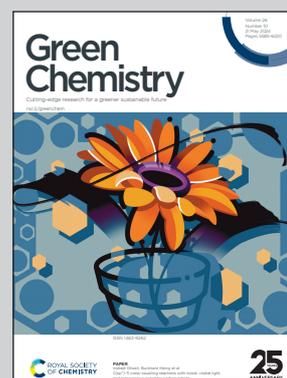


Showcasing research from Professor Waldvogel's laboratory, Max-Planck-Institute for Chemical Energy Conversion, Germany.

*E*-Dakin reaction: oxidation of hydroxybenzaldehydes to phenols with electrochemically generated peroxodicate as sustainable *ex-cell* oxidizer

Electrochemically generated peroxodicate solution efficiently oxidizes hydroxybenzaldehydes to valuable phenols. The reaction is carried out in aqueous media without solvents or additives. The reaction gives high yields of up to 97% and tolerates a broad variety of substituents, as demonstrated by 20 diverse examples. It was scaled to multi-gram range. This transformation further expands the synthetic applicability of the green oxidizer peroxodicate, which can be generated on demand from ecologically safe carbonate solutions and has a high oxidation potential at mildly basic conditions.

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# *E*-Dakin reaction: oxidation of hydroxybenzaldehydes to phenols with electrochemically generated peroxodicarbonate as sustainable ex-cell oxidizer†

Fiona Sprang,<sup>a</sup> Niclas Schupp,<sup>a</sup> Philipp J. Kohlpaintner,<sup>a</sup> Lukas J. Gooßen<sup>b</sup> and Siegfried R. Waldvogel<sup>ib</sup> \*<sup>a,c,d</sup>

Electrochemically generated peroxodicarbonate solution efficiently oxidizes hydroxybenzaldehydes to valuable phenols. The reaction is carried out in aqueous media without additional solvents or additives. The reaction gives high yields of up to 97% and tolerates a broad variety of substituents, as demonstrated by 20 diverse examples. It was successfully scaled to multi-gram range. This transformation further expands the synthetic applicability of the green oxidizer peroxodicarbonate, which can be generated on demand from ecologically safe carbonate solutions and has a high oxidation potential at mildly basic conditions.

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## Introduction

Phenols represent building blocks with fundamental importance to industry and prominently feature in pharmaceutical active ingredients and natural products.<sup>1–5</sup> Within this heterogeneous class of molecules, the dihydric members catechols and hydroquinones represent in particular valuable moieties due to their broad fields of applications (Scheme 1).<sup>6</sup>

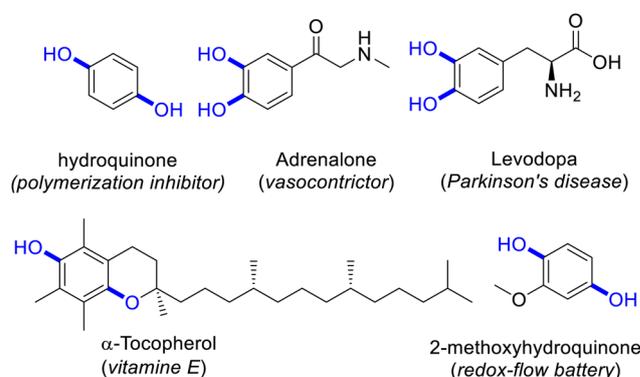
Hydroquinones exhibit remarkable redox features.<sup>7</sup> They can be reversibly oxidized into their corresponding quinone congener and subsequently be reduced again without harming their structural integrity.<sup>8</sup> The reversible redox properties open up a plethora of applications, including energy storage concepts. Successful use of all organic hydroquinone–quinone redox flow batteries has been reported.<sup>9</sup> Moreover, 2-methoxyhydroquinone was investigated as a simple lignin-derived electrolyte for sustainable future energy storage units.<sup>10</sup> Other examples of the application as redox-active molecule include the use as an inhibitor of polymerization and oxidation within the food and cosmetic industry.<sup>11</sup> Hydroquinone is used as a

reducing agent in photography due to its water soluble nature.<sup>11</sup>

Aside from that, hydroxyphenols are useful monomers for the synthesis of complex molecules.<sup>3</sup> Catechol for example is used as a starting material for the synthesis of the vasoconstrictor adrenalone while 2,3,5-trimethylhydroquinone is a precursor for the synthesis of  $\alpha$ -tocopherol (vitamin E).<sup>6,12</sup>

Due to their tremendous importance numerous strategies for the synthesis of phenols and hydroxyphenols have emerged (Scheme 2).

The aerobic C–H oxidation of non-functionalized fossil hydrocarbons arguably is the most desirable entry to phenols but suffers from a lack of selectivity. Various directing groups have been developed that enable regiospecific interaction with transition metal catalysts.<sup>13–17</sup> Still, most synthetic entries are



**Scheme 1** Selection of catechol and hydroquinone containing compounds with relevance in pharmaceutical and technical industry.

<sup>a</sup>Johannes Gutenberg-University Mainz, Department of Chemistry, Duesbergweg 10-14 55128 Mainz, Germany. E-mail: siegfried.waldvogel@cec.mpg.de

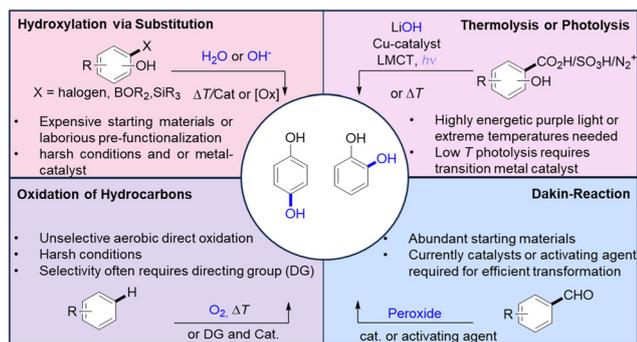
<sup>b</sup>Evonik Chair of Organic Chemistry, Ruhr-University Bochum Universitätsstraße 150, 44901 Bochum, Germany

<sup>c</sup>Institute of Biological and Chemical, Systems – Functional Molecular Systems (IBCS-FMS), Kaiserstraße 12, 76131 Karlsruhe, Germany

<sup>d</sup>Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany

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Scheme 2 State-of-the-art synthesis strategies for hydroxyphenols.

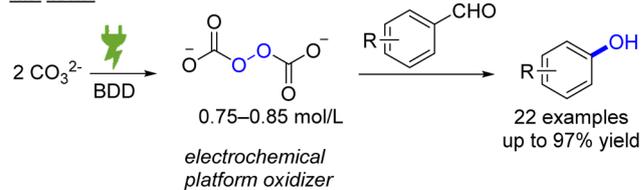
based on functional group interconversions. Common substrates are haloarenes,<sup>18–21</sup> aryl boronic acids,<sup>22–24</sup> and silylarenes.<sup>25,26</sup> In most cases, these starting materials are of non-natural origin and need to be synthesized *via* additional pre-functionalization steps, increasing their production cost and ecological footprints. One-pot transformations combining the extrusion of a volatile leaving group with hydroxylation steps allow the synthesis of phenols from benzoic acids, sulfonic acids, or diazonium salts.<sup>6,27,28</sup> The activating energy barrier is either overcome *via* photolysis or thermal energy.<sup>29</sup> The previously mentioned strategies all contradict one or more of the principles of green chemistry.<sup>30</sup> Some are limited by the problematic use of extreme reaction conditions and others by the dependence of scarce resources, the production of excessive waste in pre-functionalization steps, the use of expensive catalysts, or of ecologically questionable reagents or solvents.

An advantageous synthetic entry to phenols was already reported in the early 20<sup>th</sup> century by Dakin,<sup>31,32</sup> who demonstrated that hydroxybenzaldehydes can be converted to hydroxyphenols by treatment with hydrogen peroxide in alkaline media. However, the initial protocol calls for harsh conditions, *i.e.*, the use of excess of hydrogen peroxide at elevated temperatures, and in many cases, only modest yields were achieved.<sup>31</sup> This approach has gained renewed interest in the context of the ongoing change from fossil to renewable resources in chemical value creation, since hydroxybenzaldehydes are abundant in biogenic feedstocks.<sup>33–36</sup> The wide availability of these starting materials has prompted the development of numerous improved variants of Dakin's original method. All these variations have in common that they require activation agents, *e.g.*, boric acid, and sometimes also catalysts to ensure sufficient reactivity. Some of them require problematic or inaccessible solvents and are questionable in terms of reproducibility.<sup>6,37–44</sup>

Our goal was to develop a particularly sustainable reaction variant that involves an electrogenerated oxidizer and proceeds without organic solvents and additives.

The tremendous potential of electrochemistry in the context of green chemistry has meanwhile been widely recognized.<sup>45,46</sup> Important aspects are the replacement of stoichiometric reagents by continuously administered electric

*this work:*



Scheme 3 Electrochemical ex-cell strategy for synthesis of hydroxyphenols.

current and the resulting process safety.<sup>47–49</sup> This has paved the way to a renaissance of electrosynthesis.<sup>50,51</sup> Recently, we reported an electrosynthetic method to transform 4-hydroxybenzaldehydes into *para*-benzoquinones *via* direct anodic oxidation.<sup>52</sup> Although hydroquinones are formed as intermediates in this process, a galvanostatic electrolysis will always proceed all the way to benzoquinones. After all, the hydroquinone oxidation has a lower oxidation potential than the first step. We, thus, sought alternative pathways to gain access to valuable hydroxyphenols based on electrochemical methods. Recently, our labs established a novel protocol for efficient generation of peroxodicarbonate (PODIC) by flow electrolysis of aqueous carbonate.<sup>53</sup> This approach provides the highest peroxodicarbonate concentration so far. It is noteworthy that peroxodicarbonate is distinctly different from percarbonate in its structure and reactivity and is only accessible electrochemically.<sup>54</sup> PODIC can serve as platform oxidizer originating from alternative anodic reaction for water splitting. The use of environmentally benign alkali carbonates is a tremendous advantage over the well-established periodates.<sup>55–61</sup> Besides the advantage that PODIC is made from inexpensive and safe to store carbonate salts it does not generate toxic or problematic waste. Moreover, it is also a powerful reagent for the synthesis of various important products. Previous investigations demonstrated its unique features for the epoxidation of double bonds, the hydroxylation of boronic acids, *N*-oxidation and valorisation of lignin.<sup>53,62–64</sup>

Here, PODIC functions as an electrochemically generated ex-cell oxidant which already features the required mild base equivalent for the transformation of benzaldehydes into phenols (Scheme 3).

## Results and discussion

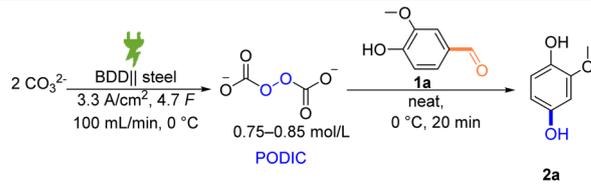
We commenced with vanillin (**1a**) as a model substrate to investigate the feasibility of a Dakin-type of reaction with electrochemically generated peroxodicarbonate in an ex-cell set-up. Vanillin is a natural product that can also be derived from the renewable feedstock lignin *via* electrochemical depolymerization.<sup>64–67</sup> Therefore, further conversion of this compound into valuable commodities is highly desirable. The resulting product of this particular Dakin reaction, 2-methoxyhydroquinone, was recently reported as a promising active electrolyte for organic flow batteries.<sup>10</sup>



Initially, various solvents were tested for their potential to facilitate the desired reaction of concentrated peroxodicarbonate solution with vanillin, starting from those that have been reported to be suitable for the Dakin reaction or to be compatible with PODIC (Table 1).<sup>37,40,41,53,62,68,69</sup> However, neither methanol or ethanol nor acetonitrile mixtures provided the desired product (Table 1, entries 1–3). In contrast, tetrahydrofuran directly gave considerable yields of **2a** (Table 1, entry 4). It is noteworthy that the reaction tolerates the presence of the stabilizer butylhydroxytoluene, which is supplemented to commercially tetrahydrofuran. After identifying a solvent which allows the desired reaction to proceed, we increased the equivalents of added PODIC to promote higher conversion to **2a**. An increase of the PODIC equivalents from 1 to 2 improved the yield from 26% to 72% (Table 1, entries 4 and 5). Driven by our intent to develop a sustainable alternative to conventional protocols, we searched for conditions without organic solvents. This was also fortified by safety concerns that arise from the combination of peroxide and cyclic ethers. Consequently, we explored different aqueous options. The use of water or carbonate solutions in place of THF gave **2a** only in lower yields (Table 1, entries 6–8). However, when treating neat **1a** with concentrated peroxodicarbonate, a satisfactory yield of 62% was achieved (Table 1, entry 9).

We next optimized all reaction parameters, such as the amount of oxidant, the reaction temperature, and the mode of addition (Table 2). Lowering of the PODIC amount from 2 eq. to 1.5 eq. led to an increase in selectivity without decreasing the conversion of **1a** (Table 2, entries 2 and 3). At even lower excess, the conversion and the overall yield decreased (Table 2, entry 4). Next, the slow addition of the oxidizer in equal portions every 5 minutes was tested (Table 2, entry 5). However, the yield was slightly lower in comparison to the original protocol in which the whole amount of PODIC is added at once (Table 2, entry 3). Moreover, a diluted peroxodicarbonate con-

**Table 2** In-depth screening of the reaction conditions



Entry	PODIC/eq.	T/°C	Deviation	Conv. <sup>a</sup> /%	<b>2a</b> <sup>a</sup> /%
1	2	rt	THF	97	72
2	2	rt	—	99	62
3	1.5	rt	—	97	80
4	1	rt	—	77	58
5	1.5	rt	Continuous addition	98	72
6	1.5	rt	c(PODIC) = 450 mM	97	66
7	1.5	rt	15 min	82	63
8	1.5	0 °C	—	81	71
9	1.75	0 °C	—	1	92 (91)

<sup>a</sup> Yield determined *via* <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard. Yield in brackets refers to isolated yield.

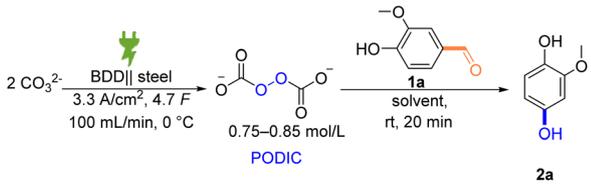
centration was used which only gave the desired compound in 66% yield (Table 2, entry 6). This control experiment clearly highlights the importance of the high concentration of peroxodicarbonate, which is currently only achievable with our previously developed protocol and flow-electrolyzer (Table 2, entry 6).<sup>53</sup> We observed that a short reaction time of 20 minutes is sufficient for the reaction to reach completion, whereas shorter reaction times led to incomplete consumption of starting material (Table 2, entries 3 and 7). It is known, that peroxodicarbonate has a decreased half-life at elevated temperatures.<sup>70</sup> Combined with the fact that an incomplete mass balance was observed, we tested a lowered temperature of 0 °C to circumvent this (Table 2, entry 8). Both the selectivity and the yield of desired product **2a** reached an optimum with the addition of 1.75 eq. PODIC at 0 °C (Table 2, entry 9; for further optimization experiments and data see ESI†).

With an optimized yield of 91% for the test substrate vanillin, we strived to explore the scope of our newly developed protocol. For this, we subjected a broad variety of substituted hydroxybenzaldehydes to our reaction protocol (Scheme 4).

Initially, we tested different alkoxyated 4-hydroxybenzaldehydes. Similar to our test substrate **1a**, ethylvanillin (**1b**) was transformed into the corresponding phenol **2b** in excellent yield. Additional combinations of substituents with dissimilar electronic effects (**1c–d**) were also well suited for our protocol and gave the phenols in 85% and 62% yield, respectively.

Next, a variety of halogenated 4-hydroxybenzaldehydes was explored including mono- and disubstituted substrates (**1e–h**). Initially, we observed very low conversion even at prolonged reaction times. This can be attributed to a poor solubility of the halogenated substrates in aqueous PODIC solution. In order to react, dissolution of the hydroxybenzaldehydes in the PODIC solution has to occur, which is then followed by deprotonation. To achieve this for compounds **1e–h**, a minor amount of methanol was employed as co-solvent.

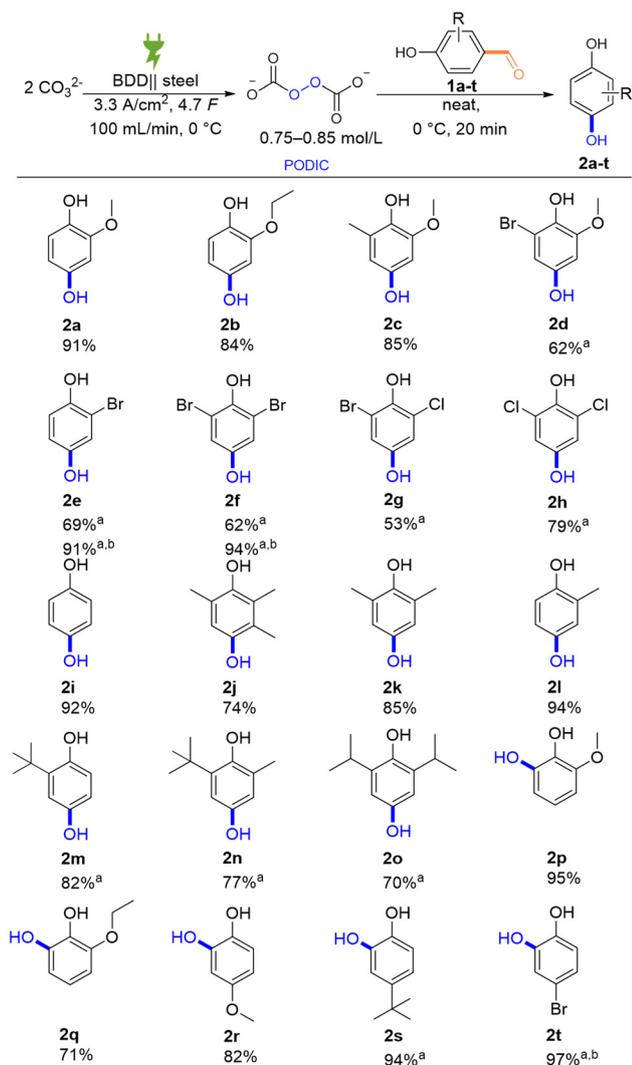
**Table 1** Initial screening of solvents



Entry	Solvent	PODIC/eq.	Conv. <sup>a</sup> /%	<b>2a</b> <sup>a</sup> /%
1	MeOH	1	22	0
2	MeOH/MeCN	1	30	0
3	EtOH	1	41	0
4	THF	1	51	26
5	THF	2	97	72
6	H <sub>2</sub> O	2	99	21
7	1 M Na <sub>2</sub> CO <sub>3</sub>	2	100	11
8	1 M NaHCO <sub>3</sub>	2	100	45
9	Neat	2	99	62

<sup>a</sup> Yield determined *via* <sup>1</sup>H NMR with 1,3,5-trimethoxybenzene as internal standard.





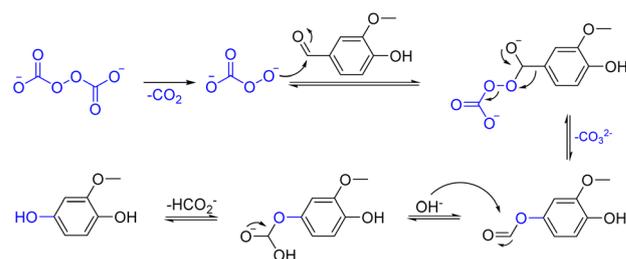
**Scheme 4** Scope of the Dakin reaction with peroxodicarbonate as oxidizer. <sup>a</sup> Substrate dissolved MeOH. <sup>b</sup> 3.5. eq PODIC.

Consequently, the conversion was significantly improved and mitigated the need for prolonged reaction times (**2e–f**). In comparison to the alkoxyated substrates, we observed slightly lower yields in the range of 69% and 79%. Usually, electron-withdrawing moieties on the substrate are detrimental and often cause diminished yields.<sup>31</sup> Nevertheless, the reaction occurred selectively under the reaction conditions established and the remaining non-converted starting material was easily recovered. The reaction can be pushed to a higher conversion by a slight increase of equivalents of PODIC, as could be demonstrated for substrates **1e** and **1f**. There, the yield could be improved from 69% and 62% to 91% and 94%, respectively.

The unsubstituted 4-hydroxybenzaldehyde was also suitable for our protocol resulting in 92% of hydroquinone (**2i**). Afterwards we explored a selection of alkyl substituted 4-hydroxybenzaldehydes. First, we applied benzaldehydes with low steric hinderance as provided by different amounts of methyl groups. The methylated phenols **2j–l** were obtained in yields of

74%, 85% and 94% yield, respectively. Subsequently, we moved to alkyl groups with a higher rate of steric hinderance such as *tert*-butyl and isopropyl substituents. A set of non-polar substituents again caused the need of a minor amount of methanol to aid their dissolution. Following this, the mono-*tert*-butylated phenol **2m** was obtained in 82% yield, the phenol with an additional methyl group **2n** was isolated in 77%, and with two isopropyl groups provided **2o** in 70% yield. Lastly, 2-hydroxylated benzaldehydes were also investigated as potential substrates. For the conventional Dakin reaction it is known that 2-hydroxybenzaldehydes are more reactive than its 4-hydroxy congeners.<sup>71</sup> Therefore, we were interested to see how these substrates perform within the conditions of our *E*-Dakin reaction. Initially, the *ortho*-isomer **1p** of our test substrate vanillin **1a** was subjected to our established conditions. The resulting catechol **2p** was obtained in 95% yield. Moreover, the ethoxylated benzaldehyde **2q**, another methoxyated isomer **2r**, as well as the *tert*-butylated **2s**, and the mono-halo derivative **2t** were successfully synthesized in 82%, 94%, and 97% yield, respectively.

Mechanistically, we propose that the reaction sequence is initiated by mono decarboxylation of the peroxodicarbonate. Subsequently, the very nucleophilic peroxide anion interacts with the carbaldehyde function. The formed tetrahedral intermediate expels a carbonate and undergoes a [1,2]-aryl shift. Finally, hydrolysis liberates phenol and formate underlining the necessity of base equivalents along with the oxidizer (Scheme 5).<sup>32</sup>



**Scheme 5** Postulated mechanism for the Dakin-reaction with PODIC.

**Table 3** Scale-up of the reaction

Entry	<i>n</i> ( <b>1a</b> )/mmol	<i>m</i> ( <b>2a</b> )/g	<b>2a</b> /%
1	1	0.128	91
2	10	1.260	90
3	20	2.464	88

Yields refer to isolated yields.



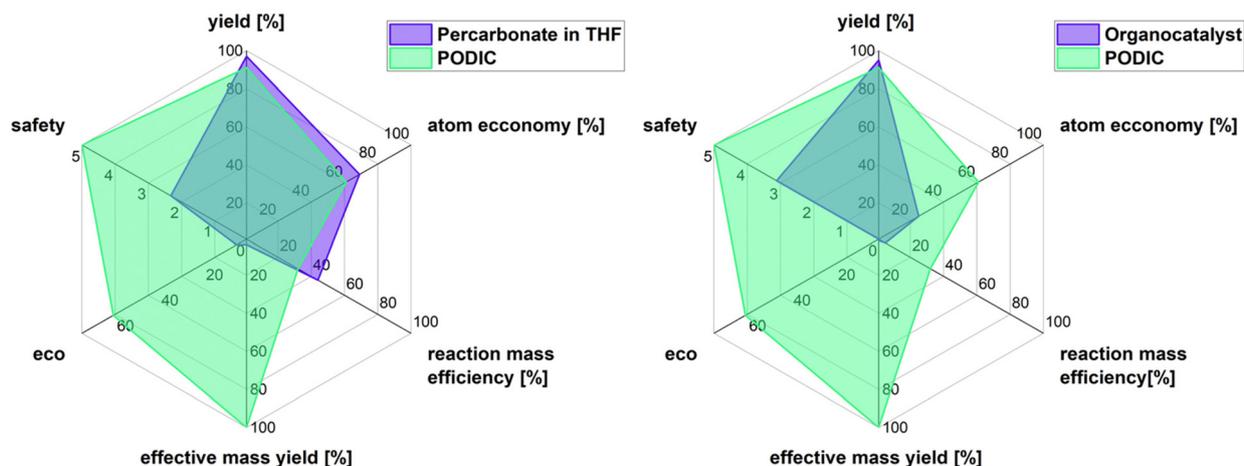


Fig. 1 Comparison of PODIC protocol (green) and published conventional methods (blue) for the oxidation of **1a** to **2a**. Left: Comparison to oxidation with percarbonate.<sup>76</sup> Right: Comparison organo-catalysed oxidation. For details on conventional methods and calculation of depicted values see ESI.†<sup>37</sup>

The mechanistic proposal also underlines the interesting chemoselectivity of the reaction. The electrochemically generated peroxodicarbonate shows high functional group compatibility and the resulting hydroxy groups remain unaffected by it. As a result of the innovative ex-cell approach, hydroquinones are exclusively obtained. In contrast to that the direct electrochemical conversion inevitably yields the benzoquinones due to the galvanostatic conditions.<sup>52,72</sup> Therefore, this novel protocol complements our previous efforts by expanding the space of obtainable products. Ultimately, we tested the scalability of our established protocol. For this, we performed the oxidation of our test substrate vanillin on 10 mmol and 20 mmol scale (Table 3).

On gram scale, the reaction proceeded smoothly in comparable yields, further underlining the synthetic utility of the *E*-Dakin reaction.

Since this research was initially motivated by the aspiration to develop a greener approach to hydroquinones and catechols *via* a Dakin-type reaction, a quantitative comparison to previous protocols was conducted (Fig. 1). To evaluate the sustainability of the reaction, we considered different established green chemistry metrics.<sup>73,74</sup> Additionally, high importance is also attributed to the economic factors, synthetic utility and safety of a reaction. Therefore, we also included such criteria in our assessment. Synthetic utility, as evidenced by the chemical yield, of all three protocols is comparably high with almost quantitative yields. Nevertheless, in times of depletion of resources and demand for more sustainable chemical transformations this single factor is no longer sufficient to rate the importance of a chemical protocol alone. Therefore, an attempt to quantify the sustainability of the protocols was undertaken. First, with the atom efficiency the molecular mass of the desired product is brought into relation to the overall mass of the formed products. Since the transformation occurs with high selectivity, but the nature of the mechanism inevitably

leads to the co-generation of formate the atom economy is high but never 100%. Next, the reaction mass efficiency was calculated. This factor puts the chemical yield and atom economy of a reaction into context with the excess reagent factor. Furthermore, the mass efficient yield, incorporating the mass of non-benign reagents, was taken into account. This is an especially important factor given the environmental problems that arise from the use of such chemicals. As is evident by Fig. 1, our protocol introduces significant advancements in this regard, since it eliminates the need for problematic organic solvents and only uses a benign carbonate-based oxidant which comes along with a mild base equivalent. Apart from this, the cost of a chemical transformation is also an important factor to consider, especially for large scale synthesis. Therefore, we also considered the generated value of the product in contrast to the cost of the used reagents. Again, an improvement to previous protocols was made, due to the inexpensive nature of the applied reagents. Finally, the safety of the protocols was evaluated based on the hazards originating from the applied chemical reagents (for details and calculation see ESI†).<sup>74,75</sup> In summary, this quantification demonstrates that our novel protocol has introduced significant advances in regards of minimization of problematic reagents while effectively lowering the cost of the transformation and improving the reaction safety.

## Conclusions

An efficient and sustainable protocol for the conversion of widely accessible hydroxybenzaldehydes into valuable hydroquinones and catechols was established. This transformation is enabled through the powerful electrochemical platform oxidizer peroxodicarbonate (PODIC), which also provides the mildly basic conditions required for the oxidation step. PODIC can be



synthesized on demand *via* electrolysis of ecologically safe aqueous carbonate solutions, circumventing the storage of potentially dangerous peroxides. The process safety is further improved due to the self-decomposition of peroxodicarbonate at room temperature preventing the build-up of peroxides in the reaction products. The reaction proceeds swiftly without an organic solvent and in the absence of any catalysts or activating agents. This simplifies the reaction work-up and minimizes waste generation. The broad applicability of the protocol was demonstrated for 20 examples with yields up to 97%. A broad variety of substituents was compatible, and the synthetic utility was proven through synthesis on a multi-gram scale.

## Author contributions

F. S. planned and conducted the optimization study and isolated the scope. N. S. and P. K. synthesized the ex-cell oxidant and were involved in the early stages of the optimization study. S. W. supervised the project and provided continuous input. L. G. planned and constructed the electrolysis cell. L. G. and S. W. acquired funding for the project. F. S. and S. W. wrote the initial manuscript, and all authors revised it. All authors listed have made a substantial, direct, and intellectual contribution to the work and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## References

- 1 K. A. Scott, P. B. Cox and J. T. Njardarson, *J. Med. Chem.*, 2022, **65**, 7044–7072.
- 2 W.-Y. Huang, Y.-Z. Cai and Y. Zhang, *Nutr. Cancer*, 2010, **62**, 1–20.
- 3 D.-P. Yang, H.-F. Ji, G.-Y. Tang, W. Ren and H.-Y. Zhang, *Molecules*, 2007, **12**, 878–884.
- 4 R. Bodoira and D. Maestri, *J. Agric. Food Chem.*, 2020, **68**, 927–942.
- 5 S. Molloy, *Nat. Rev. Microbiol.*, 2006, **4**, 880–881.
- 6 R. Bernini, A. Coratti, G. Provenzano, G. Fabrizi and D. Tofani, *Tetrahedron*, 2005, **61**, 1821–1825.
- 7 Y. Guo, D. He, A. Xie, W. Qu, Y. Tang, L. Zhou and R. Zhu, *Polymers*, 2019, **11**, 1907.
- 8 S. Patai, *The chemistry of the quinonoid compounds*, Wiley, London, 1974–1988.
- 9 X. Yang, S. N. Garcia, T. Janoschka, D. Kónya, M. D. Hager and U. S. Schubert, *Molecules*, 2021, **26**, 3823.
- 10 W. Schlemmer, P. Nothdurft, A. Petzold, G. Riess, P. Frühwirt, M. Schmallegger, G. Gescheidt-Demner, R. Fischer, S. A. Freunberger, W. Kern and S. Spirk, *Angew. Chem.*, 2020, **132**, 23143–23146.
- 11 B. Assoah, L. F. Veiros, C. A. M. Afonso and N. R. Candeias, *Eur. J. Org. Chem.*, 2016, 3856–3861.
- 12 Z. Ye, B. Shi, Y. Huang, T. Ma, Z. Xiang, B. Hu, Z. Kuang, M. Huang, X. Lin, Z. Tian, Z. Deng, K. Shen and T. Liu, *Innovation*, 2022, **3**, 100228.
- 13 L. Massignan, X. Tan, T. H. Meyer, R. Kuniyil, A. M. Messinis and L. Ackermann, *Angew. Chem., Int. Ed.*, 2020, **59**, 3184–3189.
- 14 Y.-H. Zhang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 14654–14655.
- 15 T. Jintoku, K. Nishimura, K. Takaki and Y. Fujiwara, *Chem. Lett.*, 1990, **19**, 1687–1688.
- 16 Y. Yan, P. Feng, Q.-Z. Zheng, Y.-F. Liang, J.-F. Lu, Y. Cui and N. Jiao, *Angew. Chem., Int. Ed.*, 2013, **52**, 5827–5831.
- 17 T. Yamaguchi, E. Yamaguchi, N. Tada and A. Itoh, *Adv. Synth. Catal.*, 2015, **357**, 2017–2021.
- 18 K. W. Anderson, T. Ikawa, R. E. Tundel and S. L. Buchwald, *J. Am. Chem. Soc.*, 2006, **128**, 10694–10695.
- 19 T. Schulz, C. Torborg, B. Schöffner, J. Huang, A. Zapf, R. Kadyrov, A. Börner and M. Beller, *Angew. Chem., Int. Ed.*, 2009, **48**, 918–921.
- 20 A. Tlili, N. Xia, F. Monnier and M. Taillefer, *Angew. Chem., Int. Ed.*, 2009, **48**, 8725–8728.
- 21 S. Xia, L. Gan, K. Wang, Z. Li and D. Ma, *J. Am. Chem. Soc.*, 2016, **138**, 13493–13496.
- 22 R. E. Maleczka, F. Shi, D. Holmes and M. R. Smith, *J. Am. Chem. Soc.*, 2003, **125**, 7792–7793.
- 23 J. Xu, X. Wang, C. Shao, D. Su, G. Cheng and Y. Hu, *Org. Lett.*, 2010, **12**, 1964–1967.
- 24 H.-L. Qi, D.-S. Chen, J.-S. Ye and J.-M. Huang, *J. Org. Chem.*, 2013, **78**, 7482–7487.
- 25 E. J. Rayment, N. Summerhill and E. A. Anderson, *J. Org. Chem.*, 2012, **77**, 7052–7060.
- 26 J. D. Sunderhaus, H. Lam and G. B. Dudley, *Org. Lett.*, 2003, **5**, 4571–4573.
- 27 T. Cohen, A. G. Dietz and J. R. Miser, *J. Org. Chem.*, 1977, **42**, 2053–2058.
- 28 A. A. Núñez Magro, G. R. Eastham and D. J. Cole-Hamilton, *Dalton Trans.*, 2009, 4683–4688.
- 29 W. Su, P. Xu and T. Ritter, *Angew. Chem., Int. Ed.*, 2021, **60**, 24012–24017.
- 30 P. T. Anastas and J. C. Warner, *Green chemistry. Theory and practice*, Oxford University Press, Oxford, 1st edn, 2000.
- 31 H. D. Dakin, *Am. Chem. J.*, 1909, **42**, 477–498.
- 32 Z. Wang, *Comprehensive organic name reactions and reagents*, John Wiley, Hoboken (N.J.), 2009.
- 33 V. E. Tarabanko and N. Tarabanko, *Int. J. Mol. Sci.*, 2017, **18**, 2421.



- 34 N. Zhou, W. P. D. W. Thilakarathna, Q. S. He and H. P. V. Rupasinghe, *Front. Energy Res.*, 2022, **9**, 758744.
- 35 X. Liu, F. P. Bouxin, J. Fan, V. L. Budarin, C. Hu and J. H. Clark, *ChemSusChem*, 2020, **13**, 4296–4317.
- 36 Z. Sun, B. Fridrich, A. de Santi, S. Elangovan and K. Barta, *Chem. Rev.*, 2018, **118**, 614–678.
- 37 S. Chen and F. W. Foss, *Org. Lett.*, 2012, **14**, 5150–5153.
- 38 W. Sun, L. Gao, X. Sun, H. Yang and G. Zheng, *Adv. Synth. Catal.*, 2019, **361**, 5210–5216.
- 39 B. Saikia, P. Borah and N. C. Barua, *Green Chem.*, 2015, **17**, 4533–4536.
- 40 G. W. Kabalka, N. K. Reddy and C. Narayana, *Tetrahedron Lett.*, 1992, **33**, 865–866.
- 41 A. Roy, K. R. Reddy, P. K. Mohanta, H. Ila and H. Junjappat, *Synth. Commun.*, 1999, **29**, 3781–3791.
- 42 E. T. da Silva, C. A. Câmara, O. A. C. Antunes, E. J. Barreiro and C. A. M. Fraga, *Synth. Commun.*, 2008, **38**, 784–788.
- 43 R. S. Varma and K. P. Naicker, *Org. Lett.*, 1999, **1**, 189–192.
- 44 B. Saikia and P. Borah, *RSC Adv.*, 2015, **5**, 105583–105586.
- 45 C. Schotten, T. P. Nicholls, R. A. Bourne, N. Kapur, B. N. Nguyen and C. E. Willans, *Green Chem.*, 2020, **22**, 3358–3375.
- 46 Y. Yuan and A. Lei, *Nat. Commun.*, 2020, **11**, 802.
- 47 D. Pollok and S. R. Waldvogel, *Chem. Sci.*, 2020, **11**, 12386–12400.
- 48 A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2018, **57**, 5594–5619.
- 49 S. Möhle, M. Zirbes, E. Rodrigo, T. Gieshoff, A. Wiebe and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2018, **57**, 6018–6041.
- 50 S. R. Waldvogel and B. Janza, *Angew. Chem., Int. Ed.*, 2014, **53**, 7122–7123.
- 51 M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.*, 2017, **117**, 13230–13319.
- 52 F. Sprang, J. Klein and S. R. Waldvogel, *ACS Sustainable Chem. Eng.*, 2023, **11**, 7755–7764.
- 53 A.-K. Seitz, P. J. Kohlpaintner, T. van Lingen, M. Dyga, F. Sprang, M. Zirbes, S. R. Waldvogel and L. J. Gooßen, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117563.
- 54 R. E. Dinnebier, S. Vensky, P. W. Stephens and M. Jansen, *Angew. Chem., Int. Ed.*, 2002, **41**, 1922–1924.
- 55 S. Arndt, P. J. Kohlpaintner, K. Donsbach and S. R. Waldvogel, *Org. Process Res. Dev.*, 2022, **26**, 2564–2613.
- 56 S. Arndt, D. Weis, K. Donsbach and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2020, **59**, 8036–8041.
- 57 S. Arndt, R. Rücker, A. Stenglein and S. R. Waldvogel, *Org. Process Res. Dev.*, 2022, **26**, 2447–2455.
- 58 C. M. Kisukuri, R. J.-R. Bednarz, C. Kampf, S. Arndt and S. R. Waldvogel, *ChemSusChem*, 2022, **15**, e202200874.
- 59 J. Klein, K. Alt and S. R. Waldvogel, *Adv. Sustainable Syst.*, 2022, **6**, 2100391.
- 60 J. Klein, R. Kupec, M. Stöckl and S. R. Waldvogel, *Adv. Sustainable Syst.*, 2022, **10**, 2200431.
- 61 S. Arndt, B. Grill, H. Schwab, G. Steinkellner, U. Pogorevčnik, D. Weis, A. M. Nauth, K. Gruber, T. Opatz, K. Donsbach, S. R. Waldvogel and M. Winkler, *Green Chem.*, 2021, **23**, 388–395.
- 62 P. J. Kohlpaintner, L. Marquart, L. J. Gooßen and S. R. Waldvogel, *Eur. J. Org. Chem.*, 2023, e202300220.
- 63 A.-K. Seitz, T. van Lingen, M. Dyga, P. J. Kohlpaintner, S. R. Waldvogel and L. J. Gooßen, *Synlett*, 2022, 1527–1531.
- 64 M. Zirbes, T. Graßl, R. Neuber and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2023, **62**, e202219217.
- 65 M. Breiner, M. Zirbes and S. R. Waldvogel, *Green Chem.*, 2021, **23**, 6449–6455.
- 66 M. Zirbes, L. L. Quadri, M. Breiner, A. Stenglein, A. Bomm, W. Schade and S. R. Waldvogel, *ACS Sustainable Chem. Eng.*, 2020, **8**, 7300–7307.
- 67 M. Zirbes and S. R. Waldvogel, *Curr. Opin. Green Sustainable Chem.*, 2018, **14**, 19–25.
- 68 S. Chen, M. S. Hossain and F. W. Foss, *Org. Lett.*, 2012, **14**, 2806–2809.
- 69 M. Klein, D. L. Troglauer and S. R. Waldvogel, *JACS Au*, 2023, **3**, 575–583.
- 70 C. P. Chardon, T. Matthée, R. Neuber, M. Fryda and C. Comninellis, *ChemistrySelect*, 2017, **2**, 1037–1040.
- 71 M. B. Hocking, K. Bhandari, B. Shell and T. A. Smyth, *J. Org. Chem.*, 1982, **47**, 4208–4215.
- 72 F. Sprang, J. D. Herszman and S. R. Waldvogel, *Green Chem.*, 2022, **24**, 5116–5124.
- 73 A. P. Dicks and A. Hent, *Green chemistry metrics. A guide to determining and evaluating process greenness*, Springer, Cham, 2015.
- 74 D. J. C. Constable, A. D. Curzons and V. L. Cunningham, *Green Chem.*, 2002, **4**, 521–527.
- 75 L. Goclik, H. Walschus, A. Bordet and W. Leitner, *Green Chem.*, 2022, **24**, 2937–2945.
- 76 M. Fache, E. Darroman, V. Besse, R. Auvergne, S. Caillol and B. Boutevin, *Green Chem.*, 2014, **16**, 1987–1998.

