$_2$ activation. Nanoparticle-based electrodes typically rely on a conductive carbon support for electrode fabrication, but due to the intrinsic activity of several commercially available bare supports under EC reaction conditions (Figure 6) the surface of the support should be well covered by nanoparticles to exclude its effect on the electroreduction process. Alternatively, conductive metals such as Ti with low activity towards EC and CO$_2$RR can be used as supports.

**Conclusions**

In conclusion, we performed a detailed study of the electrochemical reduction of a series of benzylic halides (benzyl bromide, 4-methylbenzyl bromide, 4-(bromomethyl)benzonitrile, (1-bromoethyl)benzene, bromodiphenylmethane, bromotriphenylmethane, benzyl chloride, and benzyl iodide) to radicals and carbanions at different metal electrodes in acetonitrile using cyclic voltammetry. A broad scope of electrodes has been screened in this work to elucidate the effect of cathode material nature on the efficiency of carbanion formation, which is the major intermediate in EC reactions.

Extensive experimental studies conducted under the same conditions along with detailed analysis of the results allowed us to map the specific electrochemical properties of different metal electrodes, such as potentials zones for the efficient one- and two-electron reductive cleavage of C-Hal bond, and the potential windows where the CO$_2$ electrochemical activation does not occur. We demonstrated that both the nature of the cathode material and the nature of an organic halide significantly affect the outcome of the reduction process. First, we showed that
the reduction of R-Hal on non-catalytic metals (Fe, Al, Sn, Zn, and Ti) requires high energy input and leads to the formation of R⁻ species. Second, we found that Ag, Au, Cu, Pt, Pd, and in some cases Ni and Pb show noticeable catalytic activity towards the reduction of Ph-CH₂Br, Me-C₆H₄-CH₂Br, Ph-CH(Me)Br, and Ph-CH₂I with ΔEₚ values of up to 0.8 V compared to non-catalytic glassy carbon. For these metals, the reduction proceeds through an initial formation of R* at the potentials ranging from -0.6 V to -1.1 V, providing a convenient route to generating radical species under mild conditions. At more negative potentials (E < -1.1 V), R* undergoes a second electron transfer yielding R⁻, which can be further coupled with CO₂ to afford carboxylic acids. In contrast to the aforementioned benzylic bromides, the reduction of NC-C₆H₄-CH₂Br requires less energy input, but still yields R⁻. However, in this case only Ag showed a moderate catalytic activity with ΔEₚ of 0.18 V. Third, we showed that, in contrast to Ph-CH₂Br, the reduction of Ph-CH₂Cl proceeds at more negative potentials and yields R⁻ without an intermediate formation of R*. We demonstrated that at high negative potentials competing CO₂ reduction to CO₂⁻ is observed, which lowers the faradic efficiencies of EC. We showed that for typical catalysts of choice for EC (e.g. Ag) the potential gap between CO₂RR and EC is narrow with ΔE < 0.3V, while for less common catalytic metals for EC such as Ni and Pb ΔE > 0.5V. Finally, potentiostatic electrolysis of Ph-CH₂Br in the presence of CO₂ at the organohalide reduction peak potentials showed that EC on the catalytic metals (Au, Cu, Pb, Ag) can proceed without any contribution of competing CO₂RR, giving rise to the target EC products with FEs of up to 81%.

Summing up, this study demonstrates the main patterns in the electrochemical reduction of organic halides at different metal electrodes in acetonitrile and opens the door for a rational catalyst design for efficient EC.

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References


10.1016/j.tetlet.2006.01.113.


[53] Hori Y. Electrochemical CO₂ Reduction on Metal Electrodes, in: Vayenas C. G., White R. E.,
Gamboa-Aldeco M.E. (Eds.) Modern Aspects of Electrochemistry. Modern Aspects of


10.1039/B513801A.

DOI: 10.1002/nano.202000001.


[58] A. Grozavu, H. B. Hepburn, E. P. Bailey, P. J. Lindsay-Scott, T. J. Donohoe, Chem. Sci. 11
(2020) 8595-8599.

10.1002/ejoc.200600070.


Figure 1. (a) Electrochemical transformation of organic halides in the presence of CO₂. The scope of electrocatalysts screened in the study (b) and molecular structures of the investigated benzylic halides (c).

Figure 2. (a,b) Cathodic sweeps of cyclic voltammograms recorded for the reduction of CO₂ in aprotic media. All voltammograms were recorded at 50 mV s⁻¹ scan rate at different bulk metal cathodes (working area ~ 0.2 cm²) in CO₂-saturated CH₃CN–0.1 M TEABF₄. (c) The activity of
different metal cathodes towards CO$_2$RR (y-axis shows the current density of CO$_2$RR at -2 V vs Ag/Ag$^+$; x-axis shows the onset potential for direct CO$_2$RR); green circles correspond to the electrodes with $E_{\text{ons}}$(CO$_2$RR) > -1.7V, while grey circles correspond to the electrodes with more negative onset potentials for CO$_2$RR.

**Figure 3.** Cathodic sweeps of CV recorded for the reduction of 100 mM solutions of primary benzylic bromides 1a-c. All voltammograms were recorded at 50 mV s$^{-1}$ scan rate at different bulk metal cathodes (working area ~ 0.2 cm$^2$) in Ar-saturated CH$_3$CN containing 0.1 M TEABF$_4$. 
Figure 4. Cathodic sweeps of CV recorded for the reduction of 100 mM solutions of secondary benzylic bromides 2a,b and 25mM solution of tertiary benzylic bromide 5 (CVs for benzyl bromide 1a are given for the reference). All voltammograms were recorded at 50 mV s\(^{-1}\) scan rate at different bulk metal cathodes (working area ~ 0.2 cm\(^2\)) in Ar-saturated CH\(_3\)CN containing 0.1 M TEABF\(_4\).
Figure 5. Cathodic sweeps of CV recorded for the reduction of 100 mM solutions of benzyl chloride 3 and benzyl iodide 4 (CVs for benzyl bromide 1a are given for the reference). All voltammograms were recorded at 50 mV s⁻¹ scan rate at different bulk metal cathodes (working area ~ 0.2 cm²) in Ar-saturated CH₃CN containing 0.1 M TEABF₄.

Figure 6. Cathodic sweeps of CVs recorded for the reduction of 100 mM solutions of benzylic halides 1a-c (a), 2a(a-c), 2b (a) and 3-5 (a). Voltammograms were recorded at 50 mV s⁻¹ scan
rate at glassy carbon (a), carbon cloth (b) and carbon paper (c) (working area ~ 0.1 cm$^2$) in Ar-saturated CH$_3$CN containing 0.1 M TEABF$_4$. Dashed lines for carbon cloth and carbon paper correspond to the electrochemical behavior of cathodes in the absence of substrate.

**Figure 7.** Cathodic sweeps of CVs recorded for the reduction of 100 mM solutions of (1-bromoethyl)benzene 2a. Voltammograms were recorded at 50 mV s$^{-1}$ scan rate at Ag-, Au- and Pd-foil cathodes (working area ~ 0.2 cm$^2$) in CO$_2$-saturated (solid red trace) and Ar-saturated (dashed black trace) CH$_3$CN containing 0.1 M TEABF$_4$. CVs for the reduction of CO$_2$ (dotted blue trace) are shown for reference.

**Figure 8.** Total Faradaic efficiencies of CO (a) and carboxylate (b) in the electrolysis of 25mM benzyl bromide + CO$_2$-saturated CH$_3$CN–0.1 M TBABr as a function of applied potential and the electrode nature. Green circles correspond to the electrodes favoring EC with minor contribution of competing CO$_2$R. (c) Faradaic efficiencies of CO in the electrolysis of 25mM benzyl bromide, chloride, and iodide performed at -1.9V as a function of charge passed.
Figure 9. The potentials of the electrochemical reduction of organic halides 1-4 and CO$_2$ at different bulk metal cathodes in CH$_3$CN containing 0.1 M TEABF$_4$. The pin colors correspond to cathode materials (see the legend on the top). The empty circles correspond to the potentials at 5mA cm$^{-2}$ for the two-electron reduction of R-Hal at GC. The filled bars correspond to the potentials at 5mA cm$^{-2}$ for the one-electron reduction of benzylic halides (R-Hal + 1e$^-$ → R$^\cdot$) 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, R$^\cdot$ + 1e$^-$ → R$. The triangles correspond to the potentials at 5mA cm$^{-2}$ for the one-electron reduction of benzylic halides for the cases when two reduction waves are overlapped. The filled circles correspond to the potentials at 5mA cm$^{-2}$ for the two-electron reduction of R-Hal to R$^-$ 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 CO$_2$ to CO$_2$$^\cdot$. 