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Direct electrochemical halogenation has appeared as an appealing approach in synthesizing organic halides where inexpensive inorganic halide sources are employed and electrical power is the sole driving force. However, the intrinsic characteristics of direct electrochemical halogenation limit its reaction scope. Herein, we report an on-site halogenation strategy utilizing halogen gas produced from halide electrolysis while the halogenation reaction takes place in a reactor spatially isolated from the electrochemical cell. Such a flexible approach is able to successfully halogenate substrates bearing oxidatively labile functionalities which are challenging for direct electrochemical halogenation. In addition, low-polar organic solvents, redox-active metal catalysts, and variable temperature conditions, inconvenient for direct electrochemical reactions, could be readily employed for our on-site halogenation. Hence, a wide range of substrates including arenes, heteroarenes, alkenes, alkynes, and ketones all exhibit excellent halogenation yields. Moreover, the simultaneously generated H_2 at the cathode during halide electrolysis can also be utilized for on-site hydrogenation. Such a strategy of paired halogenation/hydrogenation maximizes the atom economy and energy efficiency of halide electrolysis. Taking advantage of the on-site production of halogen and H_2 gases using portable halide electrolysis but not being suffered from electrolyte separation and restricted reaction conditions, our approach of flexible halogenation coupled with hydrogenation endows green and scalable synthesis of organic halides and value-added products.

Introduction

Since sustainability has become a prime direction for organic synthesis, there is no doubt that the renaissance of organic electrosynthesis will continuously attract increasing attention, in that electricity can be generated from sustainable resources while stoichiometric oxidants/reductants could be avoided in organic redox reactions.[1,2] Organic electrosynthesis also enables precise control of conversion and selectivity by adjusting multiple electrochemical parameters including electrode, electrolyte, applied potential, current, electrocatalyst, etc.[1-3] These years have witnessed impressive achievements in organic electrosynthesis from both anodic[4-6]and cathodic[7-9] perspectives, such as alcohol oxidation,[10-12] allylic C-H oxidation,[13] diazidation,[14] dichlorination,[15] and heterodifunctionalization of alkenes,[16] anodic C-C bond cleavage, [17] hydrodimerization of aldehdyes,[18] redox mediator-assisted transformations, [13, 19-21] and paired electrolysis.[22-24]

Among many important organic electrochemical reactions, direct electrochemical halogenation (*e.g.*, bromination and chlorination) holds a unique position because of the prevalence of organic halides in the synthesis of natural products, pharmaceuticals, and industrially important chemicals.[25-28] By virtue of facile electrochemical oxidation of halide anions, non-toxic and inexpensive inorganic halides can be utilized as halogen sources, representing greener alternatives to expensive and/or toxic counterparts used in conventional halogenation reactions.[29] For instance, Raju *et al* reported two-phase (chloroform/water) electrochemical bromination of aromatic compounds using NaBr as the bromine source[30] and Lei's group studied the electrochemical oxidative halogenation of heteroarenes by employing HX/NaX (X = Br, Cl) in N,N-dimethylformamide/water (Figure 1).[31] $Cu(OAc)_2$-catalyzed electrochemical bromination of amides using NH_4Br as the bromine source has also been reported.[32]

Nevertheless, due to the inherent requirements of organic electrosynthesis, several limitations exist in those aforementioned *direct* electrochemical halogenation. For instance, the oxidation potential of bromide anion dictates a small potential window for direct electrochemical bromination, which bears limited tolerance to oxidatively labile functional groups (*e.g.*, amines). Secondly, transition metal catalysts are frequently employed in various halogenation reactions, however the presence of redox-active metal species may severely interfere with direct electrochemical halogenation. In addition, aqueous or polar organic solvents are typically required in electrolyte solutions, which are not always compatible with certain halogenation reactions conducted in nonpolar organic media.[33] Furthermore, the separation of supporting electrolytes from halogenated products results in additional cost. Finally, the reduction reaction on the cathode, usually H_2 evolution, has not been well utilized in reported direct electrochemical halogenation. Overall, these collective limitations of direct electrochemical halogenation call upon a more flexible and versatile strategy for the synthesis of organic halides which can utilize both electricity and low-cost halide sources.

Inspired by decoupled water splitting,[34] paired electrolysis, [22-

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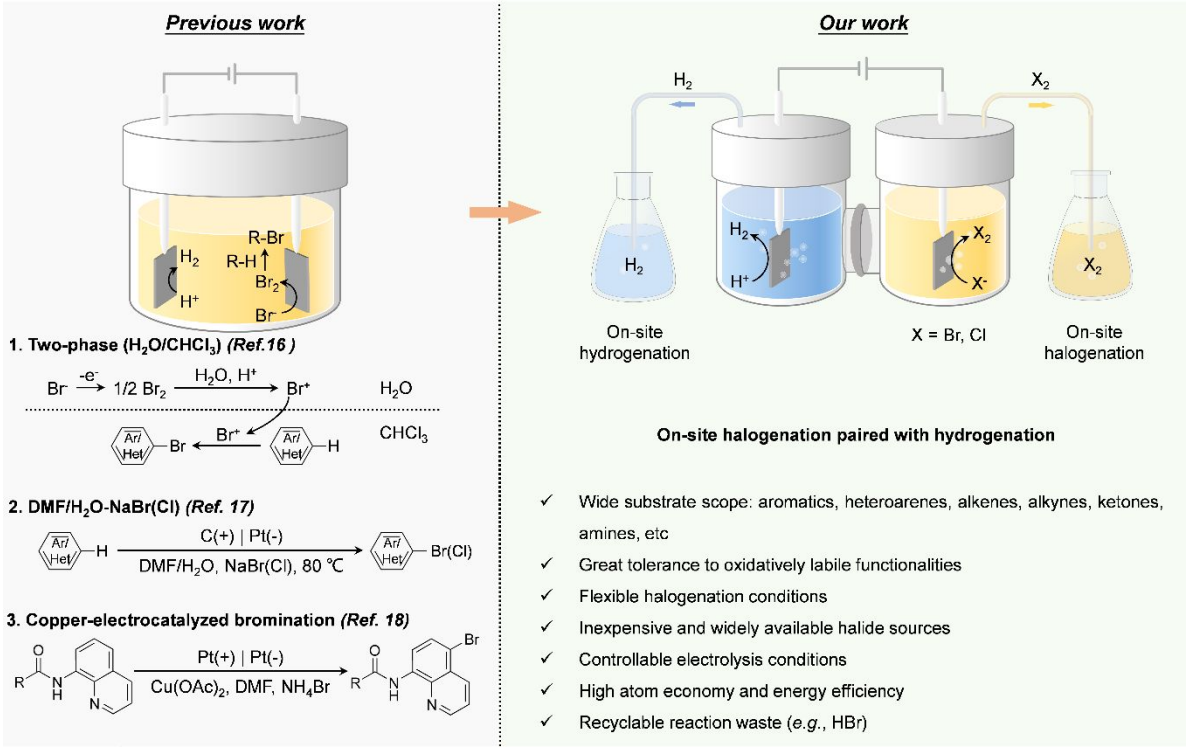


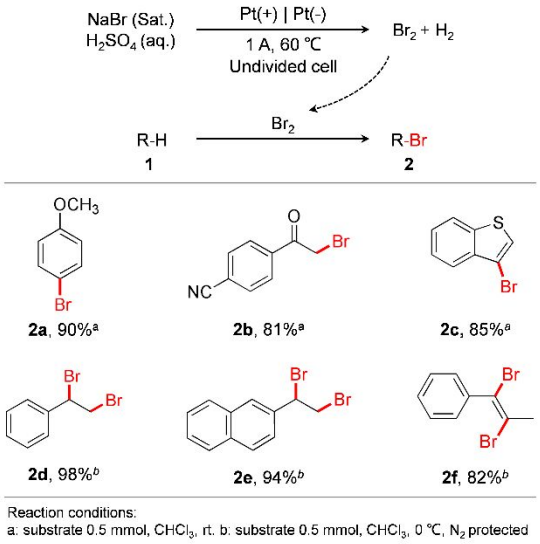
Figure 1. Reported *direct* electrochemical bromination and a schematic of paired on-site halogenation/hydrogenation described in this work.

[24]and hydrogenation in an isolated chamber utilizing electrochemically produced H_2[34-36] or Pd-adsorbed hydrogen,[37-39] we envision that it is feasible to conduct on-site halogenation employing electrochemically generated Br_2 (or Cl_2), taking advantage of the phase separation of Br_2 (or Cl_2) from the electrolyte solution. As shown in Figure 1, the one-compartment electrochemical cell in direct electrochemical halogenation is replaced by an H-type cell for the electrolysis of inorganic halides in aqueous electrolytes. The generated volatile halogen gas (Br_2 or Cl_2) will readily migrate through a Teflon tubing to an isolated chamber for on-site halogenation. In the meantime, H_2 produced on the cathode will be transported to another chamber for on-site hydrogenation. Consequently, these two spatially separated chemical reactions from halide electrolysis effectively bypass restrictions in conventional electrochemical halogenation. Herein, we will demonstrate that such a flexible on-site halogenation strategy is applicable to a wide variety of organic substrates, including those with oxidatively labile functional groups, and can also be performed under conditions incompatible to direct electrochemical halogenation, such as employment of redox-active metal catalysts and nonpolar organic solvents. Further taking advantage of H_2 produced on the cathode, our on-site halogenation can be seamlessly coupled with on-site hydrogenation, maximizing the energy return of electricity input for the halide electrolysis.

Results and discussion

Feasibility of on-site bromination using electrochemically produced Br_2

In order to prove the feasibility of our on-site halogenation strategy, an undivided cell in two-electrode configuration employing Pt as both anode and cathode was first adopted to perform the electrolysis of saturated NaBr in H_2SO_4 at a constant current of 1 A. The produced Br_2 gas in the headspace of the electrochemical cell was transported to another chamber for bromination reactions. Because of the spatial separation between organic bromination and bromide electrolysis, the bromination condition is completely independent on the electrolysis condition. As shown in Scheme 1, six representative organic substrates, including arenes, heteroarenes, aromatic ketones, alkenes, and alkynes could be successfully brominated using on-site produced Br_2. It should be noted that direct electrochemical bromination of these substrates has been reported with reasonable to excellent yields (50~98%).[32, 40, 41]Specifically, following our on-site bromination strategy, anisole (**1a**) exhibited high reactivity and the corresponding 4-bromoanisole (**2a**) was produced in 90% yield. In addition, selective bromination of aromatic ketones, such as on-site bromination on the side alkyl chain in 4-acetylbenzonitrile (**1b**)



Scheme 1. On-site bromination of representative aromatics, alkyls, alkenes, and alkynes.

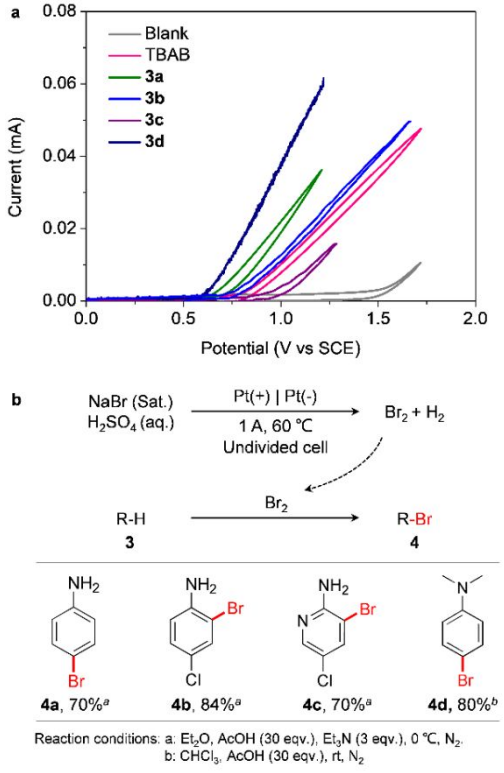


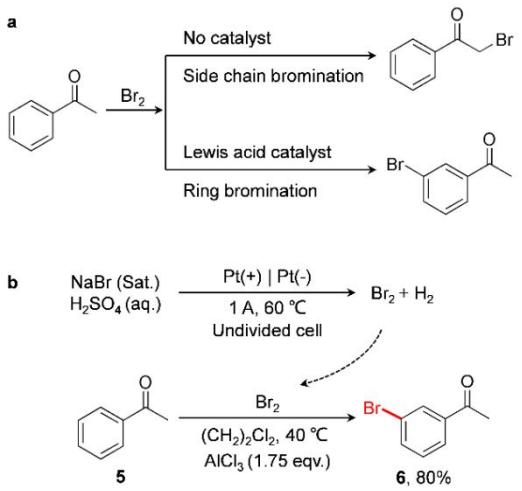
Figure 2. (a) Cyclic voltammograms of aniline (**3a**), 4-chloro-benzenamine (**3b**), 5-chloro-2-pyridinamine (**3c**), and N,N-dimethyl-benzenamine (**3d**), compared to that of tetra-*n*-butylammonium bromide (TBAB) on glassy carbon electrode (3 mm in diameter) in CH_2Cl_2. The concentration of substrate was 10 mM. Scan rate: 50 mV s^{-1}. (b) On-site bromination yields of the above four amine substrates.

to yield 4-(2-bromoacetyl)benzonitrile (**2b**) also proceeded smoothly with a decent yield of 81%. Our on-site bromination approach was also amenable to heteroarenes. For instance, benzo[*b*]thiophene (**1c**) could be brominated to produce 3-bromobenzo[b]thiophene (**2c**) with an excellent yield of 85%. It's worth noting that all these three bromination reactions were conducted at room temperature in $CHCl_3$, different from the strongly acidic condition of bromide electrolysis.

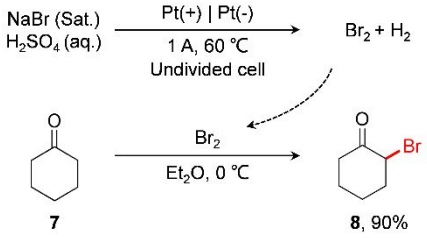
Notably, our on-site bromination was able to demonstrate exceptionally high efficiency in converting alkenes to vicinal dibromides, such as from styrene (**1d**) to (1,2-dibromoethyl)benzene (**2d**) and from 2-vinylnaphthalene (**1e**) to 2-(1,2-dibromoethyl)naphthalene (**2e**) with yields of 98% and 94%, respectively. Besides alkenes, dibromination of alkynes is fundamental to provide versatile intermediates for synthetic applications.[42, 43] A recognized challenge for the successful dibromination of alkynes is the high reactivity of the resulting dibromides bearing a C=C bond that may undergo further bromination. To our delight, on-site bromination was able to produce (1,2-dibromoprop-1-en-1-yl)benzene (**2f**) from 1-phenyl-1-propyne (**1f**) with a high yield of 82%. Such a high conversion efficiency was probably attributed to a more precise control of Br_2 feed rate in our on-site bromination. It is necessary to mention that these dibromination reactions took place in $CHCl_3$ at 0 °C, a temperature condition inconvenient for direct electrochemical bromination.

On-site bromination of organic substrates with oxidatively labile functional groups

After proving the effectiveness of on-site bromination for the aforementioned organic substrates, we next sought to explore its applicability towards those substrates which are challenging for direct electrochemical bromination. An apparent limitation of direct electrochemical bromination is the low tolerance of substrates bearing oxidatively labile functionalities, such as amine groups. For instance, the oxidation potentials of organic amines usually range from 0.3 to 1.3 V vs saturated calomel electrode (SCE),[44] however the redox potential of Br_2/Br^- is ~0.8 V vs SCE.[45] Consequently, the applied potential necessary for bromide oxidation in direct electrochemical bromination of organic amines will inevitably result in the oxidation of many amine groups, leading to side-products and low faradaic efficiency. Figure 2a presents the cyclic voltammograms of aniline (**3a**), 4-chloro-benzenamine (**3b**), 5-chloro-2-pyridinamine (3c), N,N-dimethyl-benzenamine (**3d**), and tetra-*n*-butylammonium bromide in CH_2Cl_2. The onset potential of bromide oxidation is ~0.75 V vs SCE while the onset oxidation potentials of those four amines are observed at ~0.63, 0.69, 0.90, and 0.58 V vs SCE, respectively, which are apparently less positive or close to the former. Any potential required for bromide oxidation (>0.75 V vs SCE) will definitely result in undesirable amine oxidation, as reflected in the poor yields (33-59%) from previous reports for the electrochemical bromination of these amines.[31, 46] In striking contrast, our on-site bromination completely avoids the direct interaction of amine substrates with any electrode, therefore higher bromination yields would be anticipated. Indeed, as shown in Figure 2b, on-site bromination of **3a** and **3b** both afforded decent yields of 4-bromoaniline (4a, 70%) and 2-bromo-4-chloroaniline (**4b**, 84%), respectively. The less reactive **3c** could also be on-site brominated to form 3-bromo-5-chloro-2-pyridinamine (**4c**) with a yield of 70%. Compared to aniline, **3d** achieved a higher bromination yield (80%) at the *para*-position, resulting in 4-bromo-N,N-dimethylaniline (**4d**), probably due to the steric hindrance of the dimethylamine group in preventing bromination at its *ortho*-position. Overall, no amine group



Scheme 2. (a) Different bromination pathways of acetophenone with or without a Lewis acid catalyst. (b) On-site bromination of acetophenone (**5**) using $AlCl_3$ as a Lewis catalyst.



Scheme 3. On-site bromination of cyclohexanone in diethyl ether at 0 °C.

oxidation was detected for these four amine substrates, superior to direct electrochemical bromination.

On-site bromination of organic substrates with metal catalysts

For substrates with multiple functionalities, there may exist several potential bromination sites. In order to form the desirable bromination product selectively, redox-active metal catalysts have been frequently employed. [47-50] For instance, bromination of acetophenone (**5**) may take place on the benzene ring or the side acetyl group (Scheme 2a). The deactivation effect of the acetyl group in **5** renders aromatic bromination thermodynamically challenging. Actually, aromatic bromination using the direct electrochemical method is always limited to those activated aromatics.[29,30] Instead, direct electrochemical bromination of **5** produced acetyl brominated product exclusively.[33] Nevertheless, Lewis acid catalysts such as $FeBr_3$ and $AlCl_3$ have been shown to interact with Br_2 to form strongly electrophilic brominating reagents, which are able to accomplish aromatic bromination of deactivated aromatics. [51-54] However, the redox activity of these metal catalysts may severely interfere with direct electrochemical bromination and leads to complicated product mixtures. As shown in Scheme 2b, following our on-site bromination strategy, $AlCl_3$ was introduced to the bromination reactor isolated from bromide electrolysis. Consequently, aromatic bromination of acetophenone (**5**) proceeded smoothly to deliver 1-(3-bromophenyl)ethanone (**6**) in 80% yield, comparable to reported results using conventional brominating reagents.[55] For comparison, the on-site bromination without $AlCl_3$ only produced 2-bromoacetophenone and 2,2-dibromo-1-phenylethanone (Figure S3), highlighting the important role played by the Lewis acid catalyst $AlCl_3$.

On-site bromination of substrates in solvents challenging for electrochemistry

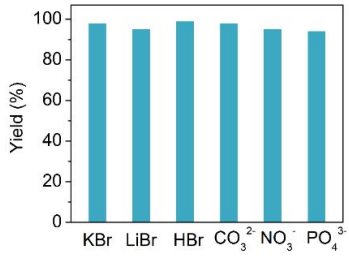
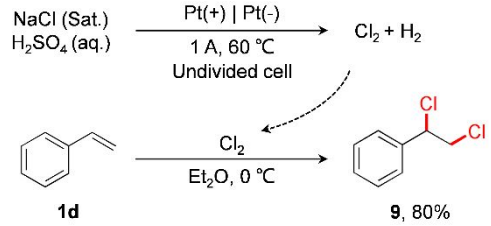


Figure 3. Dibromination yield of styrene to produce (1,2-dibromoethyl)benzene (2d) using various bromide sources and in the presence of other common anions (50 mM) for the on-site production of Br_2.



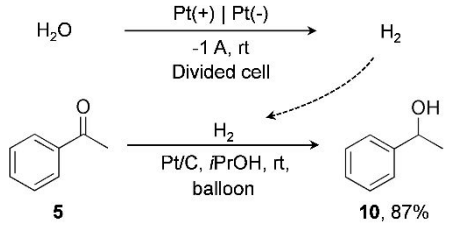
Scheme 4. On-site chlorination of styrene in diethyl ether at 0 °C.

Aqueous or polar organic solvents with supporting electrolyte are mandatory for direct electrochemical halogenation. Such a requirement of reaction medium is incompatible with certain halogenation reactions which is preferred to be conducted in nonpolar organic solvents (e.g., Et_2O and CCl_4). As an example, α-bromination of cyclic ketones exhibits faster reaction rate and higher yield in nonpolar solvents like Et_2O or CCl_4 than in polar solvents like $CHCl_3$ or MeOH.[56-58] In this regard, our on-site bromination strategy could be conveniently adopted to perform the α-bromination of cyclohexanone (**7**) in Et_2O at 0 °C as presented in Scheme 3. The desirable product of 2-bromo-cyclohexanone (**8**) was obtained with a high yield of 90%. Moreover, the absence of supporting electrolyte in the bromination chamber renders product separation/purification extremely facile.

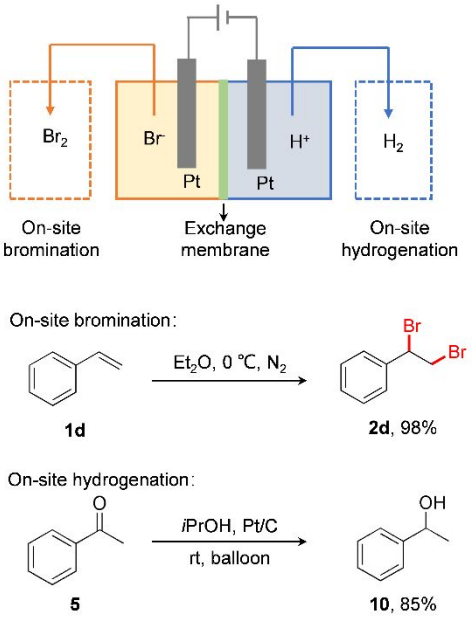
Flexibility in bromide source for on-site bromination

In addition to great suitability for challenging substrates and reaction conditions, our on-site bromination strategy also exhibits excellent flexibility in the choice of bromide source for the on-site production of Br_2. As shown in Figure 3, bromide electrolysis utilizing KBr, LiBr, and HBr all produced superior results for the on-site bromination of styrene, yields > 90%. It should be noted that HBr is actually a byproduct of many bromination reactions, hence our on-site bromination strategy realizes the recycling of HBr which is otherwise a waste, further improving atom economy and minimizing environmental impact. Due to the relatively low oxidation potential of Br_2/Br^-, the presence of common inorganic anions like CO_3^{2-}, NO_3^-, and PO_4^{3-} exerts negligible influence on the bromination performance when NaBr was used as the bromine source (Figure 3). Therefore, our on-site bromination does not require

high purity of inorganic bromides, another advantage compared to those utilizing conventional brominating reagents such as N-bromosuccinimide.



Scheme 5. On-site hydrogenation of acetophenone (**5**) to produce α-methyl-benzenemethanol (**10**) using H_2 input produced from water electrolysis.



Scheme 6. Schematic of on-site bromination paired with on-site hydrogenation with a representative example of styrene (**1d**) bromination coupled with acetophenone (**5**) hydrogenation.

Applicability of on-site chlorination

Encouraged by the above success of on-site bromination, we envisioned that such a strategy could be extended to facile chlorination taking analogous advantage of the phase separation of Cl_2 from on-site electrolysis of inexpensive inorganic chlorides. As a proof of concept, NaCl electrolysis was employed to produce Cl_2 and dichlorination of styrene (**1d**) was selected as a representative reaction (Scheme 4). To our delight, in diethyl ether at 0 °C, our on-site produced Cl_2 was able to transform styrene to (1,2-dichloroethyl)benzene (**9**) with a decent yield of 80%. Such a performance is apparently greener than those conventional chlorination approaches using expensive and/or environmentally deleterious chlorinating reagents such as $KMnO_4$/HCl[59] and $Ph_2SO/(COCl)_2$.[60] Our (1,2-dichloroethyl)benzene yield (80%) is also comparable to that (85%) of a recently reported electrosynthetic strategy using a Mn(III) complex as the electrocatalyst,[15] while much simpler product isolation and purification were inherent advantages of our approach.

On-site hydrogenation using electrochemically produced H_2

With the aim of maximizing atom economy and energy return for halide electrolysis, the byproduct H_2 formed on the cathode is better utilized for valuable synthetic applications, such as hydrogenation. It is known that ketone hydrogenation presents a straightforward access to secondary alcohols, which are useful synthons for the synthesis of pharmaceuticals, agrochemicals, and liquid crystals.[61, 62] In order to demonstrate the feasibility of on-site hydrogenation, we decided to carry out the hydrogenation of acetophenone (**5**) in an isolated chamber using H_2 stream produced from water electrolysis in a divided cell (Scheme 5). Commercially purchased Pt/C was used as the hydrogenation catalyst. A high yield of 87% was achieved for the production of α-methyl-benzenemethanol (**10**), demonstrating the success of on-site hydrogenation with electrochemically produced H_2 gas and paving the way to paired halogenation/hydrogenation.

Paired on-site bromination and hydrogenation using electrochemically produced Br_2 and H_2

The most appealing scenario of our on-site halogenation strategy is to couple with on-site hydrogenation from both atomic and economic perspectives. Eventually, we assembled a divided electrochemical cell for bromide electrolysis which could produce Br_2 on the anode and H_2 on the cathode simultaneously, which were transported to separated bromination and hydrogenation chambers, respectively. As illustrated in Scheme 6, styrene (**1d**) bromination and acetophenone (**5**) hydrogenation were selected as sample reactions. The resulting yields of (1,2-dibromoethyl)benzene (**2d**) and α-methyl-benzenemethanol (**10**) were 98% and 85%, respectively, highlighting the great efficiency of on-site bromination coupled with on-site hydrogenation using electrochemically co-produced Br_2 and H_2 from bromide electrolysis. Based on the aforementioned results, it is reasonable to envision that on-site chlorination paired with hydrogenation would be equally effective.

Conclusions

In summary, our reported on-site halogenation approach ameliorates several inherent limitations that plague direct electrochemical halogenation and hence represents a convenient and alternative strategy for electricity-driven halogenation with greater flexibility, exhibiting superior tolerance to oxidatively labile functionalities, low-polar solvents, redox-active metal catalysts, and challenging temperature conditions for electrochemistry. We further demonstrate that coupled with on-site hydrogenation, our strategy maximizes the energy return of halide electrolysis and presents exceptional greenness for organic halogenation and hydrogenation reactions. Such a strategy of chemical reactions using electrochemically generated reagents but performed in an isolated space is potentially applicable to many other organic reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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