

<https://helda.helsinki.fi>

Water tolerant base free Copper (I) catalyst for the selective aerobic oxidation of primary alcohols

Lagerspets, Emi

2022-03

Lagerspets , E , Abba , D , Sharratt , J , Eronen , A & Repo , T 2022 , ' Water tolerant base free Copper (I) catalyst for the selective aerobic oxidation of primary alcohols ' , Molecular catalysis , vol. 520 , 112167 . <https://doi.org/10.1016/j.mcat.2022.112167>

<http://hdl.handle.net/10138/341785>

<https://doi.org/10.1016/j.mcat.2022.112167>

cc_by

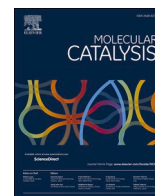
publishedVersion

Downloaded from Helda, University of Helsinki institutional repository.

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Please cite the original version.



Water tolerant base free Copper (I) catalyst for the selective aerobic oxidation of primary alcohols

Emi Lagerspets, Donatella Abba[†], Joseph Sharratt^{††}, Aleksi Eronen, Timo Repo^{*}

Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, 00014 Helsinki, Finland

ARTICLE INFO

Keywords:

Base free
Aerobic oxidation
Copper(I)
Catalyst
Water/acetonitrile mixture

ABSTRACT

We report here a base free copper(I) catalyst for the selective aerobic oxidation of primary alcohols to their corresponding aldehydes and various diols to their corresponding lactones or lactols. In the presence of the *in situ* generated Cu(I)-catalyst with 2,2'-dipyridylamine (dpa) as a ligand and 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) as a persistent radical, the oxidation reaction proceeds under true aerobic conditions, at ambient temperature, utilizing air as the oxidant and without added base. High catalytic activity without over oxidation was achieved for numerous primary alcohols (aliphatic, allylic, benzylic and diols) with different substitution patterns. The catalyst's stability is unique among reported Cu(I)-catalysts. It is not moisture or air sensitive, and is capable of *e.g.* oxidizing aliphatic and benzyl alcohols in a water/acetonitrile solution in moderate or in quantitative yield (> 99%) in 3 h.

Introduction

A fundamental and important transformation in chemistry is the selective oxidation of alcohol to aldehyde [1–6]. Although numerous methodologies have been reported for the synthesis of aldehydes, truly green catalytic oxidation reactions, according to the principles of green chemistry, that utilize air as an oxidant, are the most desirable, because they are safe and produce only water as a by-product [7–15]. Amongst others, copper-based catalysts, especially when combined with persistent radicals (such as 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)) and organic base (often N-methylimidazole (NMI)), have proven to be very effective in aerobic oxidation reactions [16–25]. The optimized conditions of these aerobic oxidations depend highly on the addition of a ligand, often used are bipyridines (5 mol% Cu-salt, 5 mol% bipy, 5, mol % TEMPO, 10 mol% NMI, 1 mmol alcohol) or Schiff bases (4 mol% Cu-salt, 4 mol% Schiff base, 5, mol% TEMPO, 10 mol% NMI, 1 mmol alcohol) [24,26]. In addition to the ligand, these Cu-catalysts require a large amount of additional organic base, such as imidazole (NMI), for optimal activity and stability [12,27–30]. The base is understood to assist the catalytic cycle through the deprotonation of the alcohol substrate, thus enhancing the substrate coordination to the Cu-center. It is further postulated, that the added base (NMI), as a weakly coordinating

ligand, stabilizes reactive monomeric Cu(I) structures and enhances activation of molecular oxygen [29,31]. Over the last two decades, these catalysts have been under intensive studies, although there has been a lot of progress, the biggest challenge in the development of copper-based oxidation catalysts remains: how to combine the high reactivity of Cu (I)-catalysts with the high stability of Cu(II)-catalysts [15]. While Cu (II)-catalysts are water stable, they are limited to only benzylic and other π -activated alcohols [32–40]. Contrariwise, Cu(I)-catalysts can oxidize even aliphatic alcohols, but their use is limited due to their air and moisture sensitivity. However, due to their highly reactive nature, Cu(I)-catalyst species are interesting for aerobic oxidation reaction [12].

Herein we report a novel Cu(I)-catalyst for the base free catalytic aerobic oxidation of various primary aliphatic and benzylic alcohols to their corresponding aldehydes. In addition to its high catalytic activity, its stability is unique among Cu(I)-catalysts. It is not moisture or air sensitive, and it can be prepared *in situ* without inert atmosphere techniques and is capable of *e.g.* oxidizing π -activated alcohols in an aqueous mixture in quantitative yields.

Experimental

Commercially available compounds were purchased from Sigma-

* Corresponding author.

E-mail address: timo.repo@helsinki.fi (T. Repo).

[†] Present address: Donatella Abba, Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

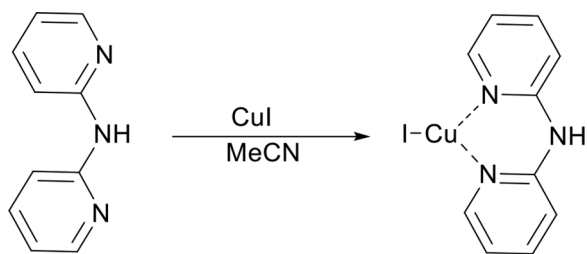
^{††} Present address: Joseph Sharratt, Department of Biotechnology, University of Manchester, 131 Princess Street, Manchester, M1 7DN, UK

<https://doi.org/10.1016/j.mcat.2022.112167>

Received 1 December 2021; Received in revised form 25 January 2022; Accepted 3 February 2022

Available online 10 February 2022

2468-8231/© 2022 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).



Scheme 1. *In situ* synthesis of the Cu(I)-iodide-2,2'-dipyridylamine (dpa) catalyst. UV-vis shows that the Cu-complex is in the oxidation state I. (See supporting information for more details.)

Aldrich except 4-fluoroaniline (from fluorochem) and benzyl alcohol (from abcr) and used without further purification unless otherwise stated. The ^1H , ^{13}C , HSQC and HMBC NMR spectra were recorded on a Bruker Avance NEO 400 MHz spectrometer. GC-FID analyses were performed on Agilent Technologies 7890B GC equipped with 5977B MSD, using an Agilent HP-MS-5-UI (30 m, 0.25 mm, 0.25 μm) column or GC-MS with an Agilent Technologies 6890 N GC equipped with 5973 MSD, using an Agilent HP-MS-5-UI (30 m, 0.25 mm, 0.25 μm) column. The oxidation products were identified via GC-MS by comparison with commercial samples. The yield determinations were conducted with the GC-FID using calibration curves with acetophenone or 1,2-dichlorobenzene as an internal standard. For the *in situ* IR measurements a Mettler Toledo ReactIRTM 15 was used with a 6.3 mm AgX DiComp as the probe.

Oxidations

Oxidation reactions were performed in 3 mL MeCN or in a mixture of 2 mL MeCN and 1 mL H₂O solutions at room temperature under open air conditions. The reaction was set up by adding 2.5 mol% of copper(I) iodide, 2.5 mol% of ligand, 3 mL solvent, 4 mol% of TEMPO and 1 mmol of alcohol into a 20 mL test tube, which was equipped with a magnetic stir bar. The reaction was stirred at 1500 rpm for 1 h, 3 h or 24 h depending on the substrate. After the reaction, the reaction solution and an internal standard (acetophenone 40 μL or 1,2-dichlorobenzene 40 μL , see ESI for more information) were diluted with EtOAc (50 mL). GC samples (1.5 mL) were prepared by filtrating the solution through a layer of silica gel (1 cm thick). The yields were determined using GC-FID with calibration curves and identified using GC-MS and/or $^1\text{H}/^{13}\text{C}/\text{HMBC}/\text{HSQC}$ NMR.

Results and discussion

Our group previously demonstrated that CuI is a highly beneficial copper source for the preparation of oxidation catalysts; CuI has a unique tendency to favor an oxidation state of +1 [26,41,42]. Although redox stability has a potentially detrimental effect on catalytic activity, by modifying Schiff base-type bidentate ligands, we have successfully developed a highly active oxidation catalysts based on CuI [26,30]. Recently we turned our focus to 2,2'-dipyridylamine (dpa) as a ligand. As a classic ligand that has been known for more than 100 years, dpa is of particular interest in coordination chemistry for its ability to act as a polyvalent ligand [43–46].

When mixed in a 1:1 ratio in HPLC grade (non-dried) acetonitrile (MeCN), dpa and CuI initially forms a yellow solution, which slowly turns green. This suggests that a Cu(I)-complex is formed (Scheme 1).

ESI-MS measurements were able to identify the presence of two different Cu(I)-complexes, one with a 1:1 ratio for dpa and Cu(I)-iodide ($[(\text{C}_{10}\text{H}_9\text{N}_3)\text{Cu}]^+$ (exact mass 234.0079 m/z)) and the one with a coordinated MeCN molecule on the Cu(I)-dpa complex ($[(\text{C}_{10}\text{H}_9\text{N}_3)(\text{C}_2\text{H}_3\text{N})\text{Cu}]^+$ (exact mass 275.0339 m/z)) (See supporting information for more details).

When the substrate and 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) are added, the system becomes catalytically active, seen by the change in color back to yellow. The oxidation reaction proceeds under truly aerobic conditions, utilizing atmospheric oxygen as an oxidant at ambient temperatures and pressures. Furthermore, there is no need for a base to proceed.

We theorize, that dpa, as a polyvalent ligand, will be able to increase the electron density at the Cu center, resulting in a more nucleophilic Cu species that promotes oxidation activity. This effect has been previously observed, when addition of base (typically NMI) yields a vastly improved activity [12,29]. The new catalyst is capable of selectively and rapidly oxidizing primary aliphatic and benzylic alcohols to aldehydes and diols are selectively oxidized to the corresponding lactols or lactones without over oxidation.

By using non-dried MeCN as the reaction medium and optimized reaction conditions (air as an oxidant, 4 mol% TEMPO, 2.5 mol% CuI, 2.5 mol% dba, 1 mmol alcohol, 3 mL MeCN and no added base), the catalyst tolerates high substrate loadings, as shown with 1-octanol (Table 1 entry 1, 1a and 1b). In addition, the blank experiments using Cu(II)Cl₂ or CuI alone gave only 2% and 7% yield in the oxidation of benzyl alcohol, respectively (see supporting information Table S1).

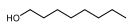

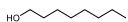

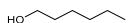
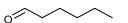
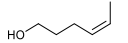
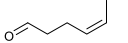
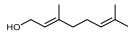
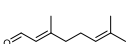
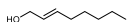
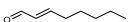
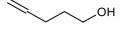
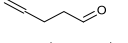
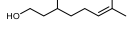
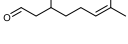
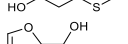
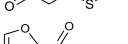



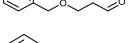
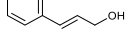
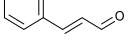
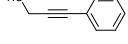
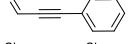
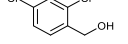
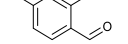
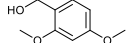
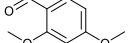
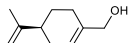
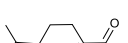
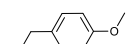
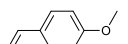
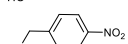
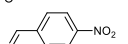
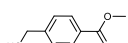
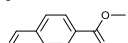
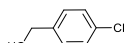
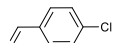
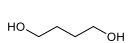
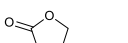
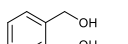
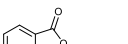

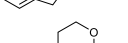
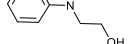
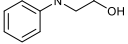
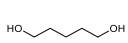
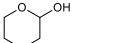
In MeCN, the substrate scope is expanded to aliphatic primary alcohols, which can be selectively oxidized under aerobic conditions (Table 1). No over oxidation is detectable, even when double or triple bonds are present in the substrates (Table 1 entry, 3–7, 11, 12 and 15). We were even able to oxidize diols selectively to form lactols and lactones (Table 1 entry 20–23). Surprisingly 1,5-pentanediol (Table 1 entry 23) yields a lactol not lactone, since this TEMPO assisted catalyst is not able to oxidize secondary alcohols, that are present in the lactone forming step. Similarly, also a valuable morpholine derivative (4-phenylmorpholin-2-ol) is formed from the oxidation of N-phenyl-diethanolamine (Table 1, entry 22). As shown in Table 1 (Table 1, entries 8–10, 14, 16–23) alcohols containing heteroatoms in various positions can be oxidized with excellent or at least moderate catalytic activity.

With this stable, easy-to-handle Cu(I)-iodide ligand system, we were able to quantitatively oxidize benzyl alcohol while using even a water/MeCN mixture as a reaction medium (see Table 2, entry 3). This is a new and exceptional finding, as previously only Cu(II)-catalysts have been reported to be capable of oxidizing alcohol in the presence of water and an external base. [38] With a reaction time of 3 h, benzyl alcohol was fully converted to aldehyde with no over oxidation (Table 2, entry 2).

It is noteworthy that doubling the amount of alcohol, in the oxidation reaction is even more efficient in a water/MeCN mixture than using pure MeCN as a solvent (Table 2, entry 5, 6). At substrate loads greater than 2 mmol, the aldehyde yield decreases in both solvents (Table 2, entry 7, 8). We were even able to use acetone as the reaction medium, but the long reaction times and open-air oxidation protocols may limit to the usefulness of this choice of solvent (Table 2, entry 4).

To gain further understanding for the catalytic system in water/MeCN mixture, we followed the oxidation of benzyl alcohol to aldehyde via *in situ* IR (Figs. 1A and B). While initially showing minor activity during the first 45 min, the aldehyde signal at 1705 cm^{-1} rapidly grows

Table 1
 Selective aerobic oxidation of primary alcohols with CuI-dpa under open air and at RT.

Entry	Substrate	Aldehyde	Yield ^a
1			98% (98%) ^b
1a			84% (85%) ^c
1b			73% (73%) ^d
1c			49% (50%) ^f
2			92% (92%) ^b
3			89%(90%) ^{b,g}
4			E:Z 98:2 ^g (100%) ^b
4a			99%(100%) ^f
5			98% (98%) ^b
6			99%(100%) ^b
7			99%(100%) ^b
7a			57% (57%) ^f
8			74% (75%) ^b
9			99% (99%) ^b
10			53% (54%) ^b
11			98% (98%) ^b
12			98% (98%) ^b
13			>99% (100%) ^e
14			>99% (100%) ^e
15			95% (96%) ^e
16			>99% (100%) ^e
17			>99% (100%) ^e
18			>99% (100%) ^e
19			>99%(100%) ^b
20			77% (100%) ^{b,g}
21			96% (100%) ^{b,g}
22			61% (65%) ^{b,g}
23			79% (100%) ^{b,g}
24			70% (100%) ^{b,g}

^a Yield calculated with GC-FID calibration curves (see supporting information) in parentheses the total conversion. Reaction conditions: 4 mol % TEMPO, 2.5 mol % CuI, 2.5 mol % dpa, 3 mL MeCN with: ^b 1 mmol alcohol, 24 h. ^c 2 mmol alcohol, 24 h. ^d 3 mmol alcohol, 24 h. ^e 1 mmol alcohol, 4 h. ^f 5 mol % TEMPO, 5 mol % CuI, 5 mol % dpa, 1 mmol alcohol, 2 mL MeCN, 1 mL H₂O, 24 h. ^g Conversion and in parentheses the total conversion calculated with GC-MS and identified with ¹H, ¹³C, HMBC and HSQC NMR (see supporting information).

Table 2

Aerobic oxidation of benzyl alcohol to benzaldehyde under open air and at RT.

Entry	Yield of benzyl aldehyde ^a	Solvent
1	> 99% (100%)	MeCN ^b
2	> 99% (100%)	MeCN ^c
3	> 99% (100%)	MeCN:H ₂ O (2:1) ^d
4	> 99% (100%)	Acetone ^c
5	56% (56%)	MeCN ^d
6	96% (96%)	MeCN:H ₂ O (2:1) ^d
7	55% (55%)	MeCN ^e
8	56% (56%)	MeCN:H ₂ O (2:1) ^e

^a Yield calculated with GC-FID calibration curves (see supporting information), in parentheses the total conversion.

^b 5 mol% TEMPO, 5 mol% CuI, 5 mol% dba, 10 mol% NMI, 1 mmol alcohol, 3 mL solvent, 1 h. Reaction conditions: 4 mol% TEMPO, 2.5 mol% CuI, 2.5 mol% dba, 3 mL solvent, 3 h.

^c 1 mmol alcohol.

^d 2 mmol alcohol.

^e 3 mmol alcohol.

after this point (Fig. 1B). Although the reason remained ambiguous, the required incubation explains the need of extended reaction time (3 h) for high yield oxidations.

The substrate scope is expandable also beyond the benzylic alcohols. Geraniol, as an example of π -activated alcohols, is oxidized in quantitative yields to citral (Table 1, entry 4a). As examples of primary aliphatic alcohols, Citronellol gave 57% yield for the corresponding aldehyde (Table 1, entry 7a) and 1-octanol gave 49% yield of 1-octanal (Table 1, entry 1c). Compared to benzyl alcohol, lower yields with aliphatic alcohols in the presence of water are associated with a slower start of the reaction and lower reaction rates.

The limits of the catalyst stability also come into play; by significantly extending the reaction times, water can immobilize the catalyst (and thus prevent higher yields). Overall, the aerobic oxidation of primary benzyl alcohols to the corresponding aldehyde in the aqueous mixture is an indication of the stability and the reactivity of this new catalytic system based on the dpa-Cu(I)-complex (see supporting information). Adding to this, no oxidation of benzylic alcohol was observed when using a Cu(II)-salt in the same conditions (see supporting information Table S1 entry 1a). Accordingly, the need of Cu(I) as the initial oxidation state of the catalyst is essential.

We propose the following mechanism for this aerobic oxidation based on Hoover *et al.* work and our previous work [26,30,31,47]. In the

beginning, in MeCN as a solvent, we have a Cu(I)-complex (supported by our ESI-MS findings, see supporting information) with one dba ligand coordinated to the Cu. The *in situ* measured UV-vis data confirms this oxidation state (see supporting information). Whereas the Cu(I)-complex is seemingly stable in MeCN, in the water/MeCN solutions the Cu(II)-signal is formed during the addition of the water. The dimeric complex between steps I to II is marked in square brackets, because the structure is hypothetical, as we cannot detect this species by UV-vis, ESI-MS, or *in situ* IR measurements (Scheme 2).

In the presence of TEMPOH/TEMPO in step II a Cu(II)-OH complex is formed. We can clearly identify it with UV-vis measurements in the water/MeCN mixture, but it remains transparent in MeCN solution. Upon addition of the alcohol substrate (step III to IV), the UV-vis signal shows a Cu(I)-signal in both solvent systems, which indicates the high turnover of the reaction towards the aldehyde and the reaction proceeds most likely *via* a transient intermediate with a coordinated alkoxide. In step IV, TEMPO participates by assisting the hydride abstraction from the alkoxide and the original Cu(I)-catalyst is regenerated together with formed aldehyde and TEMPOH.

Conclusion

In summary, we here present a new base free aerobic oxidation catalyst using the highly active Cu(I)/Cu(II)-catalytic system. It is not moisture or air sensitive, and it is able to selectively oxidize primary alcohols, including aliphatic, allylic, benzylic and diols to their corresponding aldehydes. This catalyst was studied by ESI-MS, UV-vis and *in situ* IR to gain a deeper understanding of its mechanistic function during the oxidation reaction. Moreover, the results reported here highlight the novelty of the system, since the Cu(I)-dpa-catalyst works for the aerobic oxidation even in a water/MeCN mixture: aliphatic primary alcohols are oxidized in moderate yield, and π -activated alcohols in quantitative yield. The aerobic oxidation of aliphatic primary alcohols is unprecedented in aqueous mixtures.

CRedit authorship contribution statement

Emi Lagerspets: Conceptualization, Data curation, Investigation, Writing – original draft, Writing – review & editing. **Donatella Abba:** Investigation, Data curation. **Joseph Sharratt:** Investigation, Data curation. **Aleksi Eronen:** Investigation, Writing – review & editing. **Timo Repo:** Conceptualization, Supervision, Writing – review & editing,

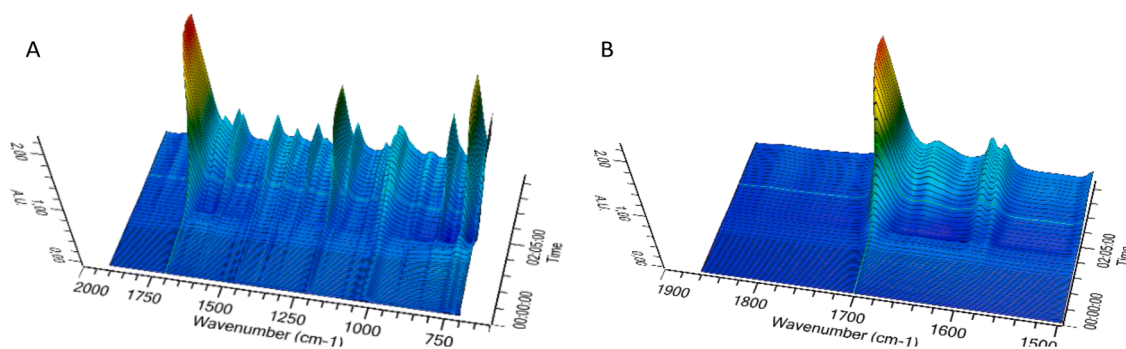
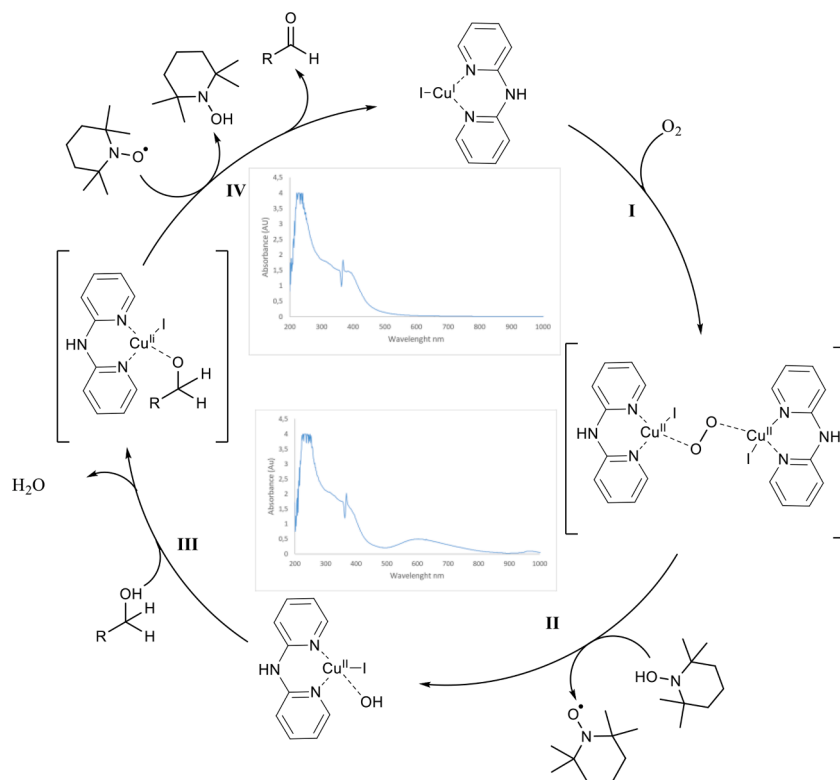


Fig. 1. *In situ* IR of the aerobic oxidation of benzyl alcohol in 3 h under open air and at RT with 4 mol% TEMPO, 2.5 mol% CuI, 2.5 mol% dba and 1 mmol alcohol. A) The whole spectra of the oxidation B) Zoom of the aldehyde-peak at 1705 cm⁻¹.



Scheme 2. The proposed reaction mechanism for the Cu(I)-catalyst. The Cu(I)-dpa is formed and stable in MeCN. In the presence of TEMPOH and air the reaction proceeds through a hypothetical Cu(II)-dpa-dimer (step I) and a Cu(II)-OH complex is formed (step II). With the added alcohol (step III), TEMPOH, aldehyde and the Cu(I)-compound are formed simultaneously (step IV).

Funding acquisition.

Declaration of Competing Interest

There are no conflicts to declare.

Acknowledgements

The financial support of this work was provided by the Academy of Finland 310767.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.mcat.2022.112167](https://doi.org/10.1016/j.mcat.2022.112167).

References

- [1] M. Hudlicky, *Oxidations in Organic Chemistry*, American Chemical Society, Washington DC, 1990.
- [2] S. Caron, R.W. Dugger, S.G. Ruggeri, J. a Ragan, D.H.B. Ripin, Large-scale oxidations in the pharmaceutical industry, *Chem. Rev.* 106 (2006) 2943–2989, <https://doi.org/10.1021/cr040679f>.
- [3] J.E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2004, <https://doi.org/10.1002/3527603689>.
- [4] D.J.C. Constable, P.J. Dunn, J.D. Hayler, G.R. Humphrey, J.L. Leazer Jr., R. J. Linderman, K. Lorenz, J. Manley, B.A. Pearlman, A. Wells, A. Zaks, T.Y. Zhang, Key green chemistry research areas—A perspective from pharmaceutical manufacturers, *Green Chem* 9 (2007) 411–420, <https://doi.org/10.1039/B703488C>.
- [5] G. Tojo, M.I. Fernandez, M. Fernández, *Oxidation of Primary Alcohols to Carboxylic Acids*, Springer New York, New York, NY, 2006, <https://doi.org/10.1007/0-387-35432-8>.
- [6] G. Tojo, M. F. M.I. Fernandez, *Oxidation of Alcohols to Aldehydes and Ketones*, Springer-Verlag, New York, 2006, <https://doi.org/10.1007/b135954>.
- [7] J.E. Steves, S.S. Stahl, Copper(I)/ABNO-catalyzed aerobic alcohol oxidation: alleviating steric and electronic constraints of Cu/TEMPO catalyst systems, *J. Am. Chem. Soc.* 135 (2013) 15742–15745, <https://doi.org/10.1021/ja409241h>.
- [8] J.E. Steves, S.S. Stahl, Copper-Catalyzed Aerobic Alcohol Oxidation, *Liq. Phase Aerob. Oxid. Catal. Ind. Appl. Acad. Perspect.* (2016) 85–96, <https://doi.org/10.1002/9783527690121.ch6>.
- [9] J.M. Hoover, B.L. Ryland, S.S. Stahl, Mechanism of copper(I)/TEMPO-catalyzed aerobic alcohol oxidation, *J. Am. Chem. Soc.* 135 (2013) 2357–2367, <https://doi.org/10.1021/ja3117203>.
- [10] I.E. Markó, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, Copper-catalyzed oxidation of alcohols to aldehydes and ketones: an efficient, aerobic alternative, *Science* 274 (1996) 2044–2046, <https://doi.org/10.1126/science.274.5295.2044>.
- [11] E.T.T. Kumpulainen, A.M.P. Koskinen, Catalytic activity dependency on catalyst components in aerobic copper-TEMPO oxidation, *Chem. A Eur. J.* 15 (2009) 10901–10911, <https://doi.org/10.1002/chem.200901245>.
- [12] T.F.S. Silva, L.M.D.R.S. Martins, Recent advances in copper catalyzed alcohol oxidation in homogeneous medium, *Molecules* 25 (2020) 1–15, <https://doi.org/10.3390/molecules25030748>.
- [13] Z. Luo, Y. Liu, C. Wang, D. Fang, J. Zhou, H. Hu, Application of the Cu(i)/TEMPO/O₂ catalytic system for aerobic oxidative dehydrogenative aromatization of pyrrolidines, *Green Chem* 21 (2019) 4609–4613, <https://doi.org/10.1039/c9gc01932d>.
- [14] M.F. Semmelhack, C.R. Schmid, D.A. Cortés, C.S. Chou, Oxidation of alcohols to aldehydes with oxygen and cupric ion, mediated by Nitrosonium ion, *J. Am. Chem. Soc.* 106 (1984) 3374–3376, <https://doi.org/10.1021/ja00323a064>.
- [15] C.L. Hill, Controlled green oxidation, *Nature* 401 (1999) 436–437, <https://doi.org/10.1038/46704>.
- [16] N.W. Lepp, *Copper. Effect of Heavy Metal Pollution on Plants. Pollution Monitoring Series*, Springer, Dordrecht, 1981, pp. 111–143, https://doi.org/10.1007/978-94-011-7339-1_4.
- [17] S.E. Kesler, B.H. Wilkinson, Earth's copper resources estimated from tectonic diffusion of porphyry copper deposits, *Geology* 36 (2008) 255–258, <https://doi.org/10.1130/G24317A.1>.
- [18] A.K. Dhara, K. Kumar, S. Kumari, U.P. Singh, K. Ghosh, Aerobic oxidation of alcohol by model complexes relevant to metal site galactose oxidase: role of copper (I) intermediate, evidence for the generation of end-on copper(II)-OOH species and catalytic promiscuity for oxidation of benzyl alcohol, catechol and, *Transit. Met. Chem.* 45 (2020) 159–172, <https://doi.org/10.1007/s11243-019-00367-7>.
- [19] R.A. Festa, D.J. Thiele, Copper: an essential metal in biology, *Curr. Biol.* 21 (2011) R877–R883, <https://doi.org/10.1016/j.cub.2011.09.040>.
- [20] R.R. Conry, *Copper: Inorganic & Coordination Chemistry Based in Part On the Article Copper: Inorganic & Coordination Chemistry by Rebecca R. Conry & Kenneth D. Karlin which Appeared in the Encyclopedia of Inorganic Chemistry, 1st Edition, John Wiley & Sons, Ltd, Chichester, UK, 2006*, <https://doi.org/10.1002/0470862106.ia052>. *Encycl. Inorg. Chem.*

- [21] M.M. Whittaker, J.W. Whittaker, The active site of galactose oxidase, *J. Biol. Chem.* 263 (1988) 6074–6080, [https://doi.org/10.1016/S0021-9258\(18\)68751-4](https://doi.org/10.1016/S0021-9258(18)68751-4).
- [22] A. Bhagi-Damodaran, M.A. Michael, Q. Zhu, J. Reed, B.A. Sandoval, E.N. Mirts, S. Chakraborty, P. Moënne-Loccoz, Y. Zhang, Y. Lu, Why copper is preferred over iron for oxygen activation and reduction in haem-copper oxidases, *Nat. Chem.* 9 (2017) 257–263, <https://doi.org/10.1038/nchem.2643>.
- [23] W. Czepa, M.A. Fik, S. Witomska, M. Kubicki, G. Consiglio, P. Pawluć, V. Patroniak, Simple Schiff-Base Cu(II) complexes as efficient catalysts for benzyl alcohol oxidation, *ChemistrySelect.* 3 (2018) 9504–9509, <https://doi.org/10.1002/slct.201801550>.
- [24] J.M. Hoover, S.S. Stahl, Highly Practical Copper (I)/ TEMPO catalyst system for chemoselective aerobic oxidation of primary alcohols, *J. Am. Chem. Soc.* 133 (2011) 16901–16910, <https://doi.org/10.1021/ja206230h>.
- [25] J.M. Hoover, J.E. Steves, S.S. Stahl, Copper(I)/TEMPO-catalyzed aerobic oxidation of primary alcohols to aldehydes with ambient air, *Nat. Protoc.* 7 (2012) 1161–1166, <https://doi.org/10.1038/nprot.2012.057>.
- [26] E. Lagerspets, E. Valbonetti, A. Eronen, T. Repo, A new catalytic approach for aerobic oxidation of primary alcohols based on a Copper(I)-thiophene carbaldimines, *Mol. Catal.* 509 (2021), 111637, <https://doi.org/10.1016/j.mcat.2021.111637>.
- [27] Q. Mei, H. Liu, Y. Yang, H. Liu, S. Li, P. Zhang, B. Han, Base-free aerobic oxidation of alcohols over copper-based complex under ambient condition, *ACS Sustain. Chem. Eng.* 6 (2018) 2362–2369, <https://doi.org/10.1021/acssuschemeng.7b03820>.
- [28] R.A. Sheldon, Recent advances in green catalytic oxidations of alcohols in aqueous media, *Catal. Today.* 247 (2015) 4–13, <https://doi.org/10.1016/j.cattod.2014.08.024>.
- [29] L. Marais, A.J. Swarts, Biomimetic Cu/Nitroxyl catalyst systems for selective alcohol oxidation, *Catalysts.* 9 (2019) 395, <https://doi.org/10.3390/catal9050395>.
- [30] E. Lagerspets, K. Lagerblom, E. Heliövaara, O.-M.M. Hiltunen, K. Moslova, M. Nieger, T. Repo, Schiff base Cu(I) catalyst for aerobic oxidation of primary alcohols, *Mol. Catal.* 468 (2019) 75–79, <https://doi.org/10.1016/j.mcat.2019.02.003>.
- [31] J.M. Hoover, B.L. Ryland, S.S. Stahl, Copper/TEMPO-catalyzed aerobic alcohol oxidation: mechanistic assessment of different catalyst systems, *ACS Catal.* 3 (2013) 2599–2605, <https://doi.org/10.1021/cs400689a>.
- [32] J.U. Ahmad, P.J. Figiel, M.T. Räisänen, M. Leskelä, T. Repo, Aerobic oxidation of benzylic alcohols with bis(3,5-di-tert-butylsalicylaldehyde)copper(II) complexes, *Appl. Catal. A Gen.* 371 (2009) 17–21, <https://doi.org/10.1016/j.apcata.2009.09.011>.
- [33] P.J. Figiel, A. Sibaoiuh, J.U. Ahmad, M. Nieger, M.T. Räisänen, M. Leskelä, T. Repo, Aerobic oxidation of benzylic alcohols in water by 2,2,6,6-tetramethylpiperidine-1-oxyl(TEMPO)/Copper(II) 2-N-Arylpyrrolocarbaldimino complexes, *Adv. Synth. Catal.* 351 (2009) 2625–2632, <https://doi.org/10.1002/adsc.200900478>.
- [34] P.J. Figiel, M. Leskelä, T. Repo, TEMPO-copper(II) diimine-catalysed oxidation of benzylic alcohols in aqueous media, *Adv. Synth. Catal.* 349 (2007) 1173–1179, <https://doi.org/10.1002/adsc.200600505>.
- [35] P. Gamez, I.W.C.E. Arends, J. Reedijk, R.A. Sheldon, Copper(II)-catalysed aerobic oxidation of primary alcohols to aldehydes, *Chem. Commun.* (2003) 2414–2415, <https://doi.org/10.1039/b305941c.13>.
- [36] W. Liu, J. Yang, J. Cai, Aerobic alcohol oxidation catalyzed by CuO-rectorite/TEMPO in water, *Res. Chem. Intermed.* 45 (2019) 549–561, <https://doi.org/10.1007/s11164-018-3618-3>.
- [37] H. Ünver, I. Kani, Homogeneous oxidation of alcohol and alkene with copper (II) complex in water, *J. Chem. Sci.* (2018) 130, <https://doi.org/10.1007/s12039-018-1439-y>.
- [38] C. Chen, B. Liu, W. Chen, Copper/imidazolium/TEMPO-catalyzed aerobic oxidation of benzylic alcohols in water, *Synthesis* 45 (2013) 3387–3391, <https://doi.org/10.1055/s-0033-1339929>.
- [39] S. Striegler, Aerobic oxidation of primary alcohols under mild aqueous conditions promoted by a dinuclear copper(II) complex, *Tetrahedron* 62 (2006) 9109–9114, <https://doi.org/10.1016/j.tet.2006.07.025>.
- [40] G. Zhang, X. Han, Y. Luan, Y. Wang, X. Wen, L. Xu, C. Ding, J. Gao, Copper-catalyzed aerobic alcohol oxidation under air in neat water by using a water-soluble ligand, *RSC Adv* 3 (2013) 19255, <https://doi.org/10.1039/c3ra43366h>.
- [41] R.H. Crabtree, The organometallic chemistry of the transition metals, 2005. 10.1002/0471718769.
- [42] G.B. Kauffman, L.Y. Fang, N. Viswanathan, G. Townsend, Purification of Copper (I) Iodide, *Inorg. Synth.* 22 (2006) 101–103, <https://doi.org/10.1002/9780470132531.ch20>.
- [43] T.J. Hurley, M.A. Robinson, Nickel(II)-2,2'-Bipyridylamine System. I. Synthesis and stereochemistry of the complexes, *Inorg. Chem.* 7 (1968) 33–38, <https://doi.org/10.1021/ic50059a007>.
- [44] J. Rogan, D. Poleti, L. Karanović, G. Bogdanović, A. Spasojević-de Biré, D. M. Petrović, Mixed ligand Co(II), Ni(II) and Cu(II) complexes containing terephthalato ligands. Crystal structures of diaqua(2,2'-dipyridylamine) (terephthalato)metal(II) trihydrates (metal=cobalt or nickel), *Polyhedron.* 19 (2000) 1415–1421, [https://doi.org/10.1016/S0277-5387\(00\)00435-6](https://doi.org/10.1016/S0277-5387(00)00435-6).
- [45] D.W. Brogden, J.F. Berry, Coordination chemistry of 2,2'-Dipyridylamine: the gift that keeps on giving, *Comments Inorg. Chem.* 36 (2016) 17–37, <https://doi.org/10.1080/02603594.2015.1079522>.
- [46] N.M. Shavaleev, A. Barbieri, Z.R. Bell, M.D. Ward, F. Barigelletti, New ligands in the 2,2'-dipyridylamine series and their Re(I) complexes; synthesis, structures and luminescence properties, *New J. Chem.* 28 (2004) 398–405, <https://doi.org/10.1039/B312647A>.
- [47] X. Xie, S.S. Stahl, Efficient and selective Cu/Nitroxyl-catalyzed methods for aerobic oxidative lactonization of diols, *J. Am. Chem. Soc.* 137 (2015) 3767–3770, <https://doi.org/10.1021/jacs.5b01036>.