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Alkoxysulfonyl radical species: acquisition and transformation towards sulfonate esters through electrochemistry†

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Sulfonyl radical mediated processes have been considered as a powerful strategy for the construction of sulfonyl compounds. However, an efficient and high atom-economical radical approach to the synthesis of sulfonate esters is still rare, owing to the limited tactics to achieve alkoxysulfonyl radicals. Herein, an electrochemical anodic oxidation of inorganic sulfites with alcohols is developed to afford alkoxysulfonyl radical species, which are utilized in subsequent alkene difunctionalization to provide various sulfonate esters. This transformation features excellent chemoselectivity and broad functional group tolerance. This new discovery presents the potential prospect for the construction of sulfonate esters, and enriches the electrochemical reaction type.

Introduction

Owing to their great importance in organic synthesis, pharmaceuticals, and materials science, studies on sulfonyl derivatives have gained remarkable attention in organic synthesis.[1–10] The construction of sulfonyl compounds through a sulfonyl radical involving process has developed rapidly over the past decades.[11–21] However, compared to the well explored sulfone radicals or sulfamoyl radicals in the construction of sulfones and sulfonamides, the study of alkoxysulfonyl radicals in the synthesis of sulfonate esters is still limited, since the pioneering work on the generation of alkoxysulfonyl radicals from chlorosulfate derivatives in 1989 by Chatgilialoglu and co-workers[22] (Scheme 1a). So far, strategies reported for the construction of alkoxysulfonyl radicals have been limited to radical exchange processes, in which radical species would react with chlorosulfonate, arylsulfonate or allylsulfonate to generate alkoxysulfonyl radicals.[23–26] With this strategy, direct synthesis of sulfonate esters could be achieved. However, pre-functionalized sulfonate esters were utilized as the alkoxysulfonyl radical sources, which restricted the applicability of these methods. The development of more direct and efficient routes to afford alkoxysulfonyl radicals is highly desirable (Scheme 1b).

In recent years, electrochemical anodic oxidation, as an alternative to chemical oxidation, represents an efficient and environmental strategy in organic synthesis.[27–40] Considering that inorganic sulfites (SO_3^{2-}, HSO_3^-, $S_2O_5^{2-}$) are cheap, easy-to-handle, and easy-to-obtain sulfur dioxide surrogates in the synthesis of sulfonyl compounds,[41,42] and based on our continuous work on the construction of sulfonyl compounds by using inorganic sulfites as sulfur dioxide surrogates, we design a direct strategy to construct alkoxysulfonyl radicals through electrochemical anodic oxidation of inorganic sulfites with alcohols. The S(IV) of inorganic sulfites could be activated by electrochemical anodic oxidation to afford corresponding radicals or radical anions (the voltammograms show that the oxidation peak of Na_2SO_3 aqueous solution is near 0.6 V).[43–45] Compared with the reported pathway to the synthesis of alkoxysulfonyl radicals, the new strategy features a more efficient and diversified route to construct alkoxysulfonyl radicals (Scheme 1b).

Given that alkenes are general radical acceptors, we conceive that this alkoxysulfonyl radical would be trapped by subsequent alkene difunctionalization to provide sulfonate esters. In 2020, Waldvogel's research group described an electrochemical reaction of electro-rich arenes with sulfur dioxide gas solution to produce alkyl arylsulfonate esters.[46,47] In this transformation, a nucleophilic addition process of alkyl sulfite with an arene radical cation is involved, rather than an alkoxysulfonyl radical process. There have been no reports on the electrochemical anodic oxidation of sulfur dioxide until now.[48] Herein, we develop an electrochemical three-component reaction of alkenes,

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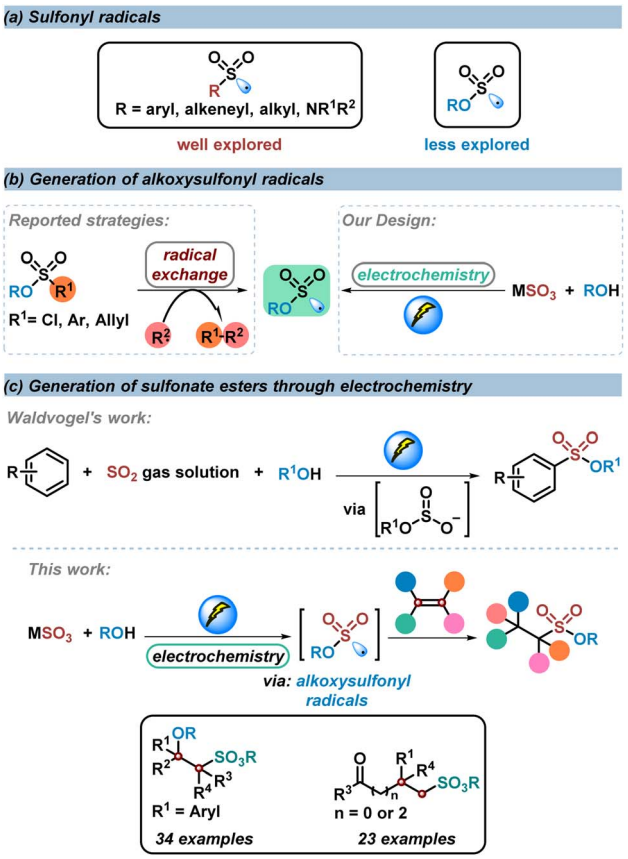


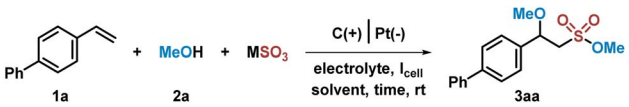
Scheme 1 Generation of sulfonate esters through electrochemistry.

inorganic sulfites, and alcohols to produce various sulfonate esters in good yields with excellent chemoselectivity and broad functional group tolerance. During this transformation, the key alkoxysulfonyl radical species was generated through an electrochemical anodic oxidation of inorganic sulfites and subsequent alcohol trapping (Scheme 1c).

Results and discussion

We commenced our design with 4-phenylstyrene **1a**, methanol **2a**, and $K_2S_2O_5$ as model substrates. Initially, this model reaction was carried out under a constant current of 4 mA for 4 h at room temperature in an undivided electrolytic cell with a graphite anode and a platinum cathode, by using $^nBu_4NBF_4$ as the electrolyte and MeCN as the solvent. Encouragingly, the desired sulfonate ester **3aa** was isolated in 33% yield (Table 1, entry 1). The yield could be improved by extending the reaction time to 12 h, giving rise to **3aa** in 81% yield (Table 1, entries 2–3). To our delight, the yield of **3aa** could be increased to 90% (in 86% isolated yield) when inorganic sulfite was changed from $K_2S_2O_5$ to $NaHSO_3$ (Table 1, entries 4–6). No better results could be obtained when other electrolytes ($LiBF_4$ or $LiPF_6$) or solvents (THF or DMAc) were tested (Table 1, entries 7–10). Changing the electric current or replacing the cathode to graphite or nickel could not give a high yield of **3aa** (Table 1, entries 11–14). Only 5% of **3aa** was obtained when the amount of methanol was reduced to 1 mL (Table 1, entry 15).

Table 1 Initial studies for the electrochemical reaction of 4-phenylstyrene **1a**, inorganic sulfite, and methanol **2a**[a]

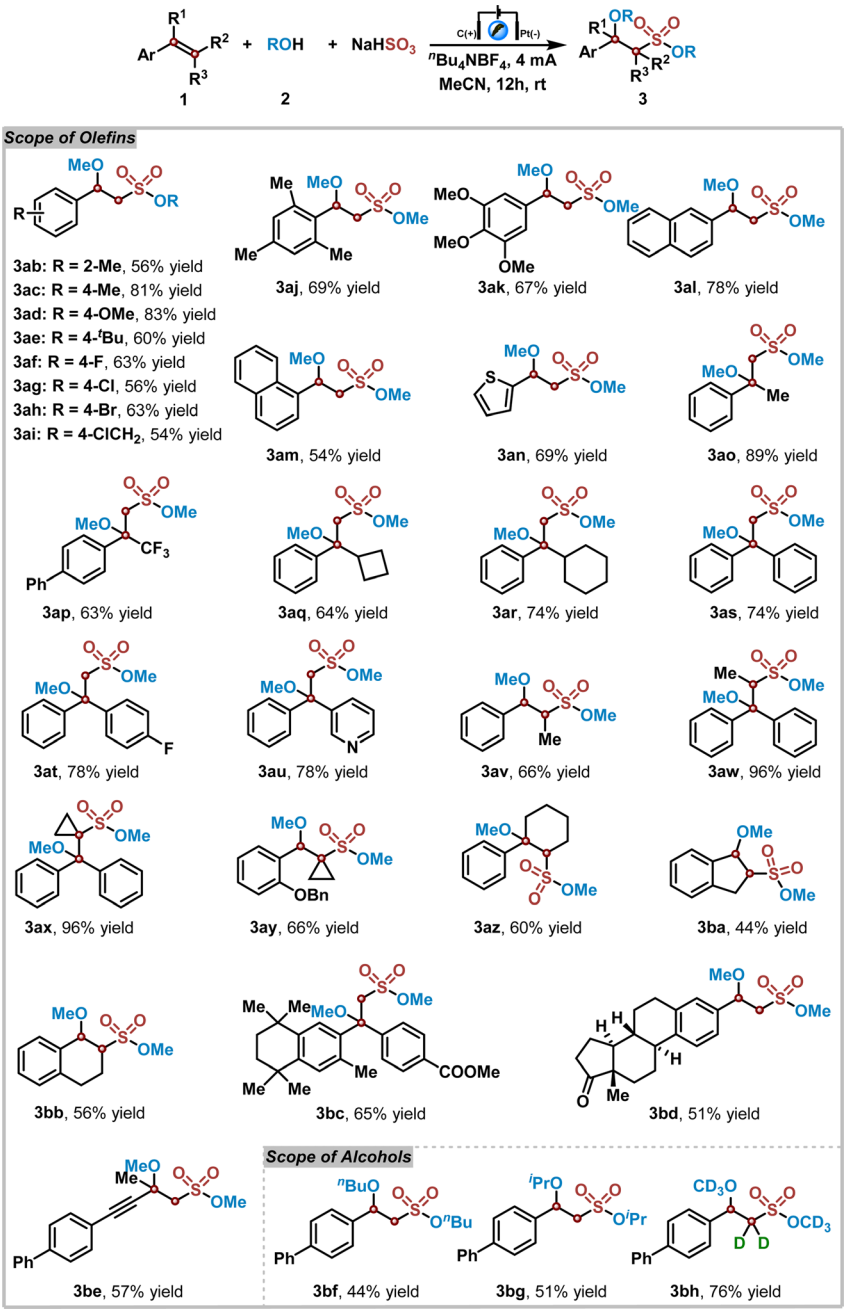


Entry	"SO_2"	Solvent	Electrolyte	I_{cell} (mA)	t (h)	Yield[b] (%)
1	$K_2S_2O_5$	MeCN	$^nBu_4NBF_4$	4	4	35 (33)
2	$K_2S_2O_5$	MeCN	$^nBu_4NBF_4$	4	8	73
3	$K_2S_2O_5$	MeCN	$^nBu_4NBF_4$	4	12	81
4	$Na_2S_2O_5$	MeCN	$^nBu_4NBF_4$	4	12	84
5	Na_2SO_3	MeCN	$^nBu_4NBF_4$	4	12	10
6	$NaHSO_3$	MeCN	$^nBu_4NBF_4$	4	12	90 (86)
7	$NaHSO_3$	MeCN	$LiBF_4$	4	12	44
8	$NaHSO_3$	MeCN	$LiPF_6$	4	12	33
9	$NaHSO_3$	THF	$^nBu_4NBF_4$	4	12	42
10	$NaHSO_3$	DMAc	$^nBu_4NBF_4$	4	12	<5
11	$NaHSO_3$	MeCN	$^nBu_4NBF_4$	2	24	64
12	$NaHSO_3$	MeCN	$^nBu_4NBF_4$	6	8	68
13[c]	$NaHSO_3$	MeCN	$^nBu_4NBF_4$	4	12	62
14[d]	$NaHSO_3$	MeCN	$^nBu_4NBF_4$	4	12	36
15[e]	$NaHSO_3$	MeCN	$^nBu_4NBF_4$	4	12	5

[a] Reaction conditions: **1a** (0.5 mmol), MeOH (2 mL), "SO_2" (4.0 equiv.), solvent (8 mL), graphite anode, Pt cathode, undivided cell, constant current, room temperature. [b] Yield determined by ^1H NMR analysis based on **1a** (using 1,3,5-trimethoxybenzene as the internal standard), isolated yield in brackets. [c] Graphite anode, Ni cathode. [d] Graphite anode, graphite cathode. [e] MeOH (1 mL), MeCN (9 mL).

Subsequently, the substrate scope of this electrochemical reaction of alkenes **1**, alcohols **2**, and $NaHSO_3$ was explored under the optimized reaction conditions. The results are shown in Table 2. At the outset, a series of substituted styrenes were examined in the reaction of methanol **2a** with $NaHSO_3$. Various electron-donating or electron-withdrawing functional groups on the styrene benzene ring were tolerated well in this reaction, yielding the corresponding products **3ab–3ak** in 54% to 83% yields. Notably, large sterically hindered styrenes, such as 2,4,6-trimethylstyrene, also participated well in this transformation, giving rise to the corresponding sulfonate ester **3aj** in 69% yield. Additionally, naphthyl and thienyl substituted vinyls were suitable for this reaction as well (**3al–3an**). Furthermore, the desired products **3ao–3av** could be obtained in good to excellent yields, when disubstituted vinylic substrates were utilized in this electrochemical reaction. The chemical structure of product **3as** was confirmed by X-ray diffraction analysis (see ESI†).[49] In contrast, tri- and even tetra-substituted vinylic substrates were compatible in this reaction, affording the corresponding products **3aw–3ay** in excellent yields. As we expected, this reaction was also compatible with cyclic styrenic substrates, leading to sulfonate esters **3az–3bb** in 44–60% yields. Moreover, bioactive molecules, such as bexarotene- and estrone-derived substrates, could provide the corresponding sulfonate ester derivatives **3bc** and **3bd** in 65% and 51% yields. An alkynyl-containing substrate was also investigated,

Table 2 Scope exploration for the reaction of alkenes **1**, alcohols **2**, and $NaHSO_3$[a]



[a] Isolated yield based on alkenes **1**.

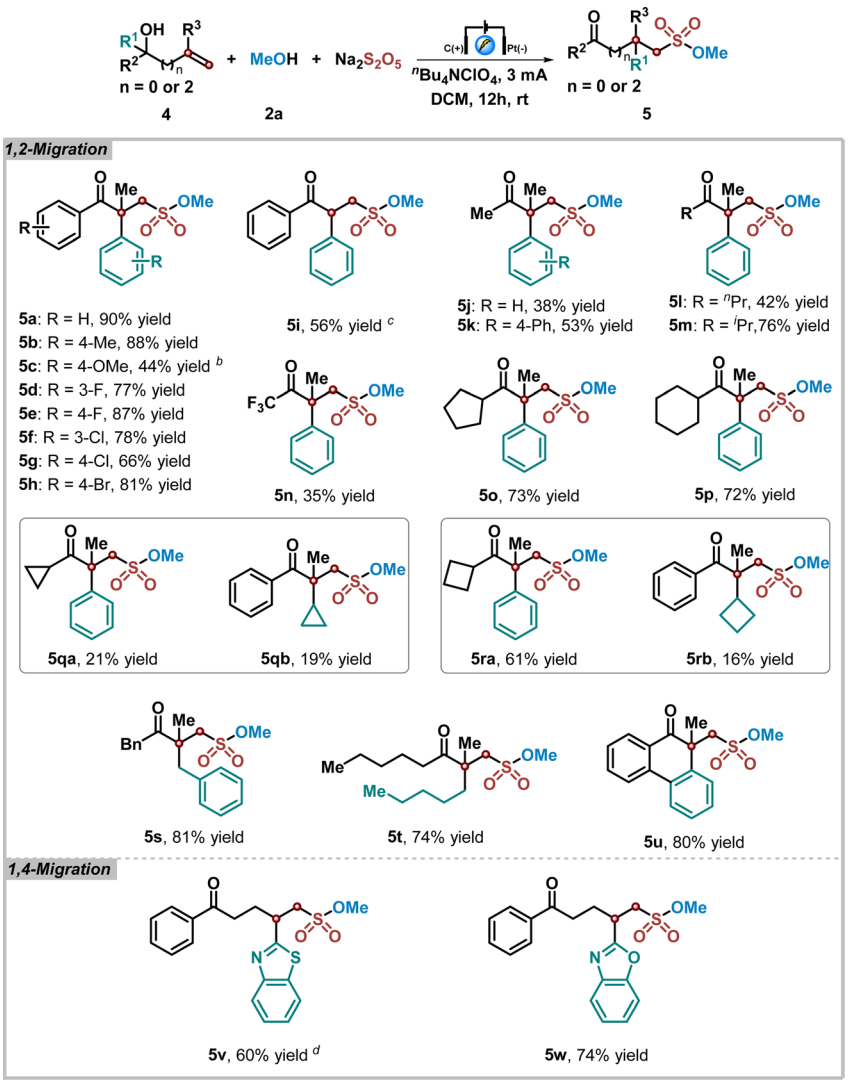
which afforded the desired product **3be** in 57% yield with excellent chemoselectivity. Next, several alcohols were utilized in the reaction of 4-phenylstyrene **1a** with $NaHSO_3$. It was found that *n*-butanol and isopropyl alcohol all worked well in this reaction, delivering the sulfonate ester products **3bf** and **3bg** in 44% and 51% yields. Interestingly, when this electrochemical reaction was carried out with deuterated methanol, the α-hydrogen deuterated sulfonate ester **3bh** was obtained in 76% yield. Further investigation indicated that the α-hydrogen of corresponding sulfonate ester could undergo a hydrogen–deuterium exchange process with deuterated methanol under the standard reaction conditions (see ESI† for details).

Considering that the intramolecular radical functional group migration process features a powerful approach for the difunctionalization of unactivated alkenes.[50–52] We proposed that the alkoxysulfonyl radical species produced by the

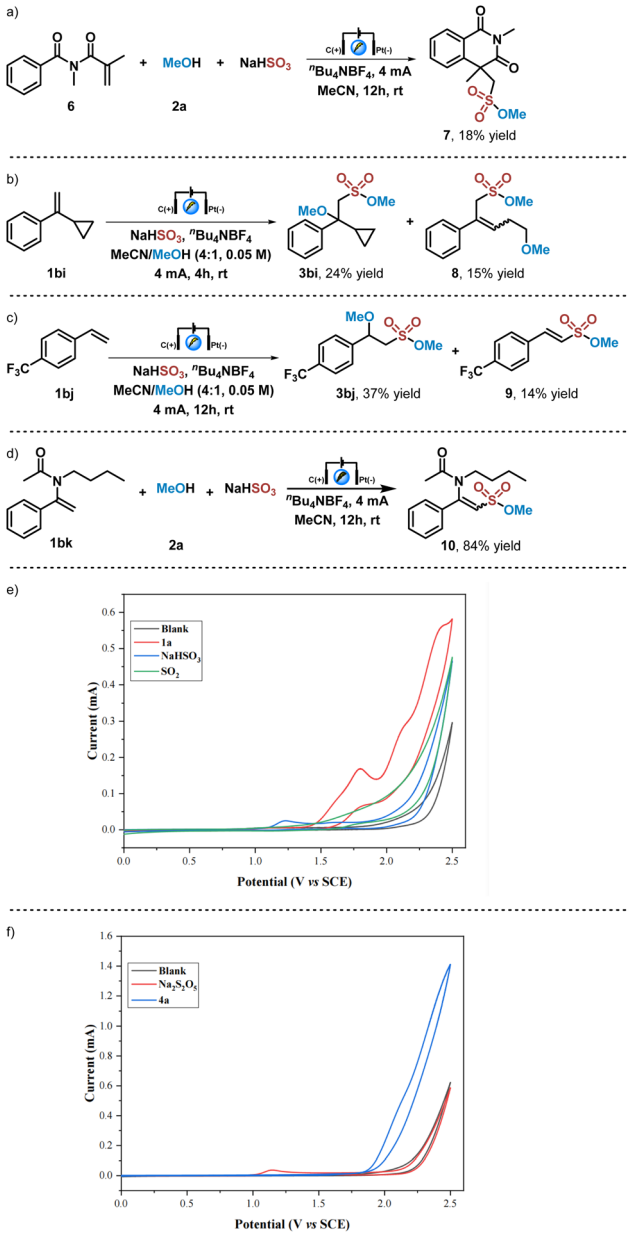
electrochemical anodic oxidation process could provide the sulfonated products of unactivated alkenes through a radical functional group migration strategy. To our delight, the sulfonated product **5a** could be achieved in 90% yield, when this electrochemical oxidative sulfonation reaction was performed by using 2-methyl-1,1-diphenylprop-2-en-1-ol **4a**, methanol **2a**, and $K_2S_2O_5$ as substrates under slightly modified reaction conditions (see ESI† for details). The reaction scope with other allyl alcohols is summarized in Table 3. It was found that 1,1-diaryl allyl alcohols with various functional groups on the aromatic ring reacted smoothly under the standard reaction conditions, giving rise to the corresponding sulfonate esters **5a–5i** in excellent yields. Additionally, 1-alkyl-1-aryl allyl alcohols were also workable in this transformation, and aryl migrated products could be produced in good yields with excellent chemoselectivity (**5j–5p**). The chemical structure of product **5m** was confirmed by X-ray diffraction analysis (see ESI†).[53] However, when this reaction was carried out with 1-cyclopropyl-2-methyl-1-phenylprop-2-en-1-ol **4q** or 1-cyclobutyl-2-methyl-1-phenylprop-2-en-1-ol **4r**, the mixture of aryl group and cycloalkyl group migrated products could be obtained (**5qa–5ra** and **5qb–5rb**). Notably, 1,1-dialkyl allylic alcohols were compatible in this reaction as well, affording corresponding products **5s** and **5t** in 81% and 74% yields. Furthermore, ring expanding product **5u** could be obtained in 80% yield through this migration process. Not only 1,2-migration, but also remote heteroaryl *ipso*-migration was realized as well, leading to the corresponding 1,4-migration products **5v** and **5w** in 60% and 74% yields.

Several control experiments were then carried out to further understand the reaction mechanism. As shown in Scheme 2a, when this electrochemical reaction was performed with *N*-

Table 3 Scope exploration for the reaction of tertiary alcohols **4**, $K_2S_2O_5$ and methanol **2a**[a]

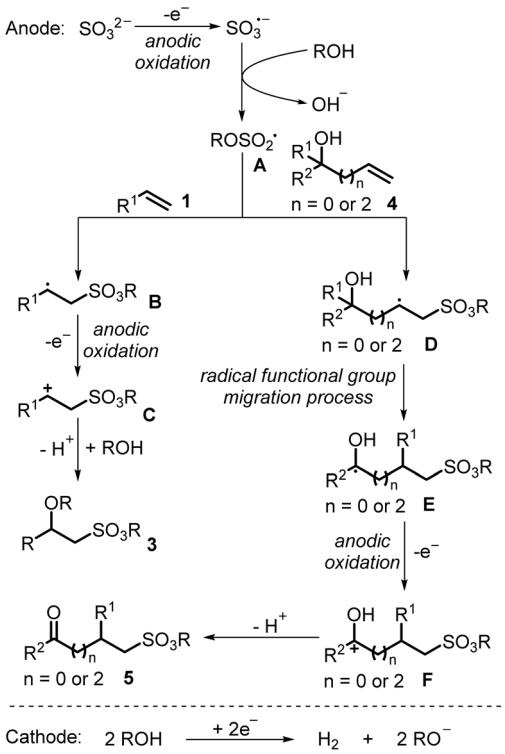


[a] Isolated yield based on tertiary alcohols **4**. [b] $I_{cell} = 2$ mA. [c] Reaction time is 8 h. [d] Reaction time is 16 h.



Scheme 2 Control experiments.

methacryloyl-*N*-methylbenzamide **6**, which has been utilized as a radical trapper in radical processing reactions,[54] the cyclized sulfonate ester **7** could be obtained in 18% yield. When cyclopropyl substituted styrene **1bi** was applied in this electrochemical reaction with methanol and $NaHSO_3$, the desired sulfonated product **3bi** and the radical ring-opening product **8** were obtained in 24% and 15% yields (Scheme 2b). These results indicated that alkoxysulfonyl radical species are generated in this electrochemical reaction, and an alkoxysulfonyl radical addition process is involved in this transformation. When this electrochemical reaction was carried out with a strong electron-withdrawing functional group substituted styrene, such as trifluoromethyl substituted styrene **1bj**, not only the difunctionalization product **3bi** could be obtained in 37% yield, but also alkene **9** could be isolated in 14% yield. Then enamide **1bk** was employed in this electrochemical reaction, giving rise to the coupling sulfonate **10** in 84% yield. These results showed that cationic species were formed by anode oxidation of radical species after the alkoxysulfonyl radical addition process, which could undergo a proton elimination process to afford corresponding coupling products. Subsequently, several CV (Cyclic Voltammetry) experiments were performed. No oxidation peak was observed when the CV experiment on the solution of sulfur dioxide gas in a mixture solvent of MeCN/MeOH (V/V = 4/1) was carried out (Scheme 2c). This result excluded the possibility of building alkoxysulfonyl radical species from the oxidation of sulfur dioxide nor alkyl sulfite (generated *in situ* from sulfur dioxide and methanol), which has been demonstrated in a previous report.[47] In contrast, inorganic sulfite anions could be easily oxidized that an oxidation peak of $NaHSO_3$ solution in MeCN/MeOH (V/V = 4/1) was found at 1.23 V (*vs.* SCE). On the other hand, the oxidation peak of olefin **1a** solution in MeCN/MeOH (V/V = 4/1) was observed at 1.80 V (*vs.* SCE), which indicated that anodic oxidation of inorganic sulfite $NaHSO_3$ is more preferential (Scheme 2c). In addition, CV experiments of inorganic sulfite $Na_2S_2O_5$ and alkene **4a** also gave similar results, showing that inorganic sulfite $Na_2S_2O_5$ could be oxidized at the anode (oxidation peak) at 1.15 V (*vs.* SCE), while no obvious oxidation peak of **4a** was found (Scheme 2d). Moreover, the CV experiment of alkene **6** showed no oxidation peak as well (see ESI† for details). All these results suggested that the alkoxysulfonyl radical species involved in this reaction are generated by electrochemical anodic oxidation of inorganic sulfites and subsequent alcohol capture.



Scheme 3 Proposed mechanism.

Based on the above results and previous reports, a possible reaction pathway for this electrochemical alkene sulfonation process is proposed in Scheme 3. The inorganic sulfite could be oxidized to the sulfite radical anion at the anode through a single-electron transfer oxidation, which would be subsequently trapped by alcohols to afford alkoxysulfonyl radical species **A**. Then, alkoxysulfonyl radical species **A** would undergo radical addition with alkene **1** to provide radical intermediate **B**. Further anodic single-electron transfer oxidation of radical intermediate **B** would provide carbocation **C**, which would subsequently react with alcohols to generate sulfonation product **3**. On the other hand, the radical addition of alkoxysulfonyl radical species **A** with alkene **4** would provide radical intermediate **D**. Followed by radical functional group migration, anodic single-electron transfer oxidation and deprotonation, the sulfonation product **5** could be obtained.

Conclusions

In summary, we have developed an efficient and applicable route to provide alkoxysulfonyl radical species *via* the electrochemical anodic oxidation of inorganic sulfites with alcohols. Various sulfonate esters could be obtained by subsequent alkene difunctionalization with these alkoxysulfonyl radical species. This method exhibits broad functional group tolerance and excellent chemoselectivity. With this new discovery, potential prospects for the construction of sulfonate esters are revealed.

Data availability

The data supporting this study are available within the article and the ESI.† The X-ray crystallography coordinates for structures of **3as** and **5m** have been deposited at the Cambridge Crystallographic Data Center (CCDC: 2131889 and 2131892).

Author contributions

S. Y. conceived the study. C. Z. and M. Y. conducted the experiments and analysed the data. Y. Q., M. S., H. W. and M. Y. conducted preparation of starting materials. S. Y. and J. W. directed the project. C. Z. and W. X. conducted the experiments during manuscript revision. S. Y. prepared the manuscript. C. Z. prepared the supplemental information. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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