

Electrochemical oxidations through hypervalent iodine redox catalysis

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ABSTRACT

In recent years, a growing number of oxidations that involve electrochemical regeneration of catalytic hypervalent iodine species has been developed. These transformations benefit from the combination of rich reactivity offered by hypervalent iodine compounds and sustainability advantage provided by electrocatalysis, which eliminates the need for any stoichiometric redox reagents. This review provides a systematic overview of this emerging field, covering the most abundant two-electron electrocatalysis with iodoarenes via I(I)/I(III) redox cycle, the isolated existing example of I(V)/I(VII) cycle, and a newly developed approach exploiting iodoarenes as I(I)/I(II) single-electron transfer mediators.

1. Introduction

Hypervalent iodine compounds have found applications in a large number of oxidation reactions. Due to a large free-energy gain associated with the loss of hypervalency, I(III), I(V), and I(VII) reagents display high potency to accept electrons from organic substrates. Despite their high oxidative power, the oxidations promoted by hypervalent iodine reagents are often very selective and confined to specific parts of substrate molecule [1]. The broad utility of hypervalent iodine reagents can also be attributed to an array of additional advantageous features, including: mild reaction conditions required, good stability toward air and moisture, reasonable cost, and low toxicity. This last property makes hypervalent iodine reagents environmentally benign alternatives for heavy-metal oxidants, such as Pb(IV), Hg(II), or Tl(III). The oxidation of alcohols with Dess-Martin iodate, an I(V) species, may serve as an excellent example illustrating above beneficial characteristics [2]. Very importantly, the oxidative processes promoted by hypervalent iodine reagents are not limited to simple functional-group interconversions, on the contrary, they often involve the formation of new chemical bonds and large increase in the molecular complexity. In addition to stand-alone applications, hypervalent iodine reagents have been also used to access higher oxidation states of transition metals, e.g., Pd(IV) or Cu(III), allowing for novel reactivity patterns in the coupling reactions catalyzed by their complexes [3]. The utility of hypervalent iodine compounds is evidenced by the widespread application of these species in the synthesis [4].

The fundamental intrinsic feature of all oxidation reactions is that

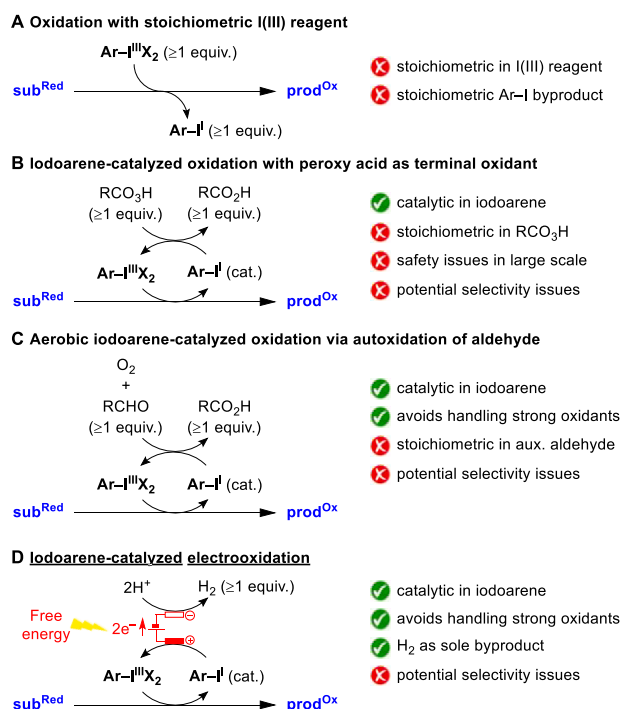
the electrons removed from the substrate need to be accommodated by the molecule of oxidant, which has to be inevitably used in a stoichiometric amount. This in turn results in the generation of the likewise amount of the corresponding reduced byproduct. This becomes a particularly pronounced inherent drawback for the oxidations with hypervalent iodine reagents. Owing to the high atomic weight of iodine and the extended structure of the reagents, typically containing at least an auxiliary aromatic ring, they are characterized by both low mass- and low atom-economy. Moreover, in the case of I(III) oxidants, the concomitant organic iodoarene byproduct is water-insoluble, creating the need for a more elaborate purification of the product. All these render the oxidations with stoichiometric hypervalent iodine reagents to be in stark contrast with the rules of green chemistry (Scheme 1A; this and other examples are illustrated with I(III) oxidations for simplicity) [5]. Therefore, although such type of processes can be deemed acceptable in laboratory applications, particularly with simple oxidants such as (diacetoxyiodo)benzene, this is clearly not the case in large-scale settings.

Initial attempts to alleviate above problem involved the preparation of recyclable versions of the reagents, for instance, polymer-supported ones or such affording the iodoarenes that can be recovered after the reaction by precipitation or extraction [6]. The key breakthrough has been, however, the introduction of iodoarene catalysis (sometimes referred to as hypervalent iodine catalysis). In this approach, only a small catalytic quantity of iodine-containing compound is utilized, combined with a stoichiometric terminal oxidant that *in situ* regenerates the hypervalent species (Scheme 1B) [7]. Over the last 20 years, a

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Scheme 1. Comparison of different variants of oxidations promoted by hypervalent iodine(III) species (X denotes additional ligands at the iodine center).

multitude of such catalytic reactions has been devised [8]. The area wherein the application of catalysis with iodoarenes has made the most significant impact are enantioselective transformations. As they employ precious complex chiral iodine-containing compounds, the issue of using these in catalytic quantities is particularly pressing. Indeed, the development of chiral iodoarene-catalyzed asymmetric oxidations has become a very active field of research [9].

Nonetheless, even if the amount of the iodine-containing reagent can be reduced by employing the catalytic approach, the terminal oxidant still needs to be used in a stoichiometric quantity. In the case of the more prevalent catalysis involving I(I)/I(III) cycle, by far the most commonly applied in this role have been peroxy acids, in particular *m*-chloroperbenzoic acid (*m*CPBA), 3 equivalents of which need to be frequently used in the practical protocols. The need to use such large quantities of highly oxidizing and potentially dangerous chemical with a record of documented explosion accidents [10], effectively prevents the widespread application of the synthetically powerful reactions catalyzed by iodoarenes, especially on a large scale. The related economic and environmental concerns are also considerable, creating further burden to translate this chemistry into industrial and semi-industrial setups. For the catalytic oxidations operating via I(III)/I(V) cycle, somewhat more benign and markedly safer inorganic peroxysulfates, mostly Oxone®, have been applied to power the reactions. Recently, there has been some progress in the use of O₂ as the terminal oxidant for the regeneration of hypervalent iodine species, both I(III) and I(V), including in actual catalytic settings [11]. However, the reported methods mostly rely on the interrupted stoichiometric autoxidation of sacrificial aldehydes to engage the triplet ground state of molecular oxygen [12], thus, they do not improve the atom-economy (Scheme 1C). Moreover, in such extended oxidation chains, the compatibility between the growing number of electron-transfer mediators and the functional groups in the substrate starts to present an issue.

Electrosynthesis is one of the techniques that allow to perform redox reactions in more environmentally friendly and sustainable manner [13]. This originates from the fact that through the application of an external potential, free energy can be injected into the system,

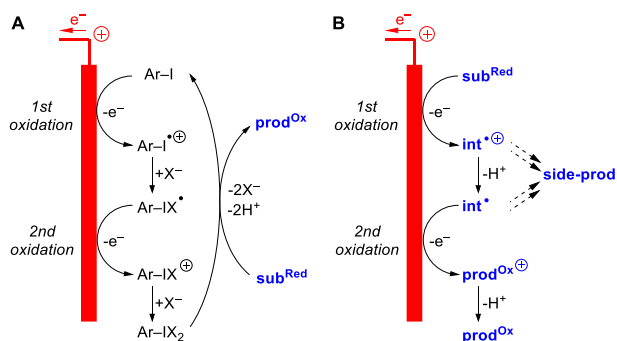
permitting to run net thermodynamically uphill transformations. Therefore, during electrolysis the role of “terminal oxidant” is limited to just accepting the electrons, whilst this process does not need to provide the driving force for the overall reaction, which is supplied by the electrical power source instead (and optimally derived from renewables). As a result, high energy (i.e., having high electron-affinity) stoichiometric oxidants, such as *m*CPBA, can be altogether avoided, as the electrons removed from the substrate can be forcefully pushed into a much more benign half-reaction, such as the reduction of protons to hydrogen [14]. In the context of hypervalent iodine-promoted oxidations, the electrochemical regeneration of the active hypervalent form of iodoarene catalyst is an excellent remedy to the key downsides characterizing the other variants of this reaction in terms of green chemistry. Namely, iodoarene is used in a catalytic amount, there is no need for a stoichiometric oxidant, the electrons are accepted by protons that originate often from the substrate itself, and the only by-product is molecular hydrogen (Scheme 1D). Naturally, the electrocatalysis with iodoarenes is not without flaws. The major challenge lies in the selective electro-oxidation of the catalyst and not the molecule of the substrate, the latter of which may lead to the formation of undesired side-products (see the next section for further discussion).

The first isolated practical realizations of the concept depicted in Scheme 1D emerged already in the 1990s, however, a sharp increase in the number of new reports has taken place during the last 5 years. This follows a more general trend of the growing interest in organic electrocatalysis observed in the recent years, motivated by both sustainability reasons and the enabling power of this technology to access novel reactivity modes [15]. The significant developments in electrocatalysis, accompanied by the introduction of standardized commercially available devices, which mitigate the barrier to adopt this technique and allow it to become the part of standard organic chemist’s toolbox [16], have undoubtedly been important factors fostering the advancements in the electrocatalysis with iodoarenes. The current review comprehensively covers the existing examples employing this approach, outlining their key advantages and weaknesses. As such, it does not include processes, wherein hypervalent iodine species are electrogenerated in stoichiometric quantities, neither ex-cell (before the addition of substrates) nor in-cell (in the presence of substrates), since those are virtually the variations of the transformation shown in Scheme 1A. That area has been extensively reviewed recently [17], so has been the traditional electrocatalysis involving non-hypervalent iodine species: I⁻/I⁺/I₂ [18].

2. Mechanistic and electrochemical considerations

The reaction depicted in Scheme 1D is an example of indirect electrolysis, wherein the role of iodoarene is to convey the electric stimulus from the electrode to the substrate [19]. The majority of (chemical) oxidations by hypervalent iodine reagents proceed through the transfers of two electrons, with the exclusive intermediacy of closed-shell species [20]. However, the redox processes at electrodes involve the transfer of a single electron per reaction event. Hence, the two-electron electrocatalyst needs to undergo two sequential single-electron oxidations (Scheme 2A).

Directly after each of the single-electron oxidation steps, an anionic ligand (X) is coordinated to the iodine center. This may be either a nucleophilic anion present in the solution (e.g., AcO⁻ or F⁻) or it may originate from the dissociation of a protic solvent (e.g., AcOH or HFIP). Importantly, the binding of the ligand takes place only after the electron transfer, since the presence of added nucleophilic anions does not affect the value of the oxidation potential measured for Ar-I by cyclic voltammetry (CV) [21,22]. However, the coordination step is fast and it most likely occurs still within the electrical double-layer surrounding the anode, which is rich in anions and highly-polarized dipoles. This is consistent with irreversible CV profiles for most iodoarenes (see Fig. 1A for a representative example) [23], testifying to a fast chemical



Scheme 2. (A) Two-electron electrocatalysis with iodoarene and (B) direct electrochemical oxidation of substrate.

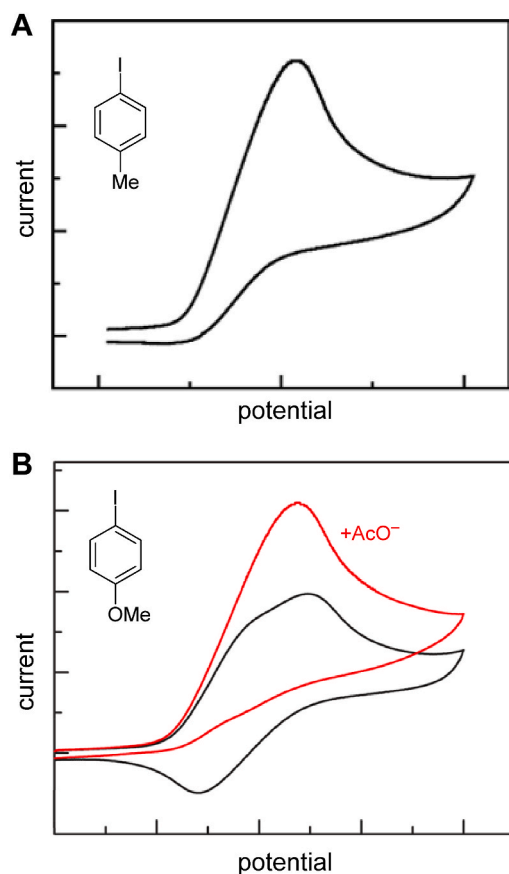


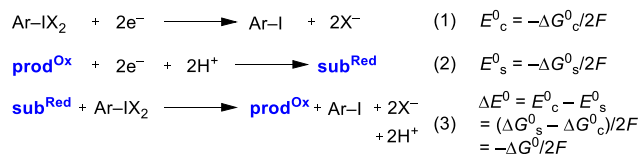
Fig. 1. (A) Representative cyclic voltammogram of iodoarene (4-iodotoluene in HFIP), showing an irreversible oxidation peak. (B) CVs of 4-iodoanisole in HFIP in the absence (black) and in the presence of 2.0 equiv. of *n*-Bu₄NOAc (red). Fig. 1A adapted with permission from Ref. [23a], © 2023 Thieme. All rights reserved; Fig. 1B adapted with permission from Ref. [21], Copyright 2020 American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

quenching of the incipient radical cation Ar-I^{•+}. Moreover, the presence of only a single oxidation peak in the CV scan evidences that the second consecutive oxidation of the resulting Ar-IX[•] to Ar-IX⁺ is taking place immediately afterwards (i.e., within the same CV wave). Therefore, the overall mechanism is of ECEC type (electron transfer/chemical step/electron transfer/chemical step) and due to the neutralization of the positive charge by coordination of an anion at the intermediate stage, the “potential inversion” occurs (that is, the second electron transfer is easier than the first) [24].

An important exception are electron-rich iodoarenes that display a reversible redox wave during CV (Fig. 1B in black), especially at fast sweep rates, pointing to the extended lifetimes of the corresponding free Ar-I^{•+} intermediates (in HFIP, in the absence of strongly coordinating species) [21,23a]. Such behavior is, however, not desirable, as iodonium (II) radical cations are prone to decomposition via deiodinative coupling or dimerization [23a]. Powers et al. have established that the addition of AcO⁻ ions to the reaction media can alleviate this problem, enabling efficient electrocatalysis with, for example, 4-iodoanisole [21]. The corresponding CV profile, exhibiting the recovery of oxidation irreversibility and the doubling of anodic current in the presence of acetate ions and other coordinating species, such as pyridine, CN⁻, F⁻, etc., indicates that these ligands have high enough affinity for iodine(II) center to coordinate to even electron-rich ArI^{•+} intermediates (Fig. 1B in red) [21]. Interestingly, this feature was, probably unknowingly, exploited in the very first reported example of iodoarene-catalyzed electro-oxidation from 1994 that utilizes 4-iodoanisole as the catalyst in the presence of Et₃N·3HF in MeCN (see Section 3.1) [25].

The mechanism of potentially competing direct stepwise electrochemical oxidation of the substrate is shown in Scheme 2B. For strictness, it has been presented with the electron transfers being interleaved with deprotonations, however, other possible alternatives for the stabilization of cationic intermediates may exist, depending on the identity of the substrate. Irrespective of this detail, it is important to note that the intermediate radical species (int^{•+} and int[•]) might give rise to the formation of entirely different product than the two-electron chemical oxidation promoted by Ar-IX₂.

In order to understand the characteristics and challenges of the two-electron electrocatalysis with iodoarenes, it is instructive to inspect the details of such reaction from electrochemical perspective. In particular, this allows for dissecting the different effects at play for both the substrate and the catalyst. In the rigors of electrochemistry, the two-electron chemical oxidation of substrate to product by Ar-IX₂, eq (3), is the difference of two formal half-reactions, eqs (1) and (2) (by convention expressed as reductions), having the corresponding standard reduction potentials and standard free-energy changes of $E_c^0/\Delta G_c^0$ and $E_s^0/\Delta G_s^0$, respectively. The potential difference for (3), ΔE^0 , is positive (i. e., $E_c^0 > E_s^0$), as the free-energy change for this thermodynamically favorable process is negative ($\Delta G^0 < 0$). This is equivalent to stating the obvious fact that Ar-IX₂ is thermodynamically a stronger oxidant than the product and, vice versa, that Ar-I is more difficult to oxidize compared to the substrate.



The steps of the sequential ECEC electro-oxidation of Ar-I are represented by equations (4)–(7). It is helpful to consider formal cumulative processes (8)=(4)–(5) and (9)=(6)–(7), having the corresponding standard reduction potentials E_{c12}^0 and E_{c34}^0 , respectively. Because (1) is the sum of (8) and (9), the standard potential for the two-electron oxidation E_c^0 is positioned exactly half-way between E_{c12}^0 and E_{c34}^0 (eq (10); Fig. 2, upper axis, in black). Consequently, the standard potentials for the actual oxidations, E_{c1}^0 for (4) and E_{c3}^0 for (6) (in blue), are shifted to higher values by $\Delta G_{c2}^0/F$ and $\Delta G_{c4}^0/F$ (blue arrows), respectively, corresponding to the affinities of X⁻ to Ar-I^{•+} and Ar-IX[•]. On top of that, the final potentials at which the electron transfers will really take place (E_{c1} and E_{c3} , in red) are further adjusted upwards due to the respective overpotentials η_{c1} and η_{c3} (red arrows).

Analogous derivation for the sequential electro-oxidation of the substrate (Scheme 2B), yields the potential picture depicted in the lower

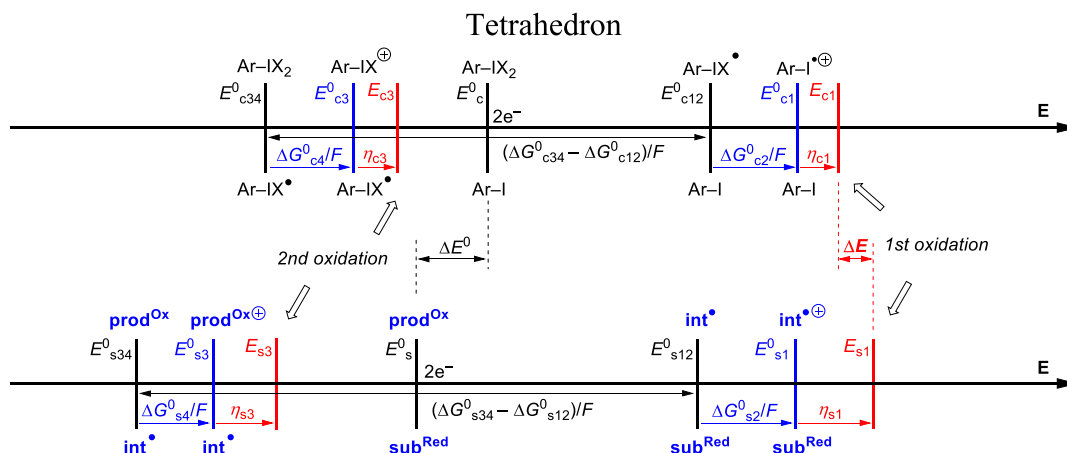
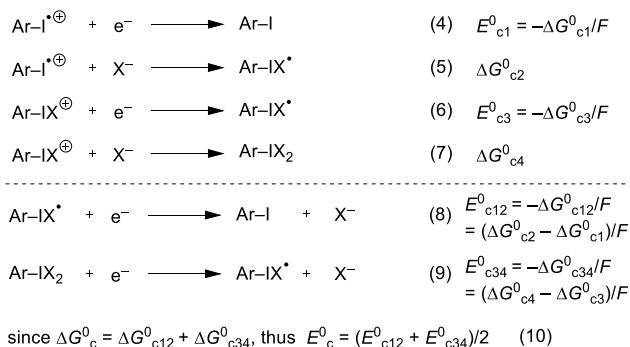


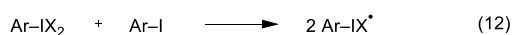
Fig. 2. Redox potential picture for two-electron electrocatalysis with iodoarene (see the text for discussion).

axis of Fig. 2. Very importantly, potential E_s^0 is shifted to a lower value relative to E_c^0 , by ΔE^0 , corresponding to the thermodynamics of the chemical oxidation (3). The size of ΔE^0 gap is one of key factors determining the viability of electrocatalysis, as will be discussed below.

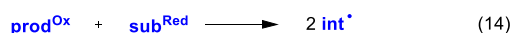


The prerequisite for two-electron electrocatalysis is that the single-electron oxidation of Ar-I occurs at a lower potential than the single-electron direct oxidation of the substrate (that is $E_{c1} < E_{s1}$). First critical quantities determining whether the above condition is going to be met are the relative separations between the standard reduction potentials: E_{c12}^0 and E_{c34}^0 for the catalyst, and E_{s12}^0 and E_{s34}^0 for the substrate (black double-headed arrows in Fig. 2). These potential "spreads" correspond to the free-energy changes for the synproportionation reactions of the respective fully-oxidized and fully-reduced species into the intermediate oxidation state (eqs. (11)-(14)). In other words, the more thermodynamically less stable is the intermediate oxidation state relative to the fully-oxidized and the fully-reduced forms, the larger the separation of the potentials for the single-electron redox processes (8) and (9) will be.

$$E_{c12}^0 - E_{c34}^0 = (\Delta G_{c34}^0 - \Delta G_{c12}^0)/F, \text{ corresponding to:} \quad (11)$$



$$E_{s12}^0 - E_{s34}^0 = (\Delta G_{s34}^0 - \Delta G_{s12}^0)/F, \text{ corresponding to:} \quad (13)$$



The potential spreads are highly relevant to the two-electron electrocatalysis. Namely, potential pairs E_{c12}^0/E_{c34}^0 and E_{s12}^0/E_{s34}^0 are centered at E_c^0 and E_s^0 , respectively, the latter having a lower value than the former due to the underlying thermodynamics of (3). Therefore, the separation between E_{c12}^0 and E_{c34}^0 (for catalyst) should be smaller than the

separation between E_{s12}^0 and E_{s34}^0 (for substrate) to offset this inherent setback due to ΔE^0 gap. In this context, a clear advantage of iodoarene catalysts is the relatively small free-energy difference between I(II) vs. I (III) species, originating from the presence of a weak 3c4e hypervalent bond in the latter, the reductive breaking of which does not require large energy input [26]. On the other hand, the large free-energy difference between I(III) and I(I) compounds, arising from the favorable exchange of a 3c4e hypervalent bond with two regular 2c2e bonds upon accepting two electrons, is an adverse feature in this respect. It directly translates into I(II) species being very thermodynamically unstable relative to I(I) counterparts, increasing the potential spread. Moreover, it also widens the basal ΔE^0 gap. Both of these effects can be somewhat alleviated by introducing electron-donating substituents into the structure of the catalyst.

Naturally, the other side of the equation is the separation of the standard potentials E_{s12}^0 and E_{s34}^0 for the formal single-electron oxidations of the substrate. For many organic compounds, the intermediate oxidation state species will be high-energy radicals, rendering E_{s12}^0 high, thus, making the reactions that involve such compounds suitable candidates for the electrocatalysis with iodoarenes. However, if an organic substrate can form a stabilized radical, the E_{s12}^0/E_{s34}^0 spread narrows and the direct oxidation will prevail. A prime example is the two-electron oxidation of phenols, which although proceeds fantastically with stoichiometric or catalytic hypervalent iodine reagents under the conditions shown in Schemes 1A-B [18,8e,27], it seems incompatible with the electrocatalytic setup in Scheme 1D. Due to the high stability of delocalized phenoxyl radical, the direct single-electron oxidation of phenols occurs at much lower potential than that of any iodoarene, precluding electrocatalysis.

The oxidation of phenols comprises also an excellent example of strikingly divergent reactivity during a two-electron chemical oxidation and a single-electron electrochemical oxidation. Namely, upon treatment with hypervalent iodine reagents, phenols undergo dearomatization with an addition of nucleophiles, yielding cyclohexadienones [27]. Conversely, when phenols are subjected to anodic oxidation, the preferential reaction pathway for the incipient phenoxyl radical (int• in Scheme 2B) leads to biphenols, instead [15i,15n,28]. For some starting materials, however, the direct electro-oxidation may, unlike in the case of phenols, give rise to exactly the same product as the chemical hypervalent iodine-promoted oxidation. In the literature, such possibility of background reaction has not always been unambiguously disproven by conducting control experiments without iodoarene electrocatalyst present, while the latter might actually turn out to be superfluous.

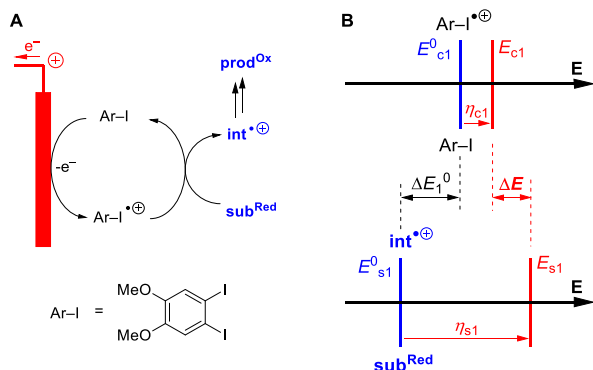
The other very important factors affecting electrocatalysis are overpotentials (Fig. 1, η ; red arrows) that establish the real experimental potentials at which the respective oxidations of the catalyst (E_{c1}) and the

substrate (E_{s1}) will take place. In contrast to all the aspects discussed so far, that were thermodynamic in nature, the overpotentials originate from the kinetic barrier for the electron transfer between species being oxidized and electrode. The height of this barrier is in part intrinsically determined by the structure of the reagent and arises from the reorganization energy as described by Marcus theory, and, thus, it is largely independent of the conditions under which the electrolysis is performed [29]. However, equally important to the size of overpotential is the contribution from electrode. In general, it is difficult to predict the effect that given electrode material will exert on the overpotential for the oxidation of a specific organic compound, including an iodoarene. Optimally, it should promote the oxidation of the catalyst and suppress the undesired direct oxidation of the starting material. For the electrocatalysis with iodoarenes, due to strongly oxidative conditions, the selection of anodes is typically limited to the different forms of carbon (graphite, glassy carbon, Reticulated Vitreous Carbon - RVC), boron-doped diamond (BDD), and platinum. In some of the existing examples, the choice of electrode material has been shown to have a profound effect on the success of electrocatalysis [21,30].

Powers and co-workers have conducted CV measurements for a large collection of iodoarenes in HFIP on a glassy carbon electrode, providing a sizeable set of reference data on the oxidation potentials of this class of compounds [23a]. The values were reported relative to ferrocenium/ferrocene couple, which in the solvent used has the redox potential of +0.42 V vs. SCE (saturated calomel electrode), should one need to recalculate them to a more generic potential scale [31,32].

The final consideration, also related to kinetics, concerns the relative rates of the chemical and electrochemical processes engaging the catalyst. Namely, a sluggish chemical oxidation of the substrate by the hypervalent form of the catalyst may lead to the accumulation of Ar-IX₂ and a parallel depletion of Ar-I. This will in turn result in the increase of potential E_{c1} (through Nernst equation) to a point at which it may surpass E_{s1} . In this respect, a possible remedy to suppress side-reactions is the application of constant-potential electrolysis, which has indeed proven advantageous in some of the reported electrocatalytic reactions with iodoarenes [21,31]. The imbalanced kinetics of the chemical and electrochemical steps may be one of the reasons why many in-cell iodoarene-mediated oxidations proceed efficiently only with ≥ 1 equiv. of the mediator, whereas they fail under a catalytic setting [33].

Very recently, Powers et al. have devised a conceptually novel catalytic application of iodoarenes in electrochemical oxidations, namely, as single-electron transfer mediators (Scheme 3A) [31,34]. It capitalizes on an increased stability of free radical cation Ar-I^{•+} derived from a specially designed iodoarene, whose catalytic utility arises from having a substantially lower overpotential compared to the substrate (Scheme 3B). This in turn allows to perform reactions initiated by a single-electron oxidation at lower applied potentials, thus, preventing undesired side-oxidations. Although using single-electron transfer mediators for indirect electrolysis is a very well-established approach [19],



Scheme 3. (A) Iodoarene as a single-electron transfer mediator and (B) the corresponding redox potential picture.

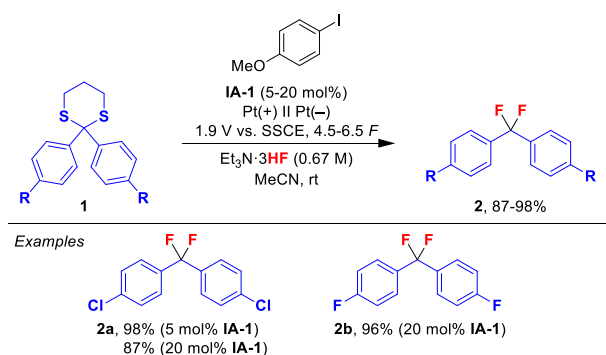
the employed iodoarene displays a considerably different oxidation potential ($E_{1/2} = 1.48$ V in HFIP vs. SCE) compared to the known electrocatalysts of this kind, [15h] possibly opening new reactivity modes. Most noteworthy, such processes will be orthogonal to the typical two-electron oxidations promoted by hypervalent I(III) and I(V) reagents.

3. Two-electron electrocatalysis

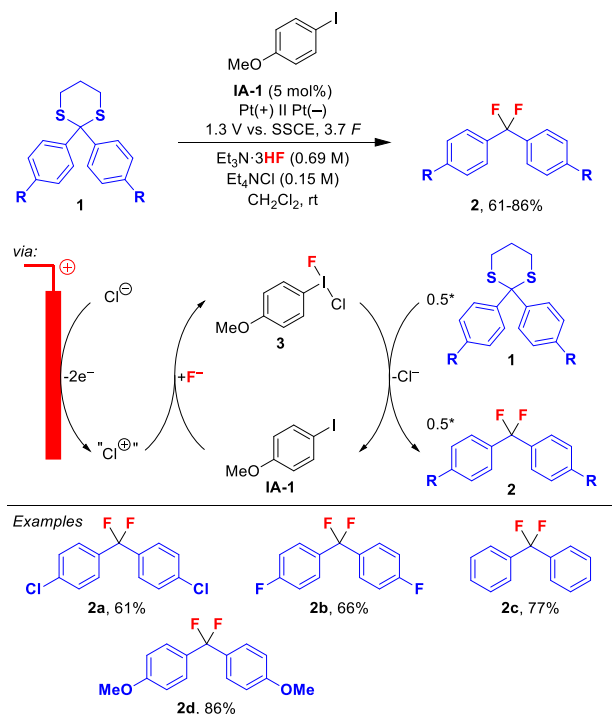
3.1. Fluorination

The seminal report in the area of electrocatalytic reactions involving hypervalent iodine oxidants has been published by Fuchigami and a co-worker in 1994 and it concerns a fluorination reaction (Scheme 4) [25]. The application of stoichiometric hypervalent iodine(III) compounds as electrophilic fluorinating reagents has been already established by then [35], and the initial intent of the authors was to electrochemically generate stoichiometric (difluoroiodo)arenes for the application in a subsequent ex-cell oxidative *gem*-difluorodesulfurization of dithioketals [36]. In the course of the investigation, however, they realized that the potential required for an efficient electro-oxidation of 4-iodoanisole (IA-1) under the reaction conditions [1.9 V vs. SSCE (saturated salt calomel electrode, having almost identical potential to SCE) on Pt anode, in MeCN in the presence of 0.67 M Et₃N·3HF] is lower than that for substrate **1** (>2.5 V vs. SSCE in DME), hypothetically enabling a selective reoxidation of IA-1 and its utilization as a catalytic mediator. The idea has proven to be correct, and two products (**2a-b**) were successfully prepared in high yields, one of which using only 5 mol% catalyst loading (Scheme 4). This achievement becomes even more notable taking into account that at least 2 equiv. of (difluoroiodo)anisole are required to effect the difluorodesulfurization of **1** under the chemical oxidation conditions. A reaction in the absence of IA-1 at 1.9 V vs. SSCE did not provide any product, while the application of a higher potential (2.5–3.0 V vs. SSCE) afforded **2**, albeit in considerably lower yields [37]. As mentioned in Section 2 above, the presence of coordinating fluoride anions in the reaction medium is the key to the effective oxidation of electron-rich IA-1 to the active I(III) form, through minimizing the life-time of the incipient free iodanyl(II) radical cation [21].

For the next 25 years since the appearance of this seminal work, the fluorination chemistry has become the only existing application of electrocatalysis with iodoarenes and the pioneering research in this area has been solely pursued by the group of Fuchigami. In 1996, they developed an extension to the original method, wherein catalyst IA-1 was utilized in a combination with chloride ions that serve as additional two-electron redox mediator (Scheme 5) [38]. In the putative mechanism, the chloride anion undergoes a two-electron oxidation at the electrode, subsequently generating (chlorofluoroiodo)anisole **3** from IA-1. The latter is the actual reagent accomplishing the *gem*-difluorodesulfurization of dithioketals. This was substantiated by



Scheme 4. Electrocatalytic *gem*-difluorodesulfurization of dithioketals employing iodoanisole IA-1.

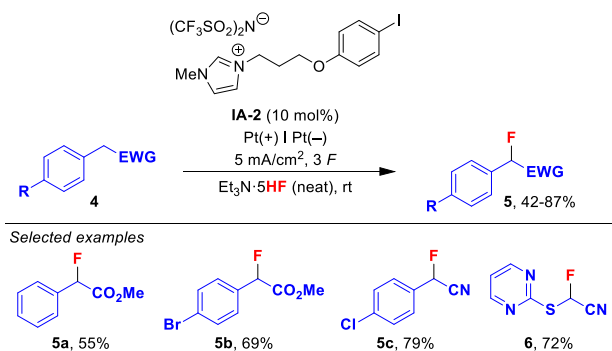


Scheme 5. *gem*-Difluorodesulfurization of dithioketals electrocatalyzed using double mediator system comprised of chlorides and catalytic iodoanisole **IA-1**.

demonstrating that stoichiometric **3** is competent to carry out the fluorination of **1a** and that the electrochemical reaction does not provide the product efficiently in the absence of **IA-1** (23 % of **2a** was obtained with only $\text{Et}_3\text{N}\cdot 3\text{HF}$ and Et_4NCl present). By the use of two-stage indirect electrolysis, the reaction could be carried out at a lower potential of 1.3 V vs. SSCE (compared to 1.9 V before). The scope of fluorination was also extended to two additional products **2c-d**.

The double, iodoarene/ Cl^- , mediator system was later employed in similar electro-driven fluorodesulfurizations and a fluorodexanthation promoted by polyiodostyrene [39]. In this case, however, the reaction was hardly catalytic, because taking into account the amount of polymer used and its degree of iodination [40], the iodoarene loading was approximately 80 mol%. On the positive side, the supported mediator could be easily recovered after the reaction and reused up to ten times without marked loss in the activity. Moreover, considerably simpler undivided cell setup and constant current electrolysis could be applied.

The final existing fluorination protocol, also developed by Fuchigami, in 2010, utilizes a derivative of 4-iodoanisole tethered to an imidazolium salt (**IA-2**) [41]. Such catalyst design allowed for conducting the electrocatalytic benzylic fluorination in neat $\text{Et}_3\text{N}\cdot 5\text{HF}$ ionic



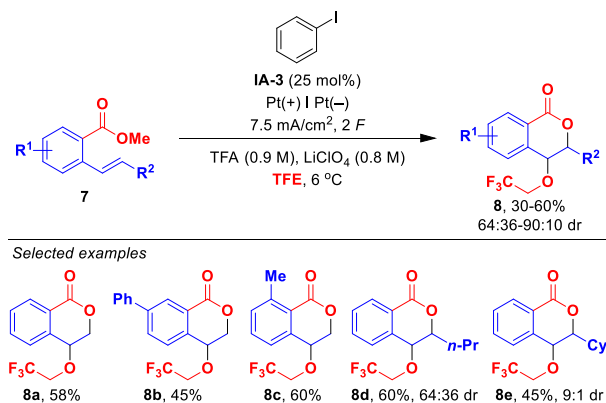
Scheme 6. Electrocatalytic benzylic fluorination in ionic liquid employing recyclable iodoarene **IA-2**.

liquid (Scheme 6). In addition to products of type **5**, compounds derived from 2-pyrimidylsulfide (**6**) [42] could also be synthesized in good yields, using just 10 mol% of **IA-2** in an undivided cell and under constant current conditions. Finally, the *gem*-difluorodesulfurization of dithioketals (similar to that shown in Scheme 4) was also accomplished in excellent yields, albeit with 20 mol% of **IA-2**. Importantly, the products of the reaction could be isolated by a simple extraction with diethyl ether, while catalyst **IA-2** remained in the ionic liquid phase that could be directly reused in another run. The clear advantage of the method employing iodoarene electrocatalysis is its high selectivity, which could not be achieved in the corresponding direct electrolysis, affording a mixture of different products [43].

3.2. Difunctionalization of alkenes

It took almost 10 years before the next method employing electrocatalysis with an iodoarene has been published. By then, in 2018, the organic electrocatalysis has already been on the rising tide, the electrogeneration of stoichiometric hypervalent iodine reagents has been relatively well-explored, and the iodoarene catalysis with chemical terminal oxidants has held a firm position as a useful synthetic approach. In particular, the latter has been notably successful in the area of oxidative difunctionalization of alkenes, including enantioselective transformations [1b,9b,44]. Under such combination of circumstances the stage was set for the (re)emergence of iodoarene electrocatalysis. The first to recognize this opportunity were Hilt and co-workers, who reported the electrochemical oxidative alkoxylation of 2-vinylbenzoates catalyzed by iodobenzene **IA-3** (Scheme 7) [45].

The reaction is based on the related processes making use of either a stoichiometric I(III) reagent or a catalytic iodoarene with *m*CPBA as a terminal oxidant [46]. Those, however, have been enantioselective transformations utilizing chiral iodine-containing compounds. In the case of the electrocatalytic version, interestingly, the authors carried out a multivariate linear regression analysis to optimize the reaction parameters and the structure of the catalyst. The scope was briefly explored and moderate yields were obtained (Scheme 7). For products where R^2 is present, the diastereomer ratio was correlated to the size of the substituent. This observation indirectly suggests that some of the product could have formed through a background direct electrolysis, since the I(III)-promoted oxidations deliver the *syn* diastereomer exclusively [46]. The oxidation potential for **IA-3** measured under the reaction conditions was 1.86 vs. Ag/AgCl/NaCl sat. (corresponding to ~ 1.8 V vs. SCE), lending support for such possibility, as the redox potentials for substituted styrenes have similar values (1.7–2.0 V vs. SCE in MeCN [47]). Unfortunately, a control experiment without **IA-3** added was not conducted (see also the discussion accompanying Scheme 11, below). Finally, based on a virtual screening, a chiral iodoarene was proposed for performing the reaction in an enantioselective fashion.

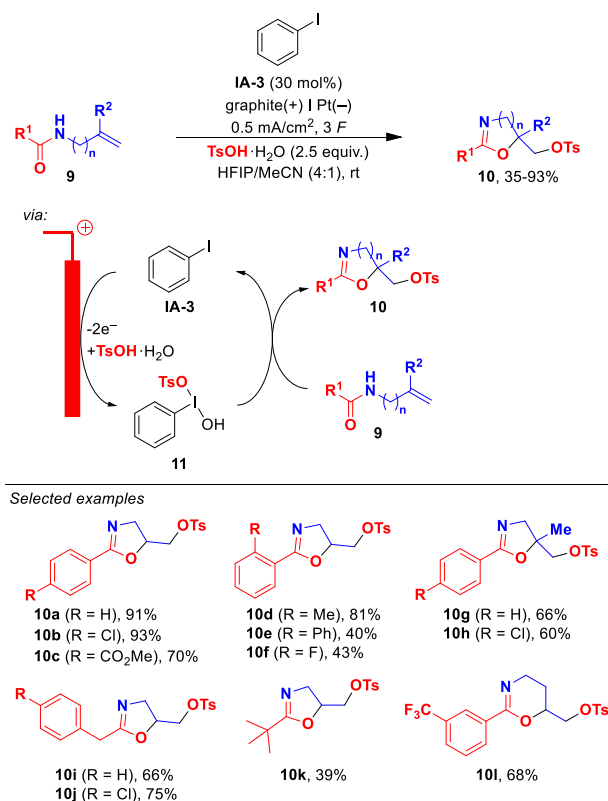


Scheme 7. Electrocatalytic alkoxylation of 2-vinylbenzoate derivatives employing iodobenzene **IA-3**.

However, this idea has never been followed up.

In 2020, He and co-workers, in their article concentrating on the electrochemical synthesis of I(III) reagents, reported a single example of the preparation of product **8a** under slightly simplified conditions than those used by Hilt [48]. Specifically, with the loading of **IA-3** reduced to 20 mol% and the current density reduced to 1.4 mA/cm², utilizing *n*-Bu₄NBF₄ as a sole additive, and performing the electrolysis at room temperature with 2.8 *F* of charge passed, **8a** could be isolated in a somewhat improved 66 % yield.

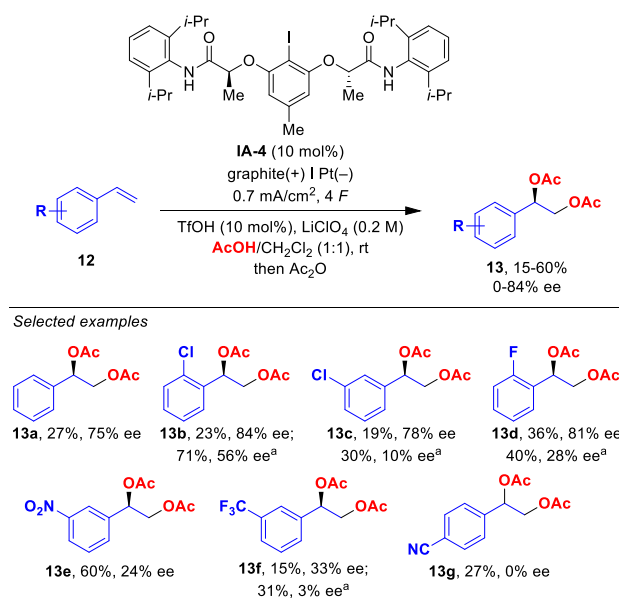
The group of Moran recently developed an electrochemical version of their iodoarene-catalyzed oxidative cyclization of unsaturated amides [49], affording tosylated oxazolines **10** (Scheme 8) [50]. The reaction employs simple iodobenzene **IA-3** as the catalyst, although as much as 30 mol% loading was found to be required to secure optimal yields. The electrolysis takes place under galvanostatic conditions in an undivided cell with HFIP/MeCN solvent mixture, in the presence of 4-toluenesulfonic acid as a sole additive. The optimization covered a number of parameters, including anode material, current density, and additives. However, no iodoarenes other than **IA-3** were reported to have been tested. Also, no control experiment in the absence of catalyst was conducted, however, the oxidation potential for non-conjugated alkene moieties, such as these as present in **9**, is as high as 2.5 V vs. SCE in MeCN [47], likely precluding direct electro-oxidation when **IA-3** is present. The scope was thoroughly explored and it includes variously-substituted *N*-allyl amides, derived from both aromatic (**10a-h**) and aliphatic carboxylic acids (**10i-k**). Moreover, oxazolines with an all-substituted carbon atom (**10g-h**) could be efficiently obtained, so could be six-membered 5,6-dihydro-4*H*-1,3-oxazines (**10l**). The yields were generally good to high. A presumed mechanism involves the formation of Koser's reagent **11** that induces the oxidative cyclization. It is worth noting that a closely related reaction involving a fluorination instead of tosyloxylation could not be turned catalytic with respect to the iodoarene mediator [33b].



Scheme 8. Electrocatalytic cyclization of unsaturated amides employing iodobenzene **IA-3**.

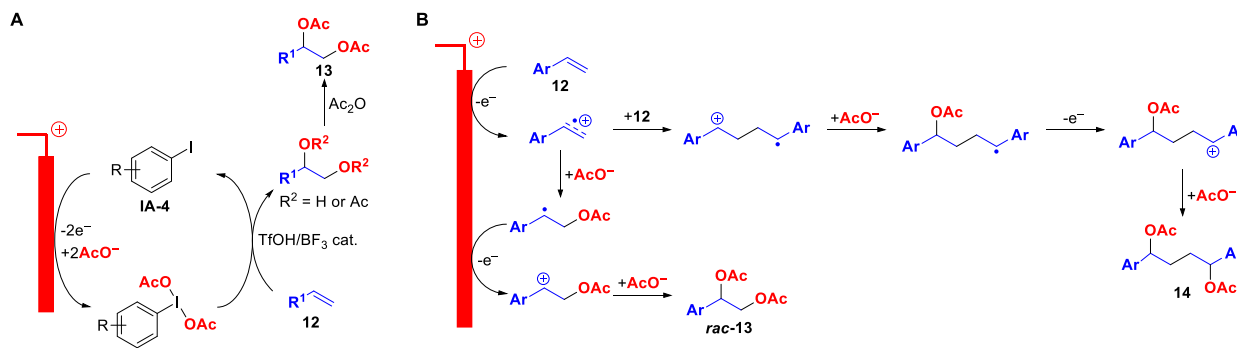
In an attempt to create a direct equivalent of the reaction powered by a chemical terminal oxidant (peracetic acid) [51], in 2023, Kalek et al. reported so far the only existing enantioselective electro-oxidation utilizing a chiral iodoarene catalyst **IA-4** (Scheme 9) [30c]. To this end, the structure of the catalyst and most of other reactions conditions were adopted from the original work. Although the asymmetric electrocatalysis has been accomplished for the first time, the attained catalytic turnovers were low, up to ~3. Moreover, some of the products were obtained not only in low yields, but also in low ee or even as racemates (e.g., **13f-g**). Both of these problems were traced to a competing direct electro-oxidation of styrene starting materials. Namely, under the conditions optimized to maximize the enantioselectivity (graphite anode), the majority of **12** was found to be converted to dimeric side-product **14** (Scheme 10B) [52]. Upon changing the anode material to glassy carbon, the formation of **14** could be somewhat suppressed. However, this caused the direct electrolytic oxidation of **12** to racemic **13** to over-compete the iodoarene-mediated process (Scheme 10A), instead, increasing the yields, but lowering the ee. The interference from the direct electro-dioxygenation of styrenes is not surprising, taking into account that processes of this type have been known [52,53]. Indeed, CV showed that catalyst **IA-4** has the onset oxidation potential ~0.2 V higher than model substrate **12b**. Specifically, **IA-4** displayed $E_{p/2} = 2.42$ V in HFIP (vs. SCE), which is among the highest values recorded for any iodoarene [23a], suggesting that the popular Ishihara-Muñiz iodoresorcinol-lactamide chiral scaffold may not be the optimal choice for electrochemically-promoted reactions. Anyhow, the reaction in Scheme 9 represents one of only few existing electrochemical asymmetric transformations, wherein the electrocatalyst itself is a chiral species and, even more unique, it is not a transition metal complex [54].

Shortly after the appearance of Kalek's report, De Vos and co-workers disclosed a general non-asymmetric protocol for iodoarene-catalyzed electrochemical diacetoxylation of alkenes (Scheme 11) [55]. The method employs iodobenzene (**IA-3**) as a catalyst and acetic acid/acetic anhydride mixture as a reaction medium. The substrate scope was explored very extensively and in the majority of cases good to excellent yields were obtained. The reaction displays tolerance to many functional groups, such as nitrile (**16f**), aliphatic bromide (**16g**), and amide (**16j**). Additionally, several examples involving combined intra- and intermolecular acyloxylation were also presented (**17a-c**). Finally,

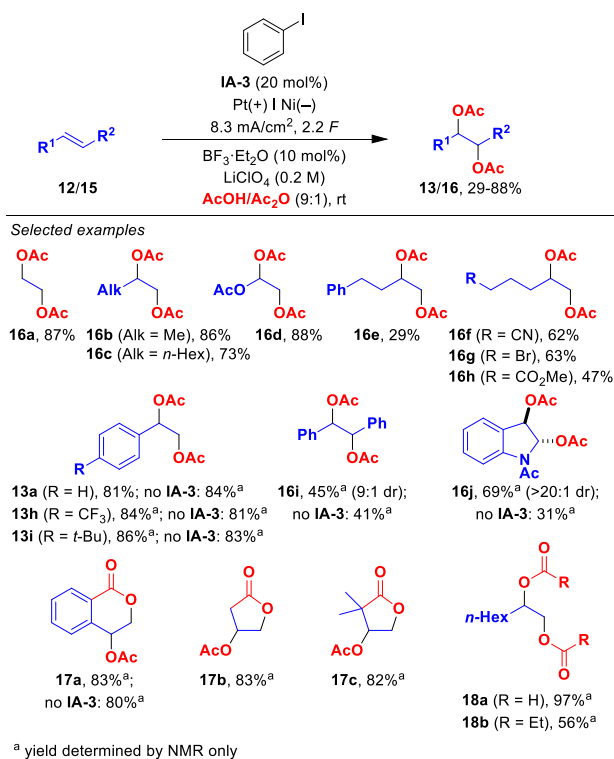


^a using GC anode

Scheme 9. Electrocatalytic enantioselective diacetoxylation of styrenes employing chiral iodobenzene **IA-4**.



Scheme 10. (A) Iodoarene-mediated diacetoxylation of alkenes and (B) possible pathways during the direct electro-oxidation of styrenes.



Scheme 11. Electrocatalytic diacetoxylation of alkenes employing iodo-benzene IA-3.

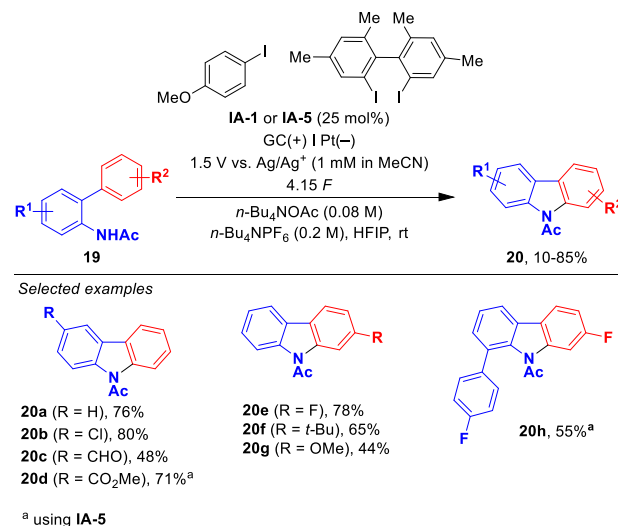
the possibility to use other carboxylic acids was demonstrated (**18a-b**). Notably, the reaction could be carried out on a gram scale without loss in the yield.

Very importantly, in the case of starting materials bearing alkene moieties non-conjugated to aromatic rings, the presence of the catalyst was proven to be necessary for the formation of the corresponding products, in line with the relatively high oxidation potentials of such olefins [47]. Conversely, for styrene derivatives, having lower potentials, practically identical yields were afforded in the presence and in the absence of IA-3 (e.g., **13a,h-i**, **16i**). This includes product **17a**, closely related to those synthesized in the 2018 report by Hilt (Scheme 7) [45]. CV measurements and an experiment with a radical clock corroborated the notion that the oxidation of isolated olefins takes place with the intermediacy of IA-3 (Scheme 10A), while for styrenes both the catalyzed and the direct (Scheme 10B) oxidation pathways contribute to the formation of products. Naturally, background oxidation leading to the same species as the catalyzed reaction does not constitute a problem in the case of non-asymmetric transformations, as the one described herein.

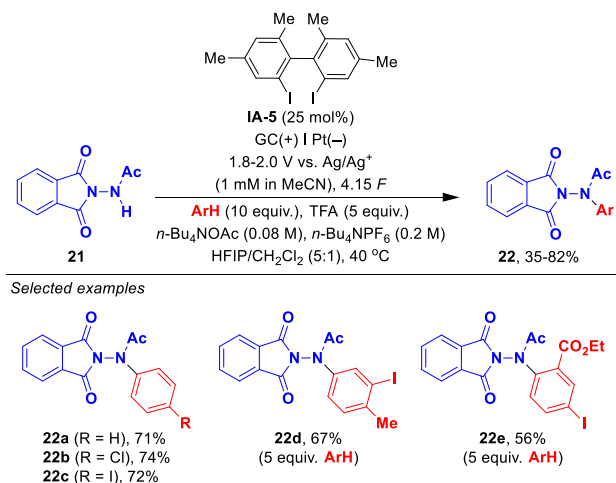
3.3. C–N coupling

The oxidative C–H/N–H coupling under the auspices of stoichiometric or catalytic hypervalent iodine reagents is an efficient method for the formation of C–N bonds [1c,56]. In 2020, Powers and co-workers have developed the first version of this reaction employing electrocatalysis [21]. Two variants were presented: an intramolecular cyclization affording N-acetylcarbazoles **20** (Scheme 12) [57] and an intermolecular N-arylation of protected hydrazines **21** (Scheme 13) [58]. Both reactions were performed under largely similar, constant potential conditions, employing either 4-iodoanisole (IA-1) or 2,2'-diiodo-4,4',6,6'-tetramethyl-1,1'-biphenyl (IA-5) as a catalyst. The latter iodoarene, being an established catalyst for the C–N bond formation in the combination with chemical oxidants [57c,58a,58c,59], had to be applied to accomplish the C–N coupling in electron-deficient carbazoles (e.g., **20d,h**) and in all hydrazines. The intramolecular reaction was found to have rather broad scope, encompassing both electron-rich and -poor substrates, while electron-rich arenes were incompatible with the intermolecular variant. The regioselectivity of the intermolecular N-arylation was found to be consistent with electrophilic aromatic substitution preferences. Interestingly, iodine-containing aryl rings could also be incorporated into the products (**22d-e**).

An admirable aspect of this work by Powers is the meticulous electrochemical characterization of all components of the reaction and thorough mechanistic investigations. Thus, CV measurements were conducted for all screened iodoarene catalysts and substrates. The substrates were additionally subjected to direct electrolysis without the



Scheme 12. Electrocatalytic synthesis of carbazoles via intramolecular C–N coupling employing iodoanisole IA-1 and 2,2'-diiodo-4,4',6,6'-tetramethyl-1,1'-biphenyl IA-5.



Scheme 13. Electrocatalytic N-arylation of protected hydrazines employing 2,2'-diiodo-4,4',6,6'-tetramethyl-1,1'-biphenyl IA-5.

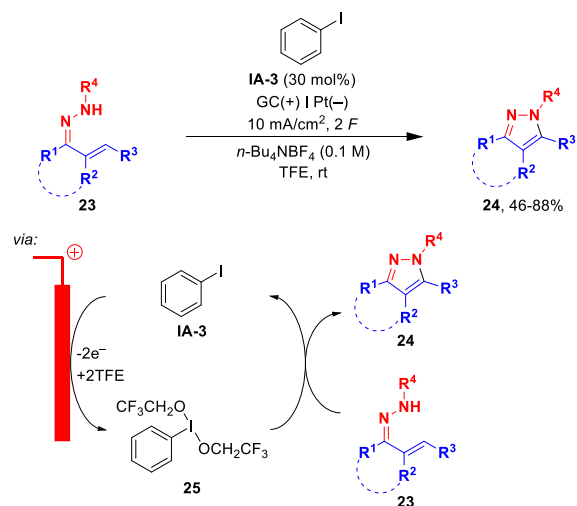
catalyst present and in most of the cases, the corresponding products were not formed (notably, Antonchick et al. have later reported alternative conditions, under which both the intra- and intermolecular variants of the reaction can be generally accomplished through the direct electrolysis [60]). However, the most significant mechanistic finding was demonstrating the role of acetate ions, which coordinate to incipient electrogenerated I(II) radical cation promoting its further oxidation to I(III) species. This both facilitates the regeneration of the active form of the catalyst as well as lessens its decomposition (see Section 2). The authors also disproved the mechanistic alternative of a direct Kolbe electrolysis of acetate under the reaction conditions.

In 2022, Terent'ev and co-workers developed an electrochemical synthesis of substituted pyrazoles from α,β -unsaturated hydrazones via intramolecular C–N coupling using iodobenzene (IA-3) as a catalyst (Scheme 14) [61]. The method is based on analogous reactions employing stoichiometric I(III) oxidants [62]. The optimized conditions consist of constant current electrolysis in an undivided cell on a glassy carbon anode, in TFE as a solvent and with Bu_4NPF_6 as a supporting electrolyte. Several iodoarenes were screened for their ability to catalyze the reaction and IA-3 was identified as the best one. The scope of the reaction is quite broad, covering substrates with differently-substituted aryl groups at both termini (24a–e, h–m), as well as with alkyl groups adjacent to the imine (24f–g). Hydrazones with carbamate and carboxylic amide protection could also be successfully employed in the cyclization (24n–o). A gram-scale synthesis of product 24a was demonstrated. Mechanistic studies revealed that the process is initiated with the anodic generation of (dialkoxyiodo)benzene 25, which effects the oxidative cyclization. A background oxidation in the absence of IA-3 provided 5 % of the product.

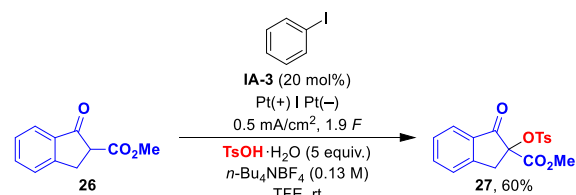
3.4. α -Functionalization of carbonyl compounds

Hypervalent I(III) compounds constitute powerful reagents for the α -functionalization of carbonyl compounds [11,63]. The first example of electrochemical reaction of this type promoted by a catalytic iodoarene was reported by He and co-workers (Scheme 15), in the same paper that included also the alkoxylation of 2-vinylbenzoate described in Section 3.2 [48]. Specifically, the tosyloxylation of a β -ketoester 26 was accomplished utilizing 20 mol% of iodobenzene IA-3, in the presence of 5 equiv. of 4-toluenesulfonic acid monohydrate in TFE.

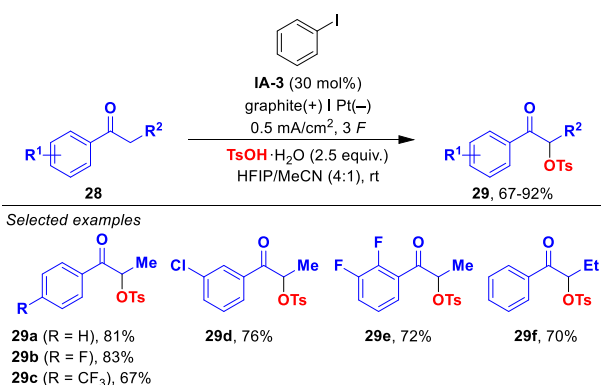
Moran and a co-worker applied the conditions developed for their dioxylation of alkenes (Scheme 8) to the α -tosyloxylation of alkyl aryl ketones 28 (Scheme 16) [50]. The reaction was shown to proceed uneventfully for a number of propiophenone derivatives having various substituents in the aromatic ring (29a–e), as well as for butyrophenone



Scheme 14. Electrocatalytic synthesis of pyrazoles via intramolecular C–N coupling employing iodobenzene IA-3.



Scheme 15. Electrocatalytic α -tosyloxylation of a β -ketoester employing iodobenzene IA-3.



Scheme 16. Electrocatalytic α -tosyloxylation of alkyl aryl ketones employing iodobenzene IA-3.

(29f). Presumably, the mechanism is similar to that depicted in Scheme 8, with Koser's reagent being the active I(III) species.

It must be noted here that there exist multiple protocols for the electrochemical α -functionalization of carbonyl compounds employing electrocatalysis with halides, including iodides, which are much easier to oxidize anodically than iodoarenes [64]. Also, a related direct α -functionalization of enol esters has been developed in the classic works by Shono as early as in the 1970s [65].

3.5. Imination of sulfur

There have been several examples in the literature, wherein electrochemically generated catalytic iodonitrene and iminoidoanone [1m] were used to effect the imination of sulfur.

In 2021, Xu and co-workers developed a method for the synthesis of NH-sulfoximines and NH-sulfonimidamides from sulfides and sulfenamides, respectively, utilizing 4-iodoanisole IA-1 as an electrocatalyst (Scheme 17) [30b]. The reaction constitutes an electrocatalytic equivalent to a similar process engaging a stoichiometric hypervalent iodine oxidant, during which sequential N and O transfers occur with high selectivity [66]. Through detailed optimization studies, the authors identified 4-iodoanisole IA-1 as the best catalyst, together with other reaction parameters. The developed conditions were applied to the synthesis of multiple NH-sulfoximines containing various combinations of aryl and alkyl substituents (31a-h). Obtained yields are good to excellent across all the scope and a number of functional groups, such as carboxylic acid (31d), benzylic alcohol (31e), ketone (31f), and allyl (31g), are well tolerated. The electro-oxidation also proceeded well for sulfenamides, providing the corresponding NH-sulfonimidamides (31i-m). Finally, a gram-scale electrolysis was successfully conducted.

Based on control experiments and CV measurements, a mechanism involving the formation of iodonitrene 33 from electrochemically

generated 4-(diacetoxyiodo)anisole 32 was proposed. Through previous mechanistic studies on the version with stoichiometric I(III) oxidant [67], it is known that 33 induces a selective sequential N and O transfers to the sulfur atom of sulfides (30), in which oxygen originates either from methanol or acetate. In the electrochemical variant, the control experiments revealed an additional possibility of the initial direct anodic oxidation of sulfides 30 to sulfoxides 34 that also undergo an efficient transformation to the final product 31 upon treatment with 33. Both of these pathways may contribute to the formation of the product.

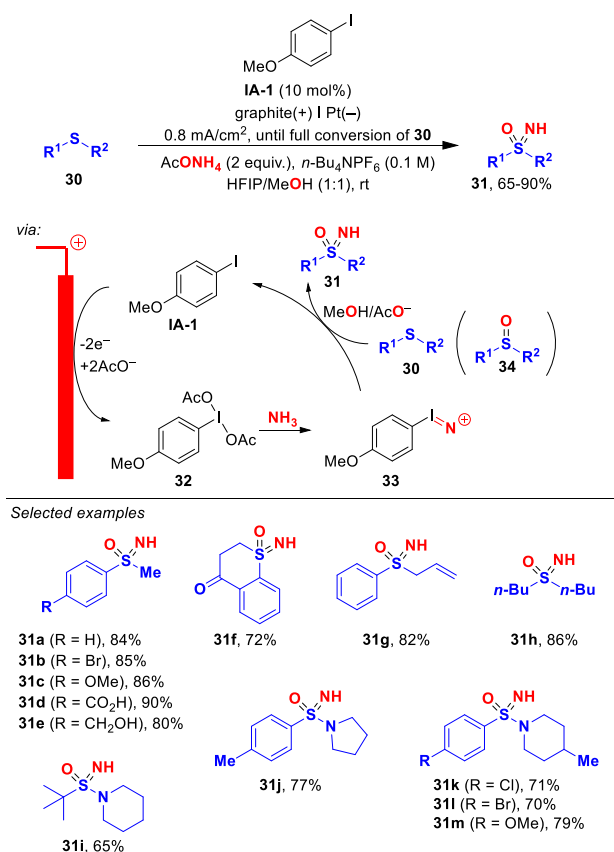
In the same article, Xu et al. further increased the scope of the electrocatalytic N,O-transfer to sulfur by combining it with an *in situ* C-N coupling (Scheme 18) [30b], as reported earlier using a stoichiometric I(III) oxidant [68]. Thus, under conditions identical to these applied before, 2-(methylsulfanyl)-1,1'-biphenyls 35 with various substituents could be transformed into dibenzothiazines 36 in good yields (Scheme 18).

Building on the work by Yoshimura [69], Wang in 2022 reported another electrocatalytic method for the imination of sulfur. Specifically, using iodobenzene IA-3 in high 40 mol% loading in conjunction with catalytic iodide, the sulfonylimination of alkyl aryl sulfides to the corresponding N-arylsulfilimines was carried out (Scheme 19) [70]. The reaction displays broad scope with the regard to sulfide partner (38a-h) and it allows for the incorporation of different arylsulfonyl moieties (38i-j). In line with the mechanistic proposal for the original chemically promoted variant, the reaction putatively takes place with the intermediacy of imidoidone 40, created *in situ* from anodically generated (dialkoxyiodo)benzene 39. Compound 40 upon reaction with molecular iodine (resulting from the electrochemical oxidation of KI) provides N, N-diiodoarylsulfonylamide 41 that is the actual iminating agent. However, under the electrochemical conditions, the presence of KI was found to be beneficial, but not essential for the formation of the product. Therefore, there is an alternative possibility of a direct imination of sulfide 37 with imidoidone 40. Conversely, iodoarene catalyst IA-3 was a crucial component of the reaction mixture, the absence of which led to exclusive oxidation of 37 to the corresponding sulfoxide.

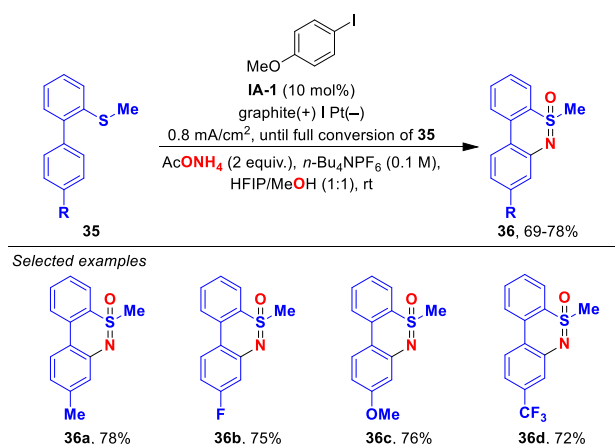
3.6. Reoxidation of ruthenium catalysts

As mentioned in the introduction, hypervalent iodine oxidants have been applied to access the higher oxidation states of transition metals, predominantly Pd(IV) or Cu(III), enabling unique reactivity modes of these metal catalysts [3]. Somewhat surprisingly in this context, the only existing examples of double redox mediator systems consisting of a catalytic hypervalent iodine compound and a transition metal complex are those involving ruthenium.

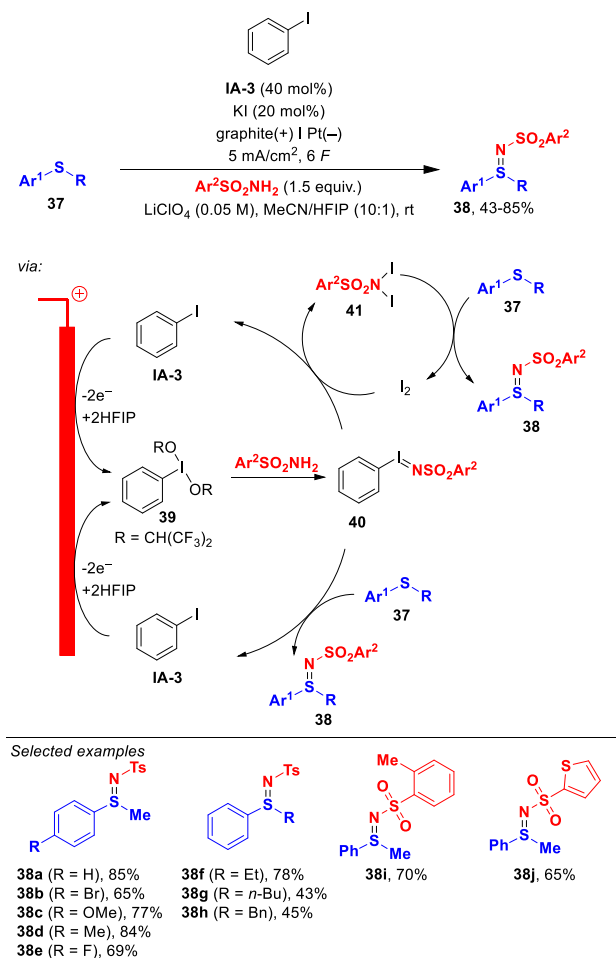
The first reported example of this kind was clearly ahead of its time



Scheme 17. Electrocatalytic synthesis of NH-sulfoximines and NH-sulfonimidamides employing 4-iodoanisole IA-1.



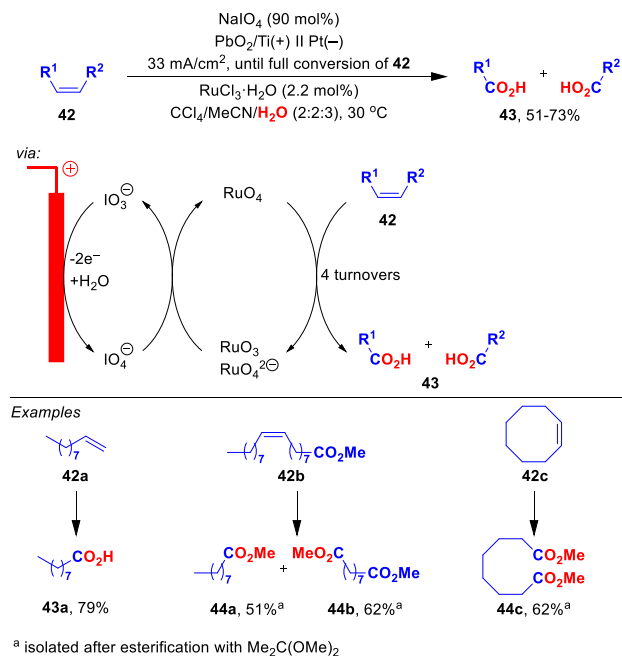
Scheme 18. Electrocatalytic synthesis of dibenzothiazines from sulfides by N, O-transfer and intramolecular C-H amination employing 4-iodoanisole IA-1.



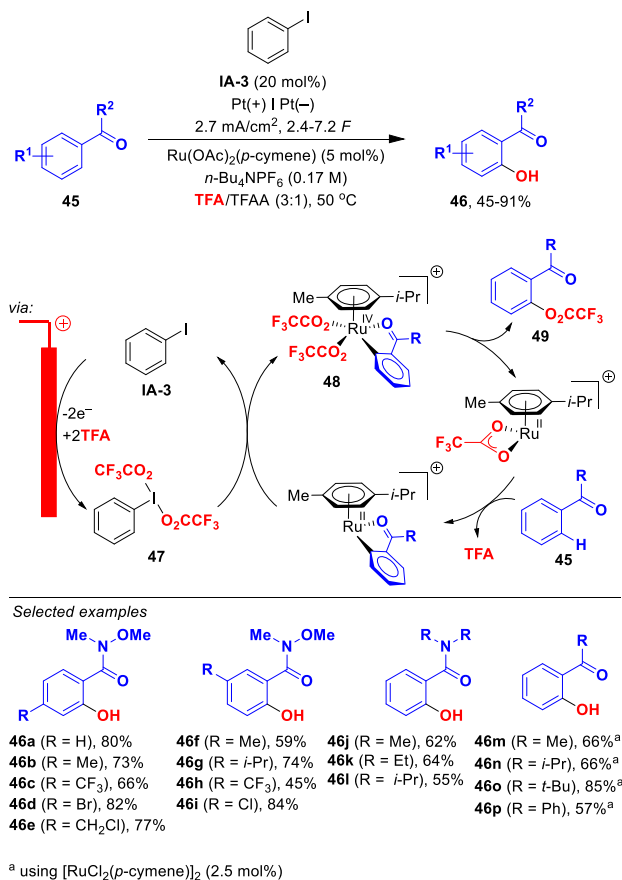
Scheme 19. Electrocatalytic sulfonylimination of alkyl aryl sulfides employing iodobenzene IA-3.

and it is also an outlier with regard that iodine cycles between I(V) and I (VII) oxidation states, rather than I(I)/I(III) as in all the instances presented so far. Namely, in the early 2000s, Schäfer and a co-worker developed an electrocatalytic method for the oxidative cleavage of alkenes using $\text{IO}_4^-/\text{RuCl}_3$ double mediator system (Scheme 20) [71]. The transformation is, thus, an electrocatalytic version of the classic Sharpless reaction [72]. The electrolysis was performed in a divided cell utilizing PbO_2 anode, which at the time was the best known material for the electro-oxidation of IO_3^- to IO_4^- [73]. Three examples were presented and the obtained yields were on the par with the equivalent reactions carried out with stoichiometric periodate. The loading of NaIO_4 applied in the electrochemical process was 90 mol% relative to the substrate, however, one has to note that as many as 4 turnovers of IO_4^- are required for the full oxidation of the substrate, therefore, less than a quarter of the amount needed in a stoichiometric reaction was used. Taking into account the methodological progress in the electrolytic synthesis of periodate, and its widespread use in synthetic organic chemistry, there is clearly a potential for the development of novel methods employing similar principle [74]. Also worth mentioning, the authors presented an interesting flow system for an ex-cell regeneration of periodate, exploiting the immobilization of the starting material. Although the experimental setup was rather complex, this approach allowed to reduce the loading of periodate to less than 5% of the amount needed in stoichiometric oxidation.

In 2020, Ackermann et al. developed an *ortho*-directed C–H oxygenation of arenes using a cooperative catalysis with Ru complex and iodobenzene IA-3 (Scheme 21) [30a]. The reaction is a direct equivalent to the earlier process reported by the same group in 2013,



Scheme 20. Electrocatalytic oxidative cleavage of alkenes employing cooperative catalysis with periodate and $\text{RuCl}_3 \cdot \text{H}_2\text{O}$.



Scheme 21. Electrocatalytic *ortho*-directed C–H oxygenation of arenes employing cooperative catalysis with iodobenzene IA-3 and Ru complexes.

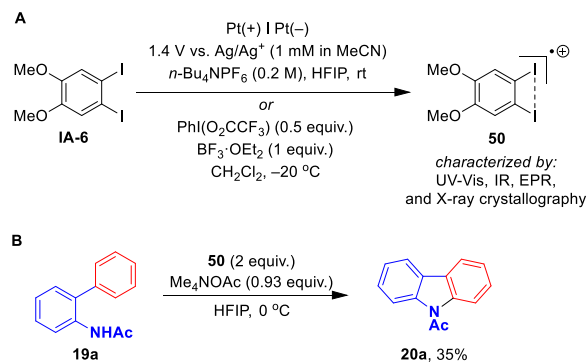
powered by a stoichiometric I(III) oxidant [75]. Notably, the replacement of electric stimulus by chemical oxidants (*m*CPBA or Oxone) drastically decreased the reaction efficiency in this case. Substrate scope

was expanded compared to the previous work, covering not only various Weinreb amides (**46a-i**), but also secondary amides (**46j-l**), ketones (**46m-p**), and pyrazoles (not shown) as directing groups. This testifies to robustness of such, rather complex, double electrocatalytic system. Mechanistically, the reaction likely proceeds through a two-stage indirect electrolysis, wherein **IA-3** is first electro-oxidized to (diacyloxyiodo) benzene **47**, which in turn generates Ru(IV) complex **48**, priming the difficult C–O forming reductive elimination. Resulting trifluoroacetic ester **49** is then cleaved during work-up to final product **46**. Two issues are of notice regarding this reaction. First, the application of iodoarene as the additional mediator is required to oxidize ruthenium to Ru(IV) that could not be achieved by a direct electro-oxidation thereof. This is in contrast to the electro-oxidation of Ru(0) to Ru(II) complexes that proceeds readily [76]. Secondly, exactly the same transformation could be later realized without iodoarene mediator, by utilizing a dinuclear rhodium complex, which efficiently undergoes the direct electrochemical oxidation to the active Rh(III)–Rh(III) form [77].

4. Iodoarenes as single-electron transfer mediators

As described in the end of Section 2, in 2022, Powers has introduced a new concept of single-electron electrocatalysis with iodoarenes [31, 34]. In this approach, the electro-oxidation of iodoarene catalyst is terminated at the stage of iodonyl(II) radical cation, which serves as a single-electron oxidant for the organic substrate (Scheme 3). Naturally, the reactions promoted by such I(I)/I(II) cycle will generally be divergent from ones employing traditional two-electron I(III) oxidants. The feasibility of an iodoarene to act as an efficient single-electron transfer mediator relies on the increased stability of the corresponding I(II) species, both to consecutive anodic oxidation and to decomposition or disproportionation [78]. In their seminal article, Powers et al. identified 1,2-diiodo-4,5-dimethoxybenzene (**IA-6**) to fulfill these criteria [31]. First, **IA-6** displayed nearly perfect reversibility of CV redox wave in HFIP, but unlike in the case of 4-iodoanisole (**IA-1**), no apparent decomposition of I(II) radical cation **50** was observed. Moreover, the addition of AcO[−] ions caused only a partial loss of reversible electrochemistry, demonstrating the robustness of **50**. Most significantly, however, **50** could be quantitatively generated, either by electrochemical or chemical oxidation, isolated, and fully characterized (Scheme 22A). The unique stability of **50** was ascribed to the presence of two methoxy substituents and the I–I interaction, allowing for the efficient delocalization of both the charge and the spin of radical cation. Finally, stoichiometric **50** was found to induce the formation of carbazole **20a** via oxidative C–N coupling (Scheme 22B), similarly to I(III) species (indirectly pointing to a universal radical mechanism of this transformation [79]).

Capitalizing on the advantageous features of **IA-6**, Powers and co-workers applied it in the electrocatalytic versions of several oxidations



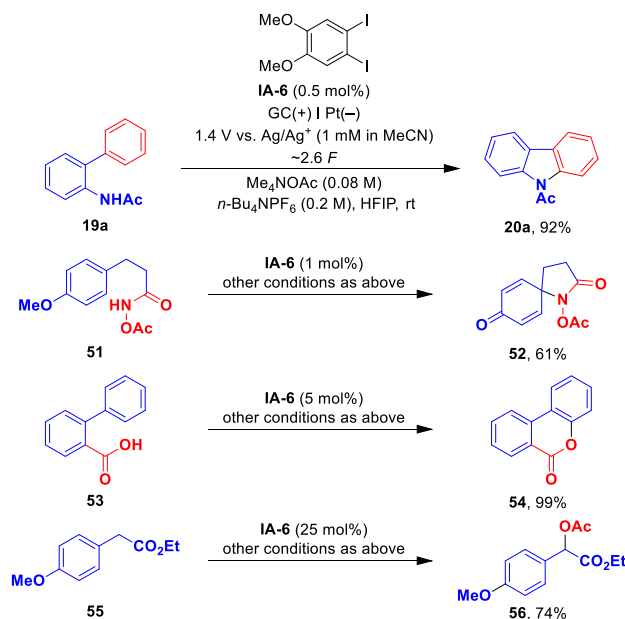
Scheme 22. (A) Oxidation of 1,2-diiodo-4,5-dimethoxybenzene **IA-6** affording stable iodonyl(II) radical cation **50**. (B) C–N coupling with stoichiometric **50** (NMR yield).

that show propensity to proceed through radical pathways (Scheme 23) [80]. Noteworthy, three of the tested reactions could be carried out with low catalyst loadings, down to 0.5 mol% for the conversion of **19a** into **20a**.

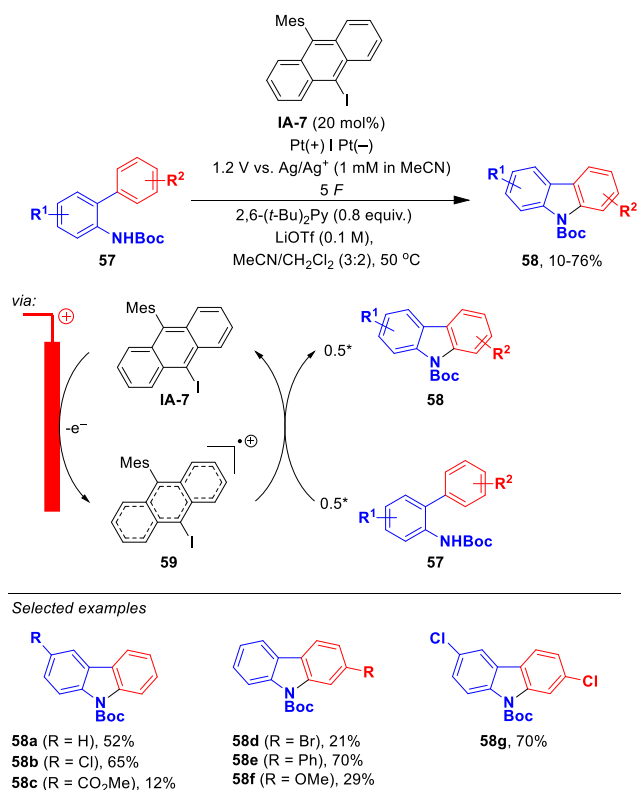
Shortly after the appearance of Powers's work, Shida and co-workers deposited a preprint describing a closely related concept, however, employing a distinctly different design of the electrocatalyst [81]. Building on the reversible electrochemistry of π -extended iodoarenes and presumably drawing inspiration from the structure of acridinium-based photoredox catalysts [82], the authors proposed 9-iodo-10-mesitylanthracene **IA-7** as a possible single-electron transfer mediator (Scheme 24). The corresponding radical cation **59** is highly stabilized due to delocalization and it was found to be sufficiently persistent to enable its quantitative electro-generation and *in situ* characterization by EPR. **IA-7** was successfully applied in the synthesis of N-Boc-carbazoles **58** through the oxidative C–N coupling (Scheme 24). However, its performance was noticeably inferior to that of **IA-6**.

5. Summary and outlook

In summary, this short review provides an exhaustive survey of electrochemical oxidations that have made use of hypervalent iodine redox catalysis. Although the first reported examples date from the 1990s, preceding iodoarene-catalyzed reactions with chemical oxidants, the field has witnessed rapid progress only over the last 5 years. Not surprisingly, the majority of developed methods mirror the most prevalent applications of hypervalent iodine reagents, that is, these involving aryl iodine(III) species. In particular, the electrocatalytic versions of some common hypervalent iodine(III)-promoted C–N couplings, olefin difunctionalizations, and α -functionalizations of carbonyl compounds have been reported. These processes rely on two-electron electrocatalysis, operating via I(I)/I(III) cycle. Although it has been sometimes argued in the literature that due to the relatively high oxidation potentials of iodoarenes, their application as electrocatalysts will be considerably hindered, the steady emergence of new methods proves quite the opposite. In fact, the possibilities for further progress on this front are evident, and it should be driven by the clear edge that the electrocatalytic approach has over the stoichiometric electro-generation of I(III) reagents. The use of chiral iodoarene catalysts to effect electrochemical enantioselective oxidations seems to be an especially



Scheme 23. Electrochemical oxidations through single-electron catalysis by 1,2-diiodo-4,5-dimethoxybenzene **IA-6** (NMR yields).



Scheme 24. Electrochemical C–N coupling through single-electron catalysis by 9-iodo-10-mesitylanthracene IA-7.

underdeveloped, while highly promising, area. Likewise, the application of iodoarene mediators to facilitate the electro-oxidation of transition metal complexes, effecting cooperative redox catalysis, is conspicuously in a nascent stage. Potential opportunities await also in the largely unexplored realms of I(III)/I(V) and I(V)/I(VII) two-electron redox chemistries. Although, the challenges associated with the required preferential electro-oxidation of catalyst over the direct oxidation of substrate are even more significant in these instances, the successful implementation of the electrocatalytic periodate/Ru-promoted cleavage of alkenes gives reasons for cautious optimism. Finally, the recent introduction of single-electron I(I)/I(II) electrocatalysis opens up possibilities for entirely new reaction designs that are not rooted in the existing processes utilizing hypervalent iodine reagents.

CRedit authorship contribution statement

Ronit S. Bernard: Writing – original draft. **Ajit Kumar Jha:** Writing – original draft. **Marcin Kalek:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization.

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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