

Electrochemical Oxidation of Benzyl Alcohols via Hydrogen Atom Transfer Mediated by 2,2,2-Trifluoroethanol

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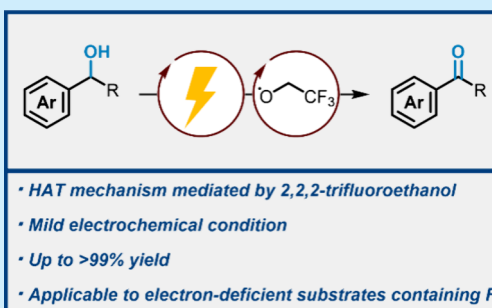


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ABSTRACT: We report a novel electrochemical oxidation of benzyl alcohols. We found that trifluoroethanol plays a role as a hydrogen atom transfer (HAT) mediator, enabling the oxidation of electron-deficient substrates that are difficult to directly oxidize on electrode surfaces. Density functional theory calculations, cyclic voltammetry measurements, and constant potential electrolysis studies supported the proposed HAT mechanism. Moreover, the obtained carbonyl compounds could be functionalized in an electrochemical one-pot manner, further highlighting their synthetic utility.



Oxidation, namely the transformation from abundant alcohols into valuable carbonyl compounds, is one of the most important reactions in organic chemistry.¹ The classical and traditional stoichiometric heavy-metal-based oxidation has been replaced by not only transition-metal-based and/or catalytic methodologies but also metal-free reactions.^{2–6} In recent years, oxidative reactions using single-electron transfer (SET) chemistry, such as photo- or electrochemistry, have been attracting attention as revival methodologies.^{7,8} In many electrochemical oxidation reactions, protons serve as the terminal electron acceptors, resulting in the exclusive generation of H₂ as the byproduct. This characteristic, coupled with no need for chemical oxidants, allows for the realization of greener reactions with exceptional atom economy and minimal waste.

In this context, the electrochemical oxidation of a hydroxy group has attracted significant attention as a subject of study. Electrochemical oxidation is classified into two types of reactions: direct and indirect oxidation. Direct oxidation, which involves the direct uptake of electrons from the substrate alcohols **1** on the anode to generate the radical cation intermediate **A**, is an ideal methodology that enables irreversible and potent electron transfer (Figure 1A); however, it often faces challenges in terms of low selectivity and reactivity, since direct oxidation heavily relies on the electronic properties of **1**.^{9,10} On the other hand, indirect electrochemical oxidation proceeds via mediators, such as halogens (I,¹¹ Br,¹² and Cl¹³) and *N*-hydroxy compounds like *N*-hydroxyphthalimide (NHPI).¹⁴ These mediators are oxidized on the anode to afford the redox active species after transformation into the corresponding anion (Figure 1B). This radical species abstracts a benzylic hydrogen atom from **1** to form intermediate **B**. This “indirect” mechanism may be advantageous with respect to the

generality of the reaction compared to direct electrolysis depicted in Figure 1A via radical cation intermediate **A**, as it is less influenced by the electronic properties of **1**.

In 2019, the direct electrochemical oxidation of alcohol combined with flow chemistry was reported to enhance reactivity (Figure 1C).¹⁵ Although the report emphasized the broad substrate scope and practicality of the approach, there was a tendency toward decreased reactivity in electron-deficient benzyl alcohols. As an example of indirect electrochemical oxidation of secondary alcohols, the reaction using bromine as a mediator was reported (Figure 1D, top).¹² Furthermore, 3,4,5,6-tetrafluoro-*N*-hydroxyphthalimide (TFNHPI), known as a kind of hydrogen atom transfer (HAT) mediator, has been reported for the indirect oxidation of propargyl alcohols (Figure 1D, bottom).¹⁶ Through the utilization of TFNHPI as a mediator, the efficiency of the desired reactions was successfully enhanced.

Here we report the electrochemical oxidation of benzyl alcohol derivatives in the presence of 2,2,2-trifluoroethanol (TFE, Figure 1E). Perfluoroalcohols, such as TFE or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), were previously reported as “effective solvents” in electrolysis; however, detailed investigations on their mechanisms are scarce.^{17–20} Through extensive mechanistic studies, we revealed that TFE functions as a HAT mediator. Additionally, the present oxidation was applicable to electron-deficient substrates.

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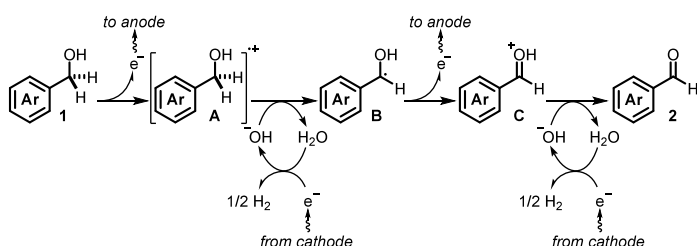
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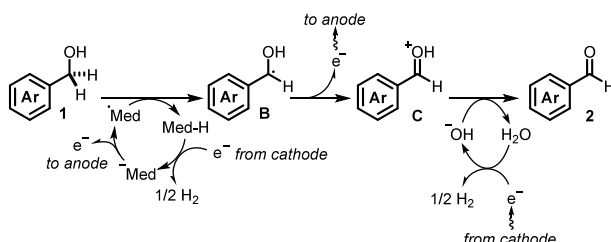
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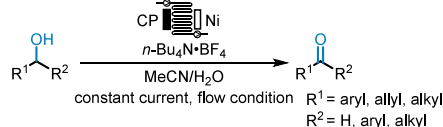
A | Direct electrochemical oxidation of benzyl alcohols



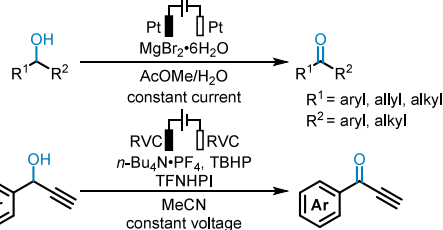
B | Indirect oxidation of benzyl alcohols via the HAT mediator



C | Prior work-1: Electrochemical oxidation on electrode surfaces



D | Prior works-2: Electrochemical oxidation using a mediator



E | This work: TFE mediated electrochemical oxidation via HAT

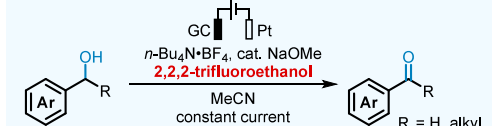


Figure 1. Mechanisms of direct/indirect electrochemical oxidation of benzyl alcohols, recent representative work on electrochemical oxidation of alcohols, and electrochemical oxidation of benzyl alcohols utilizing 2,2,2-trifluoroethanol as a HAT mediator (this work). CP = carbon paper, RVC = reticulated vitreous carbon, GC = glassy carbon, HAT = hydrogen atom transfer, and Med = mediator.

Furthermore, the obtained carbonyl compounds were successfully transformed into amines via imination, followed by electrochemical reduction in a one-pot manner, showcasing a versatile transformation pathway.

The optimization is detailed in Table 1. 4-Methoxybenzyl alcohol (**1a**) was used as the model substrate on a 0.5 mmol scale. The standard conditions are as follows: **1a** and $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$ (0.1 equiv) and NaOMe (0.5 equiv, 28% in MeOH solution) were added to a cosolvent of acetonitrile (7 mL) and

Table 1. Optimization of Electrochemical Oxidation of **1a**

entry	deviation from above	yield (%) ^a	
		1a	2a
1	none	N.D.	93
2	without NaOMe	79	15
3	LiOMe instead of NaOMe	2	84
4	MeOH instead of TFE	84	13
5	HFIP instead of TFE	34	47
6 ^b	without TFE	22	30
7	RVC (+) instead of GC (+)	N.D.	90
8	graphite (+) instead of GC (+)	15	74
9 ^{c,d}	THF instead of MeCN	N.D.	87
10 ^{c,e}	DMAc instead of MeCN	N.D.	76
11 ^c	DMSO instead of MeCN	33	43
12	without $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$	N.D.	87
13	2 F/mol instead of 4 F/mol	27	68
14	3 F/mol instead of 4 F/mol	N.D.	99 (97) ^d

^aYields were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^b0.3 equiv of NaOMe was used. ^cRVC was used instead of GC for the anode. ^dThe reaction was conducted under 10 mA. ^eIsolated yield.

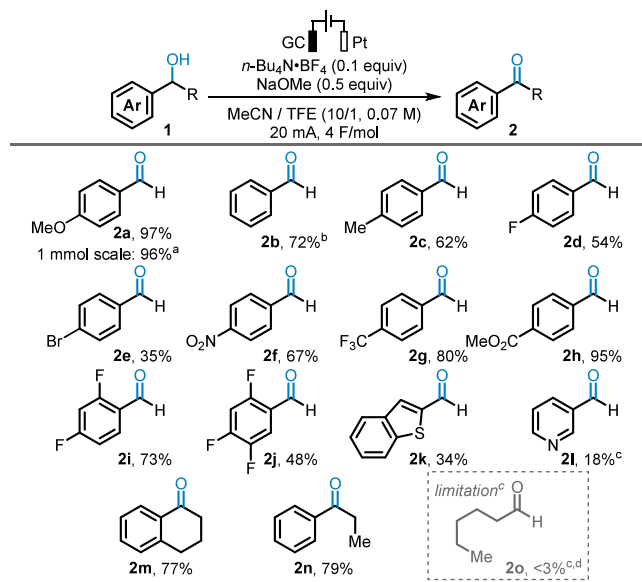
TFE (0.7 mL). Electrolysis of this mixture was conducted at a constant current of 20 mA at room temperature. An undivided cell setup was used with a glassy carbon (GC) anode and a platinum plate (Pt) cathode. As a result, 4-methoxybenzaldehyde (**2a**) was obtained in 93% yield (entry 1). Given the mechanism described in Figure 1B, the importance of bases in the regeneration of the mediator or the deprotonation of intermediate C could be inferred.²¹ In fact, in the absence of NaOMe, the reaction efficiency significantly decreased, with **1a** remaining in 79% yield (entry 2). When LiOMe was used instead of NaOMe, **2a** was also obtained in 84% yield (entry 3). Next, we investigated the effect of alcohols as cosolvents. When MeOH was used instead of TFE, 84% of **1a** remained (entry 4). Using HFIP gave **2a** in 47% yield (entry 5). In the absence of TFE, this reaction became messy, and 30% of **2a** was obtained (entry 6).

By clarifying that the base and TFE are essential for achieving this electrochemical oxidation with high efficiency, we next examined the effect of the common parameters in electrolysis. Reticulated vitreous carbon (RVC) performed well as the working electrode and yielded **2a** in 90% yield (entry 7). However, the efficiency slightly decreased when graphite plates were used as the anodes (entry 8). THF and DMAc could be used as reaction solvents instead of MeCN (entries 9 and 10). However, when using THF, a higher voltage than that under the standard conditions was observed, necessitating a decrease in the current to below 10 mA and an extension of the reaction time. On the other hand, DMSO was found to be unsuitable for this oxidation (entry 11). The electrolytes had little impact on the reaction, as high yields of **2a** were obtained using various electrolytes (see Supporting Information). Interestingly, this reaction also proceeded without additional electrolytes to afford desired **2a** in 87% yield (entry 12). This result implied NaOMe also has the role as an electrolyte. Finally, the total amount of electricity was adjusted. With a theoretical electricity of 2 F/mol, 27% of **1a** remained, but at 3 F/mol **2a** was obtained quantitatively (entries 13 and 14). Through optimization, significant discoloration or fouling on the electrode surface was not observed after the reaction, enabling

easy rinsing and wiping before reuse for further investigations. This is believed to be a clear advantage of indirect electrolysis.

With the optimized conditions in hand, we investigated the scope of alcohols (Scheme 1). The electron-rich benzyl alcohol

Scheme 1. Scope and Limitation of the Electrochemical Oxidation of Benzyl Alcohols^e



^a1 mmol of **1a** was used in MeCN/TFE (0.13 M) for 3 F/mol. ^b1.0 equiv of NaOMe was used. ^c1.5 equiv of NaOMe was used. ^dYield was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^eConditions: Unless otherwise stated, 0.5 mmol of **1** was used.

1a was cleanly oxidized even on a 1 mmol scale, and the corresponding **2a** was quantitatively obtained. The electron-donating group was not essential for oxidation, and electronically neutral benzyl alcohols were smoothly oxidized to afford the corresponding aldehydes (**2b** and **2c**) in good yields. The substrates, bearing a halogen on the aromatic ring, were also transformed into aldehydes (**2d** and **2e**) with moderate yields. Furthermore, this reaction enabled the oxidation of electron-deficient benzyl alcohols, which are unfavorable for direct electrolysis. Namely, aldehydes bearing a nitro (**2f**), trifluoromethyl (**2g**), or methyl ester group (**2h**) on their aromatic rings were synthesized in good yields. This reaction was applicable to substrates with two or three fluorine substituents (**2i** and **2j**), as well as heterocyclic-type benzyl alcohols such as thiophene and pyridine (**2k** and **2l**). Secondary alcohols were oxidized under the standard conditions to afford the corresponding ketones in 77% (**2m**) or 79% (**2n**) yields, respectively. *n*-Hexanol, an aliphatic alcohol, could not be oxidized under the optimal conditions (**2o**). In reactions using **1e**, **1l**, or **1o**, which showed low yields, byproducts were not observed and unreacted alcohols remained at the end of the reaction. Therefore, we speculate that certain substrates may hinder the HAT process by the TFE radical (the HAT mechanism will be discussed later).

To reveal the role of TFE in this electrolysis, we conducted cyclic voltammetry (CV) experiments. While no significant oxidation was observed up to 1.5 V (vs Fc/Fc⁺) for either LiOMe or TFE alone, an oxidation onset at 1.10 V was observed in their mixture (Figure 2A, left). These results seem

to suggest that the alkoxide of TFE is oxidized at a lower potential. Importantly, the TFE and LiOMe had no influence on the oxidation of **1b** (Figure 2A, middle). A similar trend was observed even with more electron-deficient substrates **1h** (Figure 2A, right). Hence, these CV measurements indicate that the TFE/base system does not facilitate the direct oxidation of the substrates on the anode but rather enables the occurrence of an alternative pathway of oxidation.

Encouraged by the results of these CV measurements, we conducted control experiments. In the case of the electronically neutral substrate **1b**, oxidation hardly occurred without TFE/NaOMe (Figure 2B, top), which was more pronounced compared to when using electronically rich **1a** that could undergo direct oxidation (see Table 1). Next, we attempted constant potential electrolysis of **1h** (Figure 2B, bottom). It proceeded at a lower potential of 1.50 V compared to the oxidation onset potential of **1h** (1.50 V) to afford **2h** in 33% yield. This result strongly suggests that the oxidation in the presence of TFE/NaOMe proceeded via a mechanism other than direct oxidation, namely via the HAT mechanism.

The results from CV measurements and control experiments indicate that TFE undergoes conversion to a radical species through electrolysis. To verify whether this radical species is capable of oxidizing benzyl alcohols, DFT calculations were employed (Figure 2C). These calculations revealed that the TFE radical, generated by the anodic oxidation of its alkoxide, can easily accept a benzylic hydrogen atom, and the energy barrier of the HAT process is 4.6 kcal/mol (Figure 2C, middle). The anodic oxidation of benzyl radical intermediate **B** smoothly proceeds, and the corresponding aldehyde is formed.²² According to the literature,²³ TFE has been found to undergo intramolecular 1,2-HAT or pseudo 1,2-HAT to generate carbon-centered radicals. The DFT calculations also showed that the carbon-centered radical can abstract the benzylic hydrogen atom to generate intermediate **B**, as well as the oxygen-centered radical of TFE (TS2 in Figure 2C, bottom). While the exact localization of the radical center in TFE remained uncertain, these mechanistic investigations strongly suggested the credibility of our hypothesis that the TFE radical can act as a HAT mediator in the oxidation of benzyl alcohols.

We further demonstrate an application of the developed electrochemical oxidation in Scheme 2A. Upon completion of the oxidation of **1a** under the standard conditions, the addition of aniline followed by electrolysis with a different electrode set (for details, see the Supporting Information) yielded the corresponding benzylamine **4a** (65% yield) in a one-pot manner. Furthermore, by leveraging the electrolysis previously reported by our group, facile cyanosilylation and alkynylation of **2b** as the substrate can be achieved (Scheme 2B).^{24,25} Conceptually, these electrochemical transformations could be combined with the present electrochemical oxidation, albeit this required tuning of the conditions such as the electrolytes and solvents. In chemical oxidation, byproducts derived from oxidants often hinder the progress of continuous reactions when attempting the transformation of the obtained carbonyl compound in a one-pot manner. Electrochemically, TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxyl) is known as an effective mediator for the oxidation of benzyl alcohols. However, it also has the ability to oxidize amines, making it difficult to achieve the transformation shown in Scheme 2A in a one-pot manner.²⁶ From these standpoints, the present methodology utilizing TFE/base offers a simple and clean oxidation, and it

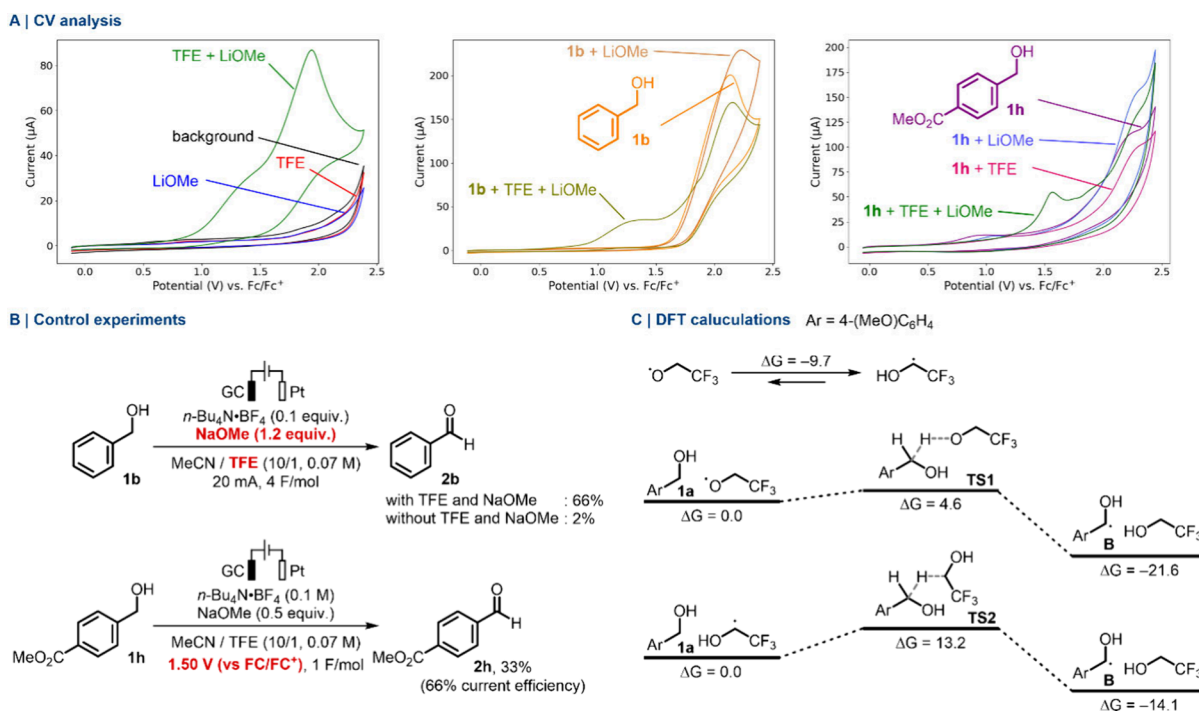
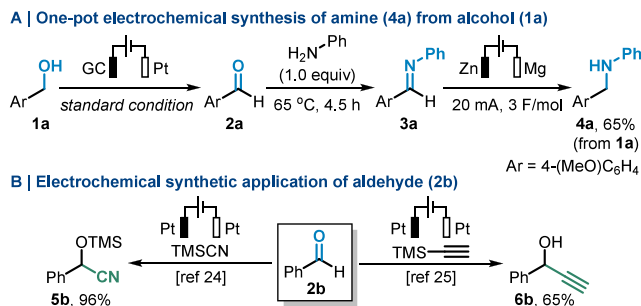


Figure 2. Mechanistic rationale of TFE-mediated electrochemical oxidation. (A) Cyclic voltammograms of the present oxidation. The following conditions were applied: substrate, **1b** or **1h**; solvent, MeCN; supporting electrolyte, *n*-Bu₄N⁺BF₄⁻ (0.1 M); working electrode, glassy carbon; counter electrode, Pt coil; reference electrode, Ag/Ag⁺; standard, Fc/Fc⁺; scan rate, 100 mV/s. (B) Control experiments using **1b** and potentiostatic electrolysis of **1h**. (C) HAT pathways by an oxygen- or carbon-centered TFE radical toward 4-methoxybenzyl alcohol (**1a**) computed at the M06-2X/6-31+G(d,p) level of theory (relative Gibbs free energies [kcal mol⁻¹]).

Scheme 2. Synthetic Application and Diversification of the Obtained Aldehydes



would be possible to enhance the complexity of benzyl alcohols either in a one-pot manner or in combination with flow chemistry.²⁷

In summary, we developed a novel electrochemical oxidation reaction utilizing TFE as a HAT mediator. Through mechanistic studies including CV measurements, constant potential electrolysis and DFT calculations, we elucidated the role of TFE. The obtained carbonyl compound was transformed to the amine derivative in an electrochemical one-pot manner.²⁸ Our group is engaged in the development of new reactions based on complete electrochemical transformations.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its [Supporting Information](#)

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.5c01138>.

Experimental details (PDF)

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Author Contributions

T.K. and M.H. contributed equally.

Notes

The authors declare no competing financial interest.

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