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Mechanistic Studies on the Anodic Functionalisation of Alkenes Catalysed by Diselenides

Mona Wilken,^[a] Stefan Ortgies,^[b] Alexander Breder*,^[b] Inke Siewert*^[a]

a) Universität Göttingen, Institut für Anorganische Chemie, Tammannstr. 4, 37077 Göttingen, Germany

b) Universität Göttingen, Institut für Organische und Biomolekulare Chemie, Tammannstr. 2, 37077 Göttingen, Germany E-Mail: alexander.breder@chemie.uni-goettingen.de; inke.siewert@chemie.uni-goettingen.de

Abstract: Herein, we present a detailed kinetic and thermodynamic analysis of the anodic allylic esterification of alkenes as well as the bulk application of the anodic amination and esterification of non-activated alkenes catalysed by diselenides. The electrochemical study led to a comprehensive picture of the coupled electrochemical and chemical reaction steps. Cyclic voltammetry measurements are consistent with a bimolecular step after initial electrochemical $1e^-$ oxidation of the diphenyl diselenide catalyst, **1a**, and therefore we postulate a dimerisation of the cation, which reacts very rapidly with the alkene forming the addition product, i.e. the selenolactone **2a**. Subsequent electrochemical oxidation of **2a** occurs at a slightly higher potential than initial oxidation of **1a**. The second oxidation is also followed by bimolecular process and we hypothesize a dimerisation of the catalysts, i.e. non-sterically demanding diaryl diselenides with electron withdrawing and donating substituents, revealed that the oxidation potential of the catalyst and the intermediate can be readily tuned by the substituents, thus, prospectively allowing for a wide application of olefinic and nucleophilic substrates. The substituent pattern at the alkene has a smaller influence on the redox potential of the adduct. Controlled potential electrolysis experiments employing different nucleophiles proved that the reaction can be run electrochemically. The functionalisation of unactivated alkenes with *N*- and *O*-nucleophiles was successfully demonstrated in several bulk electrolysis experiments and the product.

Keywords: Electroorganic synthesis, selenium, oxidative allylic functionalisation, redox catalysis, mechanism

Introduction

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The utilisation of simple, non-activated alkenes as readily available and inexpensive building blocks for the oxidative construction of (hetero)functionalised hydrocarbon architectures represents a strategically sound and highly soughtafter approach in the realm of chemical synthesis. To this date, the main part of investigations toward the development of catalytic alkene oxidations such as allylic functionalisations has centred on the use of transition metal catalysts.^[1] Due to the lack of selectivity in such processes, certain olefinic substrate classes such as internal di-, tri-, and tetrasubstituted alkenes still continue to cause severe challenges.^[1d] As a complementary approach that was frequently found to be even suitable for multisubstituted internal alkenes, a steadily increasing number of protocols involving catalysts that are derived from p-block elements such as iodine, sulphur, and selenium have been reported.^[2,3] With regard to the latter element, organic (di)selenides were recurrently shown to facilitate a diverse array of catalytic oxidation reactions including allylic alkene functionalisation .[3] Mechanistically, the oxidative allylic functionalisation of alkenes catalysed by Lewis-acidic Se-species generally was proposed to proceed through the oxidative and regiospecific formation of seleniranium intermediates I,^[4] which upon attack by given nucleophiles furnish adducts 2 (Scheme 1). Subsequent, oxidative elimination of the selenium residue eventually generates the allylic functionalisation product 4a. Due to the mechanistic idiosyncrasies of Se-catalysed π bond activations, this methodology recurrently allowed for the conversion of substrate classes that were found to be unamenable for analogous transition metal-catalysed protocols, thus, providing a complementary tool for the oxidative functionalisation of simple alkenes.[4e]

Traditional selenocatalytic procedures for the oxidative derivatization of alkenes predominantly necessitate the use of strong and in part highly corrosive oxidants such as *N*-haloamides and -imides, hypervalent iodine compounds, and certain peroxide derivatives.^[5] Despite the remarkable achievements that have been made with these oxidants, their overall utility was shown in many cases to be significantly impaired by a low degree of redox economy,^[6a] atom economy,^[6b] carbon-efficiency,^[6c] and – most importantly – a severely restricted range of applicability due to limitations in terms of chemoselectivity.^[4e] Against this background, the demand for new oxidation strategies that may offer a wider scope of application becomes lucidly evident.^[7]



Scheme 1. Proposed mechanism for the oxidative allylic functionalisation of alkenes 3 catalysed by diselenides 1.

A promising approach would be the use of electric current, i.e. free electrons and holes, as oxidant. Electrochemistry represents a versatile method for generating reactive species

under very mild conditions.^[8] The implementation of an electrochemical redox regime in the context of Se-catalysed alkene functionalisations would therefore entail significant advantages compared to previous approaches.[5c,9] For example, corresponding intermolecular processes that are driven by customary chemical oxidants very frequently suffer from insufficient chemoselectivity, since nucleophilic byproducts derived from these oxidants (i.e., endogenous nucleophiles) can superiorly compete with external nucleophiles that are actually intended to be coupled with the alkene.^[4e] Consequently, an electrochemical approach, which circumvents the transient generation of competing endogenous nucleophiles, may provide an adequate solution to this oxidant paradigm. Furthermore, the requisite redox potentials can be accurately fine-tuned under electrochemical conditions, which eliminates the risk of undesired side reactions that may proceed at potentials higher than the actual target reaction, but below the redox potential of the oxidant. Along the same lines, the targeted electrochemical process would become more energy-efficient as the applied potential matches the potential of the desired reaction. Furthermore, the stoichiometric production of multi-atomic waste derived from customary chemical oxidants would be intrinsically obviated, which would overall render the oxidation event more sustainable.^[10,11] Against this background it seems surprising that until today there is only a very limited number of studies on record showcasing that selenium-mediated allylic functionalisation of alkenes can be driven electrochemically. Torii et al. were the first to describe the anodic synthesis of allylic alcohols and ethers from simple alkenes using (PhSe)₂, **1a**, as a redox pre-catalyst.^[12] The authors postulated that phenylselanol (PhSe-OH) would serve as the actual catalytically active species. Mellor et al. later reported the stoichiometric acetamidoselenenylation of non-functionalized alkenes through anodic oxidation of 1a in acetonitrile (1.3 V vs. 0.1 M AgNO₃/Ag).^[13] In this context, the authors suggested [PhSe]⁺ to be the crucial catalytic species in these reactions.^[14] The selenenium cation was believed to be formed via sequential oxidation of 1a and proposed to react with the olefinic substrate to give an amidation adduct analogous to species 2.^[14] This mechanistic hypothesis for stoichiometric reactions was later slightly refined by Sasaki et al., who had speculated on the transient formation of iranium ion I prior to the nucleophilic attack of MeCN, and by Jouikov et al., who showed that the conversion of adducts 2 to products 4a can proceed with second order kinetics depending on the reaction medium.^[15]

Despite these very indicative yet limited reports, no comprehensive study on the anodic functionalisation of alkenes catalysed by diselenides, particularly concerning a detailed mechanistic analysis in terms of reaction kinetics and thermodynamics, has been conducted so far. We surmised that a more in-depth understanding of the reaction mechanism as well as a sound knowledge on the redox potentials of critical reaction intermediates could aid in the design of highly customised electrochemical methods for a diverse array of allylic alkene derivatisations. Aromatic diselenides seemed to be ideal candidates for a large variety of substrates, because their redox potentials should be readily tuneable by the substituents and their synthesis is straightforward.^[16] Ideally, this would make our aspired method highly adjustable to a wide scope of olefinic and nucleophilic substrates. As a consequence of these considerations, we disclose herein the results of our mechanistic investigations on the anodic allylic alkene functionalisation catalysed by **1** and the exemplification of the method in the allylic amination and esterification of olefins. The study provides the rational fundament for the design of anodic alkene functionalisations mediated by diselenide catalysts.

Results and discussion

At the outset of our investigation, we aimed to get a detailed understanding of the electrochemical and chemical reactions that are responsible for the conversion of the alkene into the functionalised product.^[17,18] As a model reaction we chose the allylic esterification of hex-3-enoic acid, **3a**, forming 5-ethylfuran-2(*3H*)-one, **4a**, catalysed by the unsubstituted diphenyl diselenide **1a** (Scheme 2).^[7f]



Scheme 2. Anodic allylic esterification of 3a.

Thus, 1a was analysed by cyclic voltammetry at first, as the cationic product of this oxidation was proposed to be the crucial species forming the intermediate 2a. The CV measurements were conducted in dry and degassed acetonitrile under a dinitrogen atmosphere employing a glassy carbon (GC) electrode. All data are referenced vs. the Fc^{+/0} redox couple. The CV of 1a in acetonitrile at 0.1 Vs⁻¹ revealed two anodic features, a shoulder at ~0.95 V and a peak at 1.04 V, and one corresponding cathodic feature at -0.43 V (Figure 1, top). This points to two subsequent oxidation processes at very similar potentials. The cathodic feature is absent, if the CV is swept cathodically at first. The CV at 0.1 Vs⁻¹ is similar to the one previously reported by Sasaki et al.,^[15a] though the authors did not observe the shoulder but only one feature around 1 V.^[14,15a] The second anodic feature and the cathodic feature at -0.43 V vanished upon increasing scan rates ($v > 2 \text{ Vs}^{-1}$), and a new cathodic feature appeared around -0.15 V ($v = 10 \text{ Vs}^{-1}$) (Figure 1, bottom). This indicates minimum two chemical reactions following the oxidation of **1a**, one fast reaction giving the redox active species with a reduction potential at -0.15 V and a slower reaction forming the species showing a reduction process at -0.43 V. The first oxidation process equals ~1 electron per **1a** (Figure S 11). When we used a Pt working electrode, the shape of the CV was very similar (Figure S 7, Figure S 8), thus the CV does not depend on the electrode material. We also studied the effect of the supporting electrolyte and the solvent on the voltammogram, because Geiger and coworkers observed significant differences in (ArS)₂ by changing from "Bu4NPF6/MeCN to "Bu4NBAr^{F/}CH₂Cl₂.^[19] However, the oxidation chemistry of **1a** was not affected by the salt and therefore we used GC/MeCN/"Bu4NPF6 for all further measurements (Figure S 8-Figure S 10).

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The peak current $i_{pa,l}$ of the first anodic feature increased linearly with the square root of the scan rate, which is characteristic for diffusion controlled conditions ($v = 0.8 - 10 \text{ Vs}^{-1}$, Figure S 11).^[20] The large separation of the cathodic and anodic wave over the whole scan rate range and the anodic shift of the peak potential $E_{pa,l}$ per ln(v) are indicative for an irreversible electron transfer process or an (ir)reversible electron transfer process followed by a fast chemical reaction (EC sequence, E = electrochemical step, C = chemical step, Figure S 12).^[20] A following chemical reaction, as already proposed previously, is very likely given the reported low stability of [(PhSe)₂]+.^[14,15,21] Suchlike radical cations were only isolable with sterically demanding residues, e.g. bis(*m*-terphenyl).^[22]



Figure 1. CV of 1a in acetonitrile at different scan rates, $I = 0.1 M^n Bu_4 NPF_6$, [1a] ~ 0.72 mM.

The second oxidation process vanished with increasing scan rates, which indicates that this oxidation process belongs to a redox active species that is formed in a rather slow chemical reaction after initial oxidation of **1a**. Furthermore, this species is also formed in smaller amounts with increasing concentrations of **1a** ([**1a**] = 0.5-2 mM), as we concluded from concentration dependent measurements. With increasing concentrations of **1a** the ratio of the second and first feature decreases, which indicates a second bimolecular route after initial oxidation of **1a** (Figure S 13).

Next, we wanted to investigate the impact of the presence of an alkene on the CV of **1a**. The addition of a 10-fold excess of **3a** significantly altered the CV of **1a** (Figure 2). The second anodic feature of **1a** ($E_{pa,I} = 1.04$ V) as well as the cathodic features at -0.43 V were no longer present but a new anodic feature appeared at 1.15 V (v = 0.1 Vs⁻¹). This second oxidation process was assigned to the oxidation of 5-methyl-4-(phenylselanyl)dihydrofuran-2(3*H*)-one, **2a**, as was confirmed from independent measurements of **2a** (Scheme 2, Figure 2). The missing cathodic features with regard to the CV of **1a** indicate a rather fast and clean chemical reaction of **3a** and the oxidised species, producing **2a**.



Figure 2. CV of **1a**, **2a** and **1a** + 10 equiv. **3a** in acetonitrile, $v = 0.1 Vs^{-1}$, $I = 0.1 M^n Bu_4 NPF_6$, **[1a]** = 1 mM, **[2a]** = 0.25 mM, the right y-axis belongs to the measurement of **2a**.

The linear shift of the first anodic peak potential $E_{pa,1}$ per $\ln(v)$ is indicative for minimum an EC mechanism, that is the oxidation product derived from 1a reacts with 3 to yield 2a (Figure S 14, Figure S 16). The current of the first oxidation process equals ~1.8 electrons according to Randles-Sevcik equation, indicating quantitative conversion of **1a** to **2a** (Figure S 14). The current ratios of $i_{pa,1}$ and $i_{pa,2}$ held constant over the whole sweep range of 0.02 Vs⁻¹ to 10 Vs⁻¹ (Figure S 17), which points to a very rapid formation of 2a after initial oxidation of 1a. Therefore, the species that was slowly formed after initial oxidation of 1a in the absence of 3a (second anodic feature, Figure 1) does not represent the kinetically relevant intermediate for the formation of adduct 2a. This particular species (i) was not detected in the CV of a mixture of 1a and 3a and (ii) is not formed at high scan rates after oxidation of 1a, whereas adduct 2a is formed quantitatively even at high scan rates. The missing reverse wave of 2a and the linear shift of its anodic peak potential $E_{pa,2}$ per $\ln(v)$ is in line with an oxidation of

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adduct **2a** followed by the elimination of a proton and 0.5 equiv. **1a**, yielding the final product **4a** (Figure S 14, Figure S 16). Notably, both redox processes are under diffusion control, since $i_{pa,1}$ and $i_{pa,2}$ increase linearly with the square root of the scan rate (Figure S 15, [1a] = 0.25 or 1mM). In other words, the CV is not recorded under catalytic conditions and k_{cat} is small in comparison to the time scale of the CV. In line with this conclusion are the facts that $i_{pa,2}$ remains the same when the concentration of **3** is doubled and that the current from the oxidation of **2a** is not altered by the presence of excesses of **3a** (Figure 2, Figure S 18, Figure S 19).

Concentration dependent measurements of **1a** and **3a** revealed that the first and second peak shift toward more cathodic potentials with increasing concentrations of **1a** (Figure 3, Figure S 20). This finding is indicative for bimolecular reactions proceeding both oxidations and thus, excludes $[(SePh)_2]^+$ as being the active species since the reaction of **1a**⁺ and **3a** would be first order in **1a**⁺.^[20]



Figure 3. Concentration dependent measurements of 1a and 5 mM 3a in acetonitrile, concentration normalised current; $v = 0.1 Vs^{-1}$, I = 0.1 M ⁿBu₄NPF₆.

In order to obtain information on the structure of the selenium intermediates that are presumably involved in the conversion of 1a into 2a, we investigated the redox properties of [PhSe]PF₆ and [(PhSe)₃]BF₄. Both cationic Se-species were speculated to be oxidation products of 1a and to serve as potent electrophiles towards 3a.^[14,15a,7f] Both species are rather unstable, but we had reasonable evidence that they can be formed *in-situ* for a limited time period. The chemical oxidation of 1a with substoichiometric amounts of NOBF4 in MeCN-d3 lead to a new species, which showed three distinctly shifted and differently split multiplets with regard to 1a in the proton NMR spectra (Figure S 2). The ⁷⁷Se NMR of the reaction mixture showed one singlet at 716 ppm (Figure S 3). A pronounced low field shift of the ⁷⁷Se resonance compared with 1a (cf. $\delta = 459 \text{ ppm})^{[23]}$ was in line with our expectation, and the shift was too low to count for other species such as [(PhSe)2]+ or fluorinated selenium species (Table S 1, Ref [22-26]). The (+)-ESI mass spectrum of the reaction mixture showed one main species, which was univocally assigned to [(PhSe)3]+ and a minor, second trinuclear species, which could not be identified (m/z = 419.0)u/e, Figure S 5). Thus, we tentatively assigned the product of the reaction of 1a and 0.66 equiv. NOBF₄ to be $[(PhSe)_3]^+$.

 $[(PhSe)_3]^+$ exhibits a reduction process at -0.38 V (v = 0.1 Vs⁻¹, Figure 4). In contrast to the CV of **1a**, this reduction process is already present when the potential is swept cathodically at first and it gets more prominent when the sweep direction is reversed (Figure S 28). The first two oxidation processes of [(PhSe)₃]⁺ occur at the same potential as in **1a** ($E_{pa,1} \sim 0.92$ V, $E_{pa,2} = 1.03$ V; v = 0.1 Vs⁻¹), but in contrast to 1a, the second process is not vanishing at high scan rates (Figure S 29). That is, the species, which is oxidised at 1.03 V, is not formed in-situ but is present already in [(PhSe)₃]⁺. The redox properties of [(PhSe)₃]⁺ in the presence of 3a are very similar to the one of the mixture of 1a and 3a and the reduction process in the reverse potential scan is no longer present (Figure S 30). The first oxidation process occurs at the same potential as in 1a and the second one as in 2a. However, the current ratio of the first and the second oxidation process increases from 150 to 180% with respect to the CV of 1a and 3a. In other words, larger amounts of adduct 2a are formed with regard to the number of injected electrons in the first oxidation process. This indicates that [(PhSe)₃]⁺ reacts initially with **3a** forming 1 equiv. 1a and 1 equiv. 2a. Subsequently, the in-situ generated 1a reacts with further equivalents of 3a upon electrochemical oxidation. However, the trimeric selenonium ion [(PhSe)₃]⁺ is most likely not the species being initially formed during the oxidation of 1a in the presence of 3a. This conclusion is based on the fact that the CV of [(PhSe)3]+ has two characteristic anodic features (cf. $E_{pa,1} = 0.94$ V; $E_{pa,2} =$ 1.04 V, v = 0.1 Vs⁻¹) on the time scale at which adduct **2a** is formed, while at the same time scale, the CV of 1a shows only the first feature.

The monomeric selenenium ion [PhSe]+ was prepared by treating PhSeBr with AgPF6 or AgBF4 in MeCN-d3. Surprisingly, the (+)-ESI mass spectrum of this reaction mixture also showed [(PhSe)₃]⁺ as the only species (Figure S 6). However, the NMR data and the redox chemistry of the reaction product derived from 1a and NOBF4 and of PhSeBr and AgPF₆ differ largely. Therefore, we assume that in the case of PhSeBr and AgPF6 serving as starting materials, the trimeric cation [(PhSe)₃]⁺ is produced under the reducing conditions of the ESI MS experiment. The proton NMR spectra of the reaction product of PhSeBr and AgPF₆ showed distinctly shifted multiplets in comparison to the spectra of 1a, PhSeBr, and [(PhSe)₃]⁺ (Figure S 4). The ¹³C NMR of the reaction mixture showed two species in a ratio of 10:1, which is similar to the ratio of the two main species in the proton NMR spectra. 77Se NMR spectra of the reaction mixture showed one slightly broadened signal at 850 ppm (Figure S 3). The signal exhibits a low field shift in comparison to $[(PhSe)_3]^+$ (cf. $\delta = 716$ ppm) and **1a** (cf. $\delta =$ 459 ppm).^[23] On the basis of our current analytical data, we tentatively assign this initially formed species to [PhSe]⁺.^[27,28] The species, which we tentatively assign to [PhSe]+, is stable for approximately 45 min, after 2 h it is fully decomposed. Time dependent MS studies revealed full conversion to a product with the composition of





Scheme 3. Proposed reaction pathways after the electrochemical oxidation of 1a in the absence (light grey) and presence of 3a (black). The green pathways describe minor pathways in the presence of 3a, as the formation of $[PhSe]^+$ and $[(PhSe)_3]^+$ is a rather slow process with regard to the formation of 2a. rds: rate-determining step.

 $C_8H_7NNaSe^+$, – a compound likely formed in a reaction of $[PhSe]^+$ with MeCN.



Figure 4. Overlay of representative CVs of $[(PhSe)_3]BF_4$, [PhSe]PF₆, and **1a** at two different scan rates, I = 0.1 M ⁿBu₄NPF₆; the right y-axis belong to the measurement of **1a**. The redox process marked with an asterisk likely belongs to PhSeBr as reasoned from independent measurements of PhSeBr under otherwise identical conditions.

[PhSe]⁺ or its very fast forming decomposition product exhibits a reduction process at -0.43 V (v = 0.1 Vs⁻¹), which is present at slow scan rates and is not affected by a preceding anodic scan (Figure S 31). The same cathodic feature is present in the CV of **1a** at slow scan rates and in [(PhSe)₃]⁺. The first oxidation process of [PhSe]⁺ occurs at ~1.01 V, which is at the same potential as the second anodic feature in the CV of 1a at slow scan rates (Figure S 32, Figure 4). Thus, we assign the species, which is formed in a slow proceeding reaction after initial oxidation of 1a, to be [PhSe]+ or its very fast forming decomposition product. The CV of [PhSe]⁺ in the presence of 3a resembles that of 2a (Figure S 33), indicating that [PhSe]+ is capable of reacting with 3a to furnish 2a. However, the rate of formation of [PhSe]+ subsequent to the oxidation of 1a is much slower compared to the rate of formation of 2a following the oxidation of 1a in the presence of **3a**. Thus, [PhSe]⁺ is rather unlikely to be a kinetically relevant species to produce 2a after initial oxidation of 1a under these conditions.

Taking all measurements together, we propose the following mechanistic scenario for the oxidation of **1a** in the absence and presence of **3a** (Scheme 3). Having in mind that adduct **2a** is formed very rapidly – more rapidly than the formation of [PhSe]⁺ – after initial one electron oxidation of **1a** in a second order process with regard to **1a** and that **1a**⁺ did not show any reversibility even at high scan rates, we propose a very rapid formation of **1a** (i.e., dimerisation of **1a**⁺).^[29] Such dimerisations of organoselenium cations have precedents in the literature.^[24,30] Dications with the generic composition [R4E4]²⁺ (R = Et, Me, E = Se, Te) were isolated and fully characterised after chemical one-electron-oxidation of the corresponding dichalcogenides (R₂E₂). Such reactivity is very similar to what is proposed herein after the

electrochemical oxidation of 1a. Notably, analogous tetrameric dications possessing non-stabilising aryl substituents were not isolable.^[24,30] This circumstance is in line with the proposed formation of [PhSe]⁺ and [(PhSe)₃]⁺ after electrochemical oxidation of 1a in the absence of 3a as well as the formation of the trimeric species after substoichiometric chemical oxidation of 1a. A dicationic tetramer could well decompose yielding [PhSe]⁺ and [(PhSe)₃]⁺, though the latter can also be formed in a reaction of in-situ formed [PhSe]⁺ and 1a.^[31] In the presence of 3a, however, the proposed transient [(PhSe)₄]²⁺ rapidly reacts with 2 equiv. of 3a, yielding 2 equiv. of 2a and 1 equiv. of 1a. Subsequent oxidation of 2a leads to the corresponding cation $2a^+$, which in turn dimerises to give $[2a-2a]^{2+}$. A second order reaction after electrochemical oxidation has been proposed previously for alkyl aryl selenoethers.^[15c] The authors proposed a disproportionation reaction. However, we assign the primary species, which is formed in a bimolecular step after oxidation of 2a, to a dimeric cation, since the dimersiation of a similar Se cation has been observed previously and a hydrolysis product of $[2f-2f]^{2+}$ has been observed recently by in-situ ESI mass spectrometry during the chemical oxidation of **2f** with NOBF₄.^[7f,32] The rate determining step under electrochemical conditions is the formation of 4a and 1a upon oxidation of 2a.[33]

Table 1. Synthesis of diaryldiselenides 1b-j.



With the idea in mind to make our anodic, selenide-catalysed alkene oxidation protocol tuneable in terms of redox potentials, our efforts turned toward the investigation of aromatic diselenides with electronically varying substitution patterns. For this purpose we synthesised a series of diselenides **1b-j**, which are readily derived from the corresponding set of aryl bromides and an aniline derivative according to literature-known procedures (Table 1).^[16]

In accordance with our expectations, the peak potentials of the first oxidation process for each diselenide **1** vary over a wide potential range (Table 2). More specifically, **1e** (*o*-MeO and *p*-OMe) exhibits the lowest peak potential of about ~0.6 V and **1j** (*m*-CF₃ and *m*-CF₃) the highest with 1.35 V ($\nu = 0.1$ Vs⁻¹, Table 2, Figure S 21, Figure S 22).

Table 2. First anodic peak potentials E_{ap} of **1** and **2** at 0.1 Vs^{-1} . If not otherwise noted, **2** have been formed in-situ by electrochemical oxidation of **1** in the presence of **3a**. I = 0.1 $M^{n}Bu_{4}NPF_{6}$, [**1**] = 0.5-0.6 mM, [**3a**] = 5 mM, MeCN.

	E_{ap} /V		E_{ap}/V
1a	~0.95	2a	1.15 ^a
1b	0.87	2b	1.08
1c	0.80	2c	0.94
1d	1.13	2d	1.35
1e	~0.6	2e	0.79
1f	0.82	2f	0.99
1g	1.20	2g	1.32 ^a
1h	1.28	2 h	1.40
1i	0.91	2i	1.11
1j	~1.35	2j	_ ^b

^a Determined by independent measurements of **2**. ^b The oxidation of **2j** is outside the potential window.



Figure 5. First anodic peak potentials E_{ap} of **1** and **2** at 0.1 $V s^{-1} vs$. Hammett's substituent parameter $\sigma^{[34]}$.

The peak potentials follow the trend of the substituent constant σ (Figure 5),^[34] meaning that electron-withdrawing groups increase the oxidation potential of diselenides 1d, 1g, 1h, and 1j relative to 1a. Analogously, electron-donating groups (e.g., 1b, 1c, 1e, 1f and 1i) markedly lower the oxidation potentials. The scan rate normalised peak currents and the scan rate dependent shifts of $E_{pa,1}$ show the expected behaviour for an EC mechanism in all derivatives. All selenides in this study show initial irreversible oxidation owing the low steric demand at the aryl substituent.^[22] 1b, 1e, and 1j each exhibit a second oxidation process near the potential of the first oxidation. These second features vanish at high scan rates – a behaviour analogous to 1a. 1g and 1h did not show any further oxidation processes within the potential window of the solvent, while 1c, 1f, and 1d exhibit

further oxidation processes at considerably higher potentials. However, the ratios of the first and the second oxidation peak in **1c**, **1f**, and **1d** are scan rate independent in contrast to ratios in **1a**. In **1i**, the second oxidation process gets more prominent with increasing scan rate, while the third one vanishes. These disparities could point to slightly different reaction kinetics after initial oxidation of **1**.

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However, upon adding an excess of alkene 3a, the first oxidation features of all diselenides 1 remain unchanged and additional features vanish. As in the case of 1a, a second oxidation process occurred in the CV of 3a in the respective presence of 1b, 1c, 1d, 1e, 1f, 1h, and 1i (Figure S 23). 1j cannot be oxidised any further within the potential window of the solvent and 1g behaves slightly different, that is a prewave occurs upon adding 3a. Thus, these two compounds are excluded from the following discussion. The second features, observed in the CV of 1 in the presence of 3a, belong to the respective adducts 2. As was already observed for 2a, the substituted analogues 2b-f, 2h, and 2i were formed very rapidly, because the current ratios of the first (1) and second (*in-situ* formed 2) oxidation peaks are very similar over the whole scan rate range (0.1-20 Vs^{-1} , Figure S 24). The peak current normalised by the square root of the scan rate for each diselenide 1 and *in-situ* formed adduct 2 is very similar, which is indicative of diffusion controlled conditions rather than catalytic conditions as in 1a.

The oxidation potentials of **2** vary over a wide range (0.70-1.40 V). However, the peak potential differences between **1** and their respective **2** are relatively invariant for all compound pairs, ranging from 0.12 V in **1g/2g** to 0.22 V in **1d/2d** (Table 2, Figure 5). The very similar behaviour of all diselenides suggests a very similar mechanism independent from the respective substitution pattern. The species that are formed after initial oxidation of **1** – most likely tetrameric dications – react very fast with **3a** to form **2**, which in turn are further oxidised at slightly higher potentials than **1**.

Next, we wanted to analyse the influence of electronically varied substituents embedded in the alkene-derived carbon backbone of selenoacetoxylation adducts 5a-h on the redox potential (Scheme 4). We surmised that the corresponding redox potential would more strongly depend on the substituents on the aryl group and less on the substituents incorporated in the alkene-derived carbon backbone, as the former is spatially nearer to the redox active Se centre. Accordingly, we synthesised adducts 5a-h through the conversion of alkenes with PhSeBr and potassium acetate in a 10:1 mixture of acetic acid and acetic anhydride, furnishing the target structures in 54-97% yield (Scheme 4). CV of 5a**h** revealed a first oxidation feature in a potential range similar to the oxidation potential of 2a, i.e. 5g exhibits the lowest peak potential at 1.03 V, while the peak potential of 1.22 V for 5c represents the upper limit within this series (Scheme 4, $v = 0.1 \text{ Vs}^{-1}$). The electron-withdrawing substituents within 5c and 5f shifted the potentials anodically relative to 2a. An analogous trend toward lower oxidation potentials was recorded for adducts possessing electron-donating groups (e.g., 5e, 5g, and 5h). Scan rate dependent data revealed diffusion controlled oxidation processes for all derivatives, and the missing reverse feature as well as the potential shift of $E_{pc,1}$ with v is in line with an EC process (v = 0.1-20 Vs⁻¹, Figure S 26, Figure S 27).

In summary, we can conclude that the electronic nature of the substituents within the carbon backbone of **5** has a smaller influence on the redox potential than the substituents on the ArSe groups. This finding appears plausible, since the selenium atom is the redox active centre and should therefore experience stronger electronic effects exerted by the substituents of the adjacent aryl groups.

R ²				OAc R [∠]	
~			KOAc	Ϋ́	
R ¹ + PhSeBr		РПЗерг	AcOH/Ac ₂ O (10 : 1)	Ĩ	
3	(1 equiv)		SePh	
		E _{pa,1} /V		rac -5	
	5a:	1.10	5a: R ¹ = 4-tolyl,	$R^2 = CO_2Et$	
	5b:	1.10	5b: R ¹ = Ph,	$R^2 = CO_2Et$	
	5c:	1.22	5c: R ¹ = 4-CF ₃ -C ₆ H	H₄, R ² = CO ₂ Et	
	5d:	1.13	5d: R ¹ = Et,	$R^2 = CO_2Et$	
	5e:	1.07	5e: R ¹ = Et,	R ² = OH	
	5f: ^a	1.21	5f: ^a R ¹ = Et,	$R^2 = CN$	
	5g:	1.03	5g: R ¹ = Et,	R ² = Me	
	5h:	1.08	5h: syn isomer of 5	5h: syn isomer of 5g (from Z-alkene)	

Scheme 4. Synthesis and peak potentials of 5 at 0.1 Vs⁻¹. I = 0.1 MⁿBu4NPF₆, [5] = 1 mM; ^a5f corresponds to syn-isomer derived from Z-alkene.

Electrosynthesis

Finally, the question remained, if the catalysis can be successfully conducted under electrochemical conditions. Therefore, controlled potential electrolysis experiments (CPE) were run. All CPE have been conducted in a one-compartment cell under air with dry and degassed acetoni-trile (Figure S 1). At first, the reaction of **1a** and **3a** in a 1 to 10 ratio was investigated. CPE at the half peak potential of the first oxidation process of **1a** and **3a** was conducted in order to confirm the electrosynthesis of **2a**. After injection of ~2 charge equivalents with regard to **1a**, the yellow colour of **1a** disappears and the CV lacks the first oxidation wave (Figure S 35). The ¹H NMR spectrum of the reaction mixture showed **2a** as the sole product after work-up, which confirmed the electrosynthesis of **2a** after initial oxidation of **1a** (Figure S 49).

Subsequently, we applied a potential in the CPE, which matches the half peak potential of the second oxidation wave, i.e. 1.10 V. The *i* vs. *t* curve showed that the current drop is pronounced during the first 60 minutes of the electrolysis and then rather slow (Figure S 37). Within the first 60 minutes the yellow colour of **1a** disappeared. This behaviour is in line with the observation that the formation of **2a** is rather fast and subsequent formation of **4a** is the rate limiting step in the electrocatalytic cycle. In a large-scale experiment, **4a** was isolated in 78% yield. Notably, no conversion was observed in the absence of the Se-catalyst at the same applied potential. In line with this, the charge transfer at a set potential of 1.10 V was negligible.

Subsequently, we tested the applicability and tunability of the method to a representative set of alkenes and nucleophiles (Table 3). Electrolysis of hex-3-enedioic acid, **3i**, with 0.1 equiv. **1a** at a potential of 1.10 V led to the formation of 2-(5-oxo-2,5-dihydrofuran-2-yl)acetic acid, **4i**, in isolated yield of 86% (Table 3 entry 2, Figure S 38, Figure S 39).

4-(*p*-tolyl)but-3-enoic acid, **3j**, is readily oxidised at an onset potential of 1.1 V similar to the oxidation of **2a** (Figure S 40). Indeed, the CV of **1a**, and **3j** showed that the oxidation of the respective selenofunctionalisation intermediate and the starting material overlap, which could lead to undesired background reactivity during catalysis.^[35] Therefore, we switched to **1c** as catalyst, since it has a lower oxidation potential than **1a** and thus, undesired oxidation of **3j** could be avoided. Indeed, the oxidation peaks of the intermediate and the alkene were well separated in the CV and electrolysis at an applied potential of 0.95 V led to the conversion of **3j** to **4j** with an isolated yield of 58% (Table 3 entry 3, Figure S 40, Figure S 41, Figure S 42).

Table 3. Overview of the electrosynthesis experiments, E vs. $Fc^{+,0}$, Conditions: 0.7-1 Mmol alkene, 0.1 equiv. cat, MeCN, 0.1 M "NBu4PF6.



The method is not restricted to internal *O*-nucleophiles as demonstrated by the functionalisation of 1,6-diphenylhex-3-ene, **3k** with acetic acid and formic acid. Electrolysis of **3k**, with 0.1 equiv. **1a** and 20 equiv. acetic acid and 30 equiv. formic acid at a set potential of 1.05 V for both cases, led to the desired products **6k** and **6l** in yields of 59% and 40%, respectively (Figure S 43, Figure S 44, Figure S 45, Figure S 46). Notably, such intermolecular allylic aceloxylations, in which the alkene substrates do not possess any directing or activating groups, are known to be difficult to perform regioselectively when resorting to palladium catalysis (Table 4).^[1d,36] In our case, however, products **6k** and **6l** were isolated as single regioisomers.^[37]

Table 4. Representative comparison of regioselectivities observed in Pd- and Se-catalyzed acyloxylations of internal, undirected alkenes. ^aThe number refers to conversion into the depicted mixture of isomers.



Finally, the electrocatalytic conversion of N-(2,2-dimethylhex-4-en-1-yl)-4-methylbenzenesulfonamide, 3l, forming 4,4-dimethyl-1-tosyl-2-vinylpyrrolidine, 7 was investigated. Amination reactions are of considerable importance since the C-N bond motif can be found in numerous organic compounds associated with biological, pharmaceutical, or material scientific applications.^[38] The CV of 1a and 3l showed one oxidation feature at a peak potential of 1.06 V (Figure S 47, $v = 0.1 \text{ Vs}^{-1}$). Applying a potential of 1.00 V to a solution of 0.1 equiv. of 1a and 3l leads to the conversion of **31** to **7** as anticipated. The *i* vs. *t* curve showed that the current drop is pronounced during the first 60 minutes of the electrolysis and then rather slow, indicating a similar reaction cascade as was observed for 1a and 3a (Figure S 48). The electrosynthesis yielded analytically pure 7 in 64%.

Conclusion

A detailed mechanistic analysis of the anodic allylic esterification of alkenes led to a comprehensive picture of the proceeding electrochemical and chemical steps. Initial electrochemical oxidation of the catalyst is followed by a bimolecular reaction, likely the dimerisation of the cation [(PhSe)₂]⁺. The cationic tetramer reacts very rapidly with the alkene forming the selenooxylation adduct **2**. The adduct is electrochemically oxidised at a slightly more anodic potential than **1**, and the cation reacts in a bimolecular reaction step producing the dimer. The last chemical step, that is the deprotonation and regeneration of the catalyst, is the rate determining step of the catalysis.

The redox potential of the catalyst, 1, and the intermediate, 2, can be tuned readily by electron-withdrawing or donating groups at the aryl residues. The potential of 2 is always slightly higher than the one of the respective diselenide **1**. The potentials of **1** and **2** increase with increasing Hammett's substituent parameters. On the other hand, the redox potentials of the intermediates are rather insensitive to the electronic nature of the substituent at the alkene. This can be rationalised by smaller distance between the redox active selenium centre and the substituent at the aryl residue with regard to the distance between the Se atom and the residue at the alkene.

We demonstrated in six proof-of-principle electrolysis experiments that the anodic functionalisation of (unactivated) alkenes can be used successfully in organic electrosynthesis using different nucleophiles, namely an amine and various acids. Internal and external O-nucleophils were used and the functionalisation products were isolated in good yields. Such C-O and C-N bond motifs are particular important for various organic compounds applied in material or pharmaceutical science. The electrochemical functionalisation provides significant benefits with regard to classical oxidation protocols, since the required potential to drive the reaction can be adjusted easily. The tunability of the catalyst's redox potential makes the methods very versatile with potential applications for a larger variety of nucleophiles and alkenes including those, which are susceptible to oxidation as demonstrated by the reaction of the 3j forming 4j. Our kinetic and thermodynamic study provides a blueprint for such transformations.

Experimental Section

Electrochemical Studies. All electrochemical measurements were carried out using Gamry Reference 600, Gamry Reference 600+, or Gamry Interface 1010B Potentiostats using dried, degassed acetonitrile from an MBraun Solvent Purification System. We utilised a common three electrode setup for CV measurements consisting of a glassy carbon or platinum working electrode (GC: CH Instruments, ALS Japan; $A = 7.1 \text{ mm}^2$, Pt: ALS Japan; $A = 2.0 \text{ mm}^2$), a platinum wire as a counter electrode, and a silver wire or diluted Ag/AgNO3 electrode as pseudo reference electrode. All CV data except those prior and after the bulk electrolysis experiments were collected under nitrogen atmosphere. The data were referenced vs. the Fc^{0/+} redox potential. The potentials can be converted to the SCE scale by adding 0.40 V.^[39] In the [(PhSe)₃]PF₆ and [PhSe]PF₆ measurements we utilised a freshly prepared Ag⁺/AgNO₃ electrode (~0.01 M AgNO₃ in MeCN/nBuPF6) and referenced the potential of the electrode vs. Fc^{+/0} at the end of each CV series, since both species react with Fc. "Bu4NPF6 was used as supporting electrolyte, I = 0.1 M. Some of the experiments were conducted in the glove box.

Bulk Electrolysis Experiments: The Electrolysis was carried out in a custom-made cell in dry and degassed acetonitrile under air with a GC-rod working electrode (diameter 7 mm), a Pt-spiral counter electrode and an Ag/AgNO₃ reference electrode (Figure S 1). The CV prior and after the electrolysis were collected with a disk electrode (A = 7.1 mm²).

General procedure for the bulk electrolysis experiments: 1 (10 mol%) was dissolved in 30 mL MeCN with 0.1 M NBu₄NPF₆ as electrolyte. After addition of the substrate (and, if applicable, the nucleophile) the solution was electrolysed at a set potential for several hours. The electrolysis experiments were interrupted, when more than 105% of the required charge for full conversion were injected (theoretically needed for full conversion: 212 C for 1 mmol of substrate). The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography on silica gel.

4a: **1a** (31.3 mg, 100 µmol, 10 mol%), **3a** (113 mg, 1.01 mmol, 1 equiv.), E = 1.10 V vs. Fc^{+/0} for 17 h, 341 C, eluted with *n*-pentane/EtOAc (3:1) (88.1 mg, 784 µmol, 78%, colourless liquid); the analytical data matched those reported in the literature.^[7f]

4i: 1a (31.0 mg, 99.3 µmol, 10 mol%), **3i** (145 mg, 1.00 mmol, 1 equiv.), E = 1.10 V vs. Fc^{+/0} for 16 h, 311 C eluted with EtOAc/AcOH (100:1) (122 mg, 858 µmol, 86%, white solid); the analytical data matched those reported in the literature.^[7f]

4j: **1c** (37.2 mg, 99.9 µmol, 10 mol%), **3j** (177 mg, 1.00 mmol, 1 equiv.), E = 0.95 V vs. Fc^{+/0} for 15 h, 405 C eluted with *n*-pentane/EtOAc (5:1) (101 mg, 580 µmol, 58%, yellow liquid); the analytical data matched those reported in the literature.^[35]

6k: 1a (31.4 mg, 101 µmol, 10 mol%), 3k (239 mg, 1.01 mmol, 1 equiv.), acetic acid (1.15 mL, 1.21 g, 20.1 mmol, 20 equiv.) E = 1.05 V vs. Fc^{+/0} for 68 h, 224 C, diluted with DCM (50 mL) and washed with sat. aq. Na-HCO₃-soltn. (50 mL), eluted with *n*-pentane/EtOAc (20:1) (175 mg, 594 μ mol, 59%, colourless oil); TLC: $R_f = 0.40$ (*n*-pentane/EtOAc, 10:1); **IR** (neat): $\tilde{\nu} = 3451, 3061, 3025,$ 2926, 1732, 1602, 1494, 1453, 1369, 1231, 1018, 968, 743, 696 cm⁻¹; ¹**H-NMR** (300 MHz, CDCl₃): δ (ppm) = 1.81-2.15 (m, 5 H), 2.54-2.71 (m, 2 H), 3.33-3.45 (m, 2 H), 5.28 (tdd, J = 7.1, 6.0, 0.9 Hz, 1 H), 5.50 (ddt, J = 15.3, 7.1, 1.5 Hz, 1 H), 5.88 (dtd, J = 15.3, 6.8, 0.9 Hz, 1 H), 7.08-7.37 (m, 10 H); ¹³C-NMR (126 MHz, CDCl₃): δ (ppm) = 21.3, 31.6, 36.1, 38.6, 74.0, 125.8, 125.9, 126.1,128.2, 128.3, 128.4, 128.4, 129.5, 132.6, 139.6, 141.2, 170.1; HR-MS (ESI): [C₂₀H₂₂NaO₂]⁺ ([M + Na]⁺): obs.: m/z = 317.1512, calcd.: m/z = 317.1512.

6I: 1a (31.3 mg, 100 μmol, 10 mol%), **3k** (237 mg, 1.00 mmol, 1 equiv.), formic acid (1.13 mL, 1.38 g, 30.0 mmol, 30 equiv.) E = 1.05 V *vs*. Fc^{+/0} for 110 h, 244 C, diluted with DCM (50 mL) and washed with sat. aq. Na-HCO₃-soltn. (50 mL), eluted with *n*-pentane/EtOAc (20:1) (113 mg, 403 μmol, 40%, colourless oil); **TLC**: $R_f = 0.41$ (*n*-pentane/EtOAc, 20:1); **IR** (neat): $\tilde{\nu} = 3061$, 3025, 2921, 1718, 1602, 1494, 1453, 1163, 1028, 1007, 970, 908, 739, 696 cm⁻¹; ¹**H-NMR** (400 MHz, CDCl₃): δ (ppm) = 1.83-2.17 (m, 2 H), 2.53-2.78 (m, 2 H), 3.31-3.47 (m, 2 H), 5.38 (m, 1 H), 5.51 (ddt, J = 15.2, 7.3, 1.5 Hz, 1 H), 5.93 (dtd, J = 15.3, 6.8, 0.9 Hz, 1 H), 7.03-7.38 (m, 10 H), 8.08 (s, 1 H); ¹³**C-NMR** (101 MHz, CDCl₃): δ (ppm) = 31.4, 36.0, 38.5, 74.1, 126.0, 126.2, 128.3, 128.4, 128.5, 128.5, 128.9,

133.6, 139.4, 141.0, 190.4; **HR-MS** (ESI): $[C_{19}H_{20}NaO_2]^+$ ([M + Na]⁺): obs.: m/z = 303.1356, calcd.: m/z = 303.1356. **7**: **1a** (22.2 mg, 71.1 µmol, 10 mol%), **3l** (200 mg, 0.71 mmol, 1 equiv.), E = 1.00 V vs. Fc^{+/0} for 22 h, 211 C, eluted with *n*-pentane/EtOAc, 10:1, yield: 127 mg, 455 µmol, 64%, colourless oil); the analytical data matched those reported in the literature.^[40]

Conflicts of interest

The authors declare no competing financial interest.

Supporting Information

Experimental details, synthesis and characterisation (NMR, IR, HR-ESI-MS) of **1**, **2**, **3**, **5**; *in-situ* synthesis, NMR and ESI-MS data of the selenium intermediates; additional CV and electrosynthesis data; NMR and IR spectra of the diselenides and selenolactones.

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