

This item is the archived peer-reviewed author-version of:

Cooperative electrocatalytic and chemoselective alcohol oxidation by Shvo's catalyst

Reference:

Lybaert Jeroen, Trashin Stanislav, Maes Bert, De Wael Karolien, Abbaspour Tehrani Kourosch.- Cooperative electrocatalytic and chemoselective alcohol oxidation by Shvo's catalyst
Advanced synthesis and catalysis - ISSN 1615-4150 - 359:6(2017), p. 919-925
Full text (Publisher's DOI): <http://dx.doi.org/doi:10.1002/ADSC.201600783>
To cite this reference: <http://hdl.handle.net/10067/1397950151162165141>

Cooperative electrocatalytic and chemoselective alcohol oxidation by Shvo's catalyst

Jeroen Lybaert,^{a,b} Stanislav Trashin,^b Bert U. W. Maes,^a Karolien De Wael^{b*} and Kourosh Abbaspour Tehrani^{a*}

^a Organic Synthesis, Department of Chemistry
University of Antwerp

Groenenborgerlaan 171, 2020 Antwerp (Belgium)

E-mail: kourosch.abbaspourtehrani@uantwerpen.be Phone: +3232653226; Fax: +3232653233

^b AXES, Department of Chemistry
University of Antwerp

Groenenborgerlaan 171, 2020 Antwerp (Belgium)

E-mail: karolien.dewael@uantwerpen.be Phone: +3232653335; Fax: +3232653233

Received: ((will be filled in by the editorial staff))



Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201#####>. ((Please delete if not appropriate))

Abstract: A new electrocatalytic conversion of alcohols to ketones and aldehydes was developed based on an electrochemical study of the Shvo's complex. The oxidation of secondary alcohols was efficiently performed under mild conditions using a catalytic amount of the Shvo's catalyst, in combination with a sub-stoichiometric amounts of 2,6-dimethoxy-1,4-benzoquinone in *N,N*-dimethylformamide at 80 °C. The hydroquinone thus formed is continuously reoxidized with the aid of an electrochemical device. Excellent yields for different ketones, aromatic as well as aliphatic and α,β -unsaturated ketones, are obtained. In addition, chemoselectivity towards oxidation of the secondary alcohol is achieved when converting vicinal diols such as 1,2-octanediol and 1,2-decanediol.

Keywords: Alcohols; Oxidation; Green chemistry; Ruthenium complex; Quinones

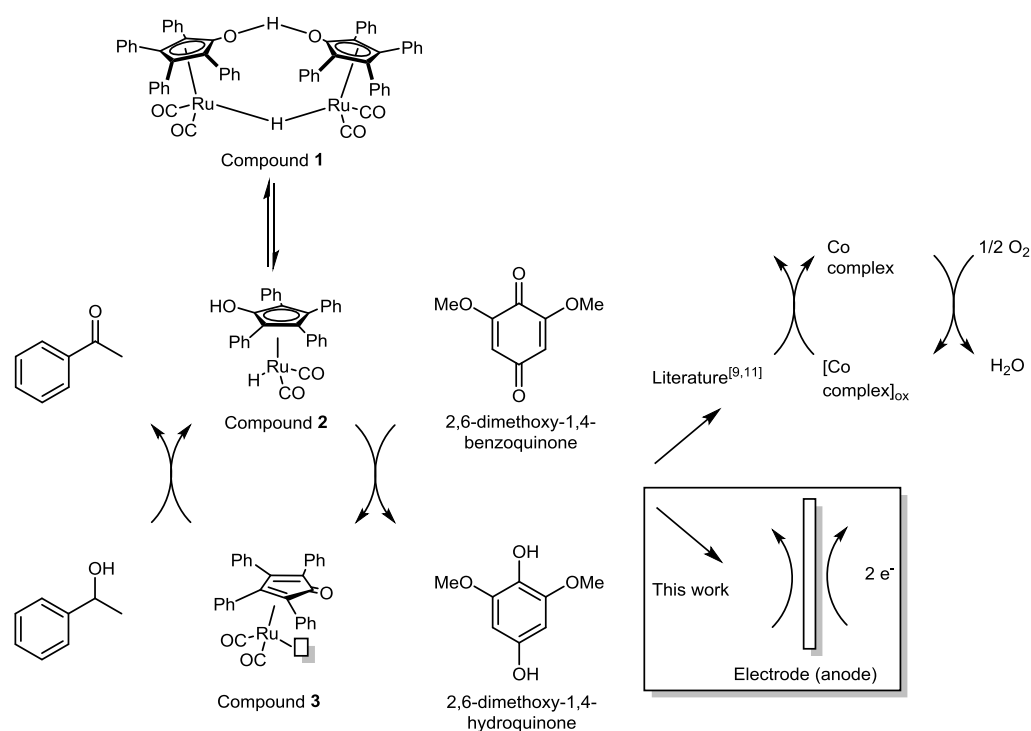
The Shvo complex (Scheme 1, compound 1) is a versatile ruthenium catalyst used in organic synthesis. The discovery in the middle eighties of its unique stable dimer structure by Shvo and coworkers^[1] was the beginning of a search to the borders of his applicability and the exact mechanism of the reactions in which the catalyst is involved. Because of the dimer structure, it has the possibility to dissociate in two different monomer forms, one (compound 2) can be used for reduction reactions while the other (compound 3) for oxidation reactions. They can convert into each other by the loss or addition of hydrogen gas. The dissociation is the key to the broad applicability of the complex^[2], for example it can be used for the oxidation of alcohols to ketones^[3], the oxidation of amines into imines^[4],

the alkylation of amines with amines^[5], the hydrogenation of ketones and alkenes^[6]. In combination with lipases Shvo's catalyst has been used for the dynamic kinetic resolution of secondary alcohols^[7].

Nowadays the interest of making efficient reactions more environmentally friendly is of unremitting importance. In the framework of alcohol oxidation reactions the use of molecular oxygen as the final hydrogen acceptor is the natural solution and low-cost alternative for toxic chemicals or catalyst materials.^[8] In combination with the Shvo's complex, an aerobic oxidation of secondary alcohols has been observed by Bäckvall and coworkers.^[9] More specific, a biomimetic coupled catalytic system, in which the alcohol is oxidized by the Shvo's complex was employed. The reduced Shvo's complex in his turn gets oxidized by benzoquinone, followed by an oxidation of the in situ formed hydroquinone via a cobalt-salen complex. Finally, this cobalt complex is oxidized by oxygen (Scheme 1).^[9] Similarly the oxidation of amines to imines is possible using the same catalyst system.^[4] In a later stage, the complexity of the system could be reduced by linking the hydroquinone and the cobalt complex in one compound resulting in high yields of ketones.^[10] Despite the green properties of molecular oxygen as an oxidant, it has some drawbacks, the solubility is low in organic solvents and there is always a risk in mixing extra oxygen with hot organic solvents, especially in the context of upscaling. The limiting oxygen concentration (determining the flammability) of organic solvents is rather low and therefore in industry it involves strict safety rules when performing reactions in organic solvents under oxygen atmosphere. The chance of ignition is

avoided at all time by operating well below the limiting oxygen concentration. For example it has

been shown that the



Scheme 1. Possible pathways for alcohol oxidation via Shvo's catalyst.

limiting oxygen concentration is below 10% (vol. percent) for toluene at 100 °C at normal pressure.^[11] This is more or less half the concentration of oxygen present in ambient air. To overcome the drawback of using oxygen as a stoichiometric oxidant, an interesting alternative is the use of electrochemistry for the conversion of alcohols to ketones or aldehydes.^[12] So far, no literature is available on the combination of Shvo's complex and electrocatalysis. In an electrocatalytic oxidation reaction, a mediator will be oxidized at the surface of the electrode at a low potential followed by the oxidation of the target molecule.^[13] Ruthenium oxides can be used as a mediator. For example RuO₂ can be directly oxidized at the electrode surface to a Ru⁷⁺ species in an alkaline acetonitrile/water mixture, followed by the Ru⁷⁺ promoted oxidation of alcohols.^[14] Alternatively, the popular perruthenate anion^[15] or TEMPO^[16] can be used as mediators for the oxidation of alcohols. Another possible mediator is benzoquinone, together with palladium acetate as a catalyst, it can be used for a Heck-type reaction between an arene and an alkene in acetic acid^[17], for an electro-oxidative homocoupling between arylboronic acids or arylboronates^[18] and for the oxidation of alcohols^[19]. Aldehydes and ketones could be obtained in moderate yields using this method. Drawbacks are the necessity to add equivalent amounts of base and eventual catalyst decomposition because of redox active intermediates at the potentials necessary to oxidize the hydroquinone.

Inspired by all these approaches, a combination of the Shvo's complex and the electrochemical oxidation of hydroquinone is examined and proposed as a new environmentally friendly method for high yield conversion of secondary alcohols into ketones. With this method the applicability of quinones as mediators for the regeneration of the redox catalyst in organic-electrochemical synthesis of ketones will be extended. Also the chemoselectivity of the method is addressed, especially for diols. The selective oxidation of vicinal diols directly to α -hydroxy ketones is of utmost importance in the development of atom-economical reactions.^[20] The chemoselective oxidation of diols is for example possible with a cationic palladium catalyst in combination with air^[21] or RuCl₃ as a catalyst in combination with buffered oxone^[22]. Interesting is also the electrocatalytic method where a carbon supported platinum electrode is modified with bismuth to get a direct selective oxidation of glycerol at the electrode surface.^[23] Also the use of TEMPO as a mediator is reported for the selective oxidation of glycerol but only in 25% yield.^[24] Only very recently, Pd-supported nanoparticles have been applied as catalysts for a non-selective glycerol electro-oxidation in an aqueous NaOH solution.^[25] A selective electrochemical oxidation of diols under mild conditions and in high yield is now presented.

The critical reaction at the anode surface (Scheme 1) is the oxidation of hydroquinone to 1,4-benzoquinone. In the cathodic compartment acetic

acid is added in order to reduce the protons to H_2 at the platinum electrode. To avoid pressure build-up by the hydrogen gas the cathodic part of the divided cell is left open under atmospheric pressure. For an optimization of the HOAc amount see the SI. Since 2,6-dimethoxy-1,4-benzoquinone was one of the most active benzoquinones for the oxidation of the Shvo complex^[9], this compound was selected as a mediator for the following reactions. Another advantage is the lower oxidation potential of 2,6-dimethoxyhydroquinone compared to hydroquinone. The electrochemical behavior of 2,6-dimethoxyhydroquinone was screened in different solvents in order to identify the most stable redox process at the lowest oxidation potential (Table 1). Dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) gave the best results, the oxidation in these solvents occurs at a potential of ca. 0.55 V (Table 1, Entry 1 and 2). It is known that the basicity of these two solvents is able to lower the oxidation potential of hydroquinones.^[26]

Table 1. Oxidation peak potential of 2,6-dimethoxyhydroquinone in different solvents.^[a]

Entry	Solvent	Oxidation peak potential (V) ^[b]
1	<i>N,N</i> -Dimethylformamide	0.6
2	Dimethyl sulfoxide	0.5
3	Sulfolane	1.0
4	1,1,1,3,3,3-Hexafluoro-2-propanol	1.2
5	2-Methyltetrahydrofuran (2-MeTHF)	1.1
6	Dimethyl carbonate	1.0
7	<i>n</i> -Butyl acetate	> 1.4
8	Acetonitrile	0.8
9	Propionitrile	0.9

^[a] In an 0.1 M Bu_4NBF_4 solution at 20 °C with glassy carbon (GC) working electrode.

^[b] Versus an Ag/AgCl reference electrode

Aiming at the use of the Shvo's complex in an electrochemical synthesis procedure, the redox behavior of the complex has been further investigated using cyclic voltammetry. The Shvo's complex was examined in a DMF solution at a glassy carbon (GC) working electrode in the presence of 0.1 M of Bu_4NBF_4 as supporting electrolyte. Figure 1 represents the redox behavior of the Shvo catalyst at room temperature, no oxidation or reduction process is observed in a potential window from -0.4 V until 1 V (Figure 1, black curve). Higher potentials are avoided because the oxidation of the solvent may interfere with the catalytic cycle. At lower potentials starting around -0.7 V, different reduction processes of the catalyst, explained as redox chemistry of the ligand, can be detected (see supporting information) so these potentials are avoided. The temperature of the Shvo catalyst solution was raised to 80 °C as a higher temperature is typically required for the

reaction between the Shvo catalyst and the alcohol^[27]. The higher temperature did not affect the current-potential behavior of the complex. In a next step an excess of 1-phenylethanol was added, allowing the Shvo catalyst to react with the alcohol turning the Shvo catalyst into its reduced form. However, no change in the current-potential behavior is observed (Figure 1, blue curve), since no direct oxidation of the reduced form of the Shvo catalyst is possible in this potential range. Additionally, the alcohol cannot be oxidized in this potential window, as much higher overpotentials are needed.^[28] It is clear that there is a need for a mediator such as a benzoquinone to facilitate the electrochemical regeneration of the Shvo catalyst.

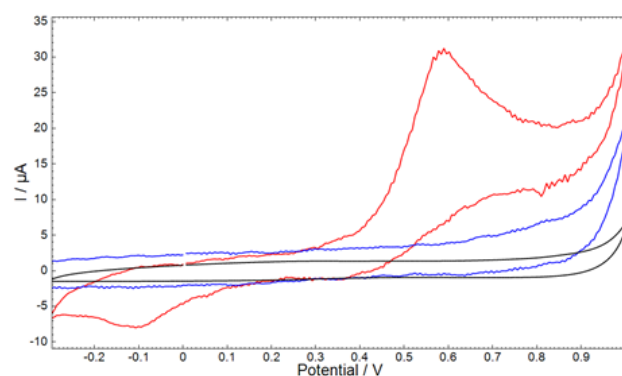


Figure 1. Cyclic voltammograms of 0.75 mM Shvo catalyst in an 0.1 M Bu_4NBF_4 DMF solution at 20 °C with a scan rate of 0.1 V/s (Black curve); at 80 °C with addition of 33 mM 1-phenylethanol (Blue curve); with addition of 1.1 mM 2,6-dimethoxybenzoquinone (Red curve).

When 2,6-dimethoxybenzoquinone is added to a solution containing alcohol and Shvo catalyst, an oxidation process at ca. 0.6 V appears, i.e. the oxidation peak of 2,6-dimethoxyhydroquinone to 2,6-dimethoxybenzoquinone. The formation of 2,6-dimethoxyhydroquinone observed by the oxidation peak in Figure 1 (red curve) is a strong indication for the Shvo's catalyst mediated oxidation of 1-phenylethanol. Even more, this catalytic cycle can now be implemented in an electrochemical setup for electrosynthesis conversion. In brief, the oxidation of the alcohol by the Shvo catalyst generates the hydrogenated form of the Shvo catalyst, which is oxidized by the 2,6-dimethoxybenzoquinone forming the 2,6-dimethoxyhydroquinone which in its turn is oxidized at the electrode surface at a potential of 0.6 V. This potential corresponds to the oxidation peak potential of the 2,6-dimethoxyhydroquinone in DMF, as confirmed in Table 1. A control experiment was performed leaving the Shvo catalyst out of the catalytic cycle, no oxidation processes were detected in the range of -0.4 V until 1.0 V (similar as Figure 1, blue curve). Since no 2,6-dimethoxyhydroquinone is formed, this excludes the mechanism where a direct

oxidation of the alcohol by the 2,6-dimethoxybenzoquinone occurs.

Encouraged by the results of the cyclic voltammetry study, electrolysis experiments were performed. An airtight homemade electrolysis cell was used with a working electrode with high surface area. Using this setup, the electrolysis was tested for the oxidation of the model alcohol 1-phenylethanol to acetophenone. Different catalyst loadings were tested and the addition of 5 mol% of Shvo catalyst and 25 mol% of 2,6-dimethoxybenzoquinone followed by a constant potential of 0.7 V for 6 hours at 80 °C is sufficient to give a yield of 82% of acetophenone (Figure 2). When using 1 mol% of Shvo catalyst in combination with 10 mol% of 2,6-dimethoxybenzoquinone the yield of the ketone dropped drastically to 25% (for further optimization see the Supporting Information). In the literature^[2] Shvo catalyst promoted oxidations require loadings of 1%, which is rather low compared to the optimal catalyst loading of 5 mol% (10 mol% Ru) in the present study. Most Ru-catalyzed dehydrogenations take place in aromatic solvents at high temperatures, but in order to ensure the solubility of the electrolyte (Bu_4NBF_4) in the electrocatalytic oxidation DMF was used as the solvent. The higher catalyst loading may therefore be explained by a faster degradation of the Shvo complex in DMF. A qualitative rationalisation of this was made by means of IR spectroscopy of a solution of Shvo catalyst in 2-MeTHF. By adding DMF after 3.5 hours to this stable 2-MeTHF solution the characteristic peaks for compound **2**^[6] at 2036 cm^{-1} , 2005 cm^{-1} and 1976 cm^{-1} decreased.

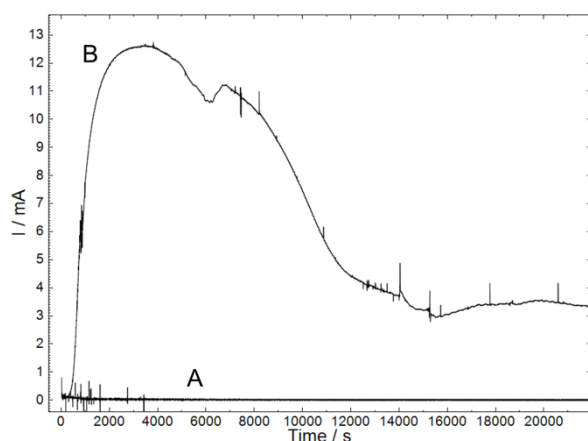
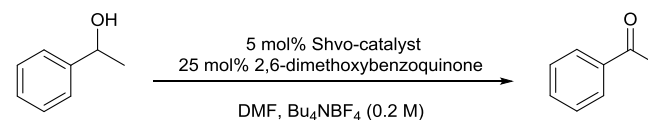


Figure 2. Current in function of time for electrolysis of 1-phenylethanol (0.7 mmol) in 0.2 M Bu_4NBF_4 DMF solution at 80 °C at a constant potential of 0.7 V (A); with Shvo catalyst (0.035 mmol) and 2,6-dimethoxybenzoquinone (0.175 mmol) (B).

After 6 hours of electrolysis, the current dropped steadily and hence also the efficiency of the electrolysis. By further electrolysis to a total reaction time of 24 hours (Table 2, entry 6) only a small increase of the yield to 88% was observed. This can

be partially explained by electro-osmotic phenomena, a small part of the solution migrated during electrolysis through the frit into the compartment of the cathode, and so a small part of the alcohol becomes unavailable together with a small loss of catalyst.

Table 2. Oxidation of 1-phenylethanol with electrochemical regeneration of the Shvo catalyst via 2,6-dimethoxybenzoquinone.



Entry ^[a]	Potential [V]	Time [h]	Yield [%] ^[b]	Recovered alcohol [%] ^[b]
1	0.7	0.5	30	65
2	0.7	1.5	56	38
3	0.7	4	72	21
4	0.7	6	82	11
5	0.7	7	84	10
6	0.7	24	88	5
7	No	7	25	61
8 ^[c]	0.7	16	0	94
9	0.8	7	78	9
10 ^[d]	0.7	7	81	7
11 ^[e]	0.7	7	70	16

^[a] Reaction conditions: 0.7 mmol 1-phenylethanol with 0.05 equivalents of Shvo complex and 0.25 equivalents of 2,6-dimethoxybenzoquinone in 14 mL DMF with 0.2 M Bu_4NBF_4 at 80 °C with constant potential.

^[b] NMR yields calculated after extraction with the addition of 1,3,5-trimethoxybenzene as an internal standard.

^[c] Without Shvo catalyst and 2,6-dimethoxybenzoquinone.

^[d] At 100 °C.

^[e] No acetic acid added to the cathodic compartment.

Control electrolysis experiments were performed in order to confirm the proposed oxidation mechanism (Scheme 1). When the electrolysis of 1-phenylethanol was performed without the Shvo catalyst, no current increase was observed and no oxidation of the alcohol could be detected (Table 2, entry 8). In case no potential was applied, only the stoichiometric oxidation of the alcohol could be detected (Table 2, entry 7), giving an expected yield of acetophenone of 25%. An electrolysis experiment with a constant potential of 0.8 V was performed but no change of the yield could be observed (Table 2, entry 9). Also the influence of the temperature was examined by performing an experiment at 100 °C, again no significant influence on the yield was observed (Table 2, entry 10). When acetic acid in the cathodic part was omitted the yield dropped from 82% to 70% (Table 2, entries 4 and 11).

In Figure 3 the progress of the oxidation of 1-phenylethanol has been plotted in function of the charge passed during the electrolysis (Figure 3). This

makes clear that after adding 135 Coulombs of charge (approximately 7 h of electrolysis) the effectiveness of the catalytic cycle drops. Extending the time of electrolysis does not much improve the yield of the reaction.

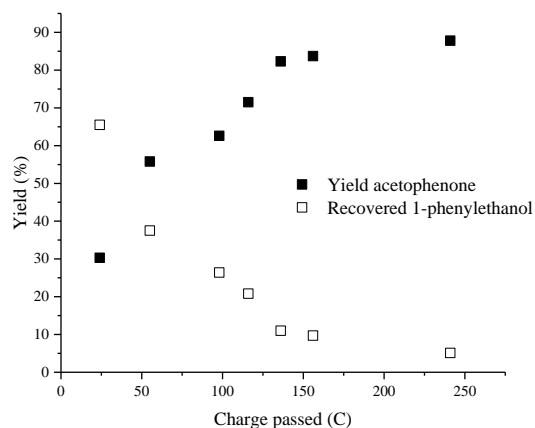


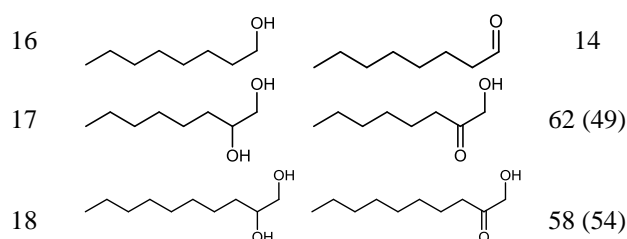
Figure 3. Yield of acetophenone in function of total charge passed during electrolysis; Reaction conditions: 0.7 mmol 1-phenylethanol with 0.035 mmol of Shvo complex and 0.175 mmol of 2,6-dimethoxybenzoquinone in 14 mL DMF with 0.2 M Bu_4NBF_4 at 80 °C with a constant potential of 0.7 V. Yields are the average of two runs.

To study the substrate scope a variety of alcohols were electrolysed during 5 h at 0.7 V. Various secondary alcohols were oxidized to ketones with a sufficient yield. A range of substituted 1-phenylethanols gave good yields for methyl (Table 3, entry 2) and methoxy (Table 3, entries 3 and 4) derivatives. A more challenging oxidation was found with an electron withdrawing group at the para position, for example *para*-chloro and *para*-nitro (Table 3, entries 5 and 6) derivatives only gave moderate yields. The oxidation of allylic alcohols, 3-octene-2-ol and 1-cyclohexyl-2-buten-1-ol (Table 3, entries 9 and 10), also furnished the corresponding ketone in good yields. During this process the stereochemistry of the alkene was conserved. Further, no ruthenium catalyzed isomerization of the allylic alcohols to the saturated ketone was observed under these conditions.^[29,30] Most likely, the reason for this selectivity is the fact that the present system runs without any additional base.^[29] Also more resistant aliphatic secondary alcohols were investigated and good yields of ketones were obtained for 2-nonanol, dicyclohexylmethanol and 4-*tert*-butylcyclohexanol (Table 3, entries 10, 11 and 12). The more sterically demanding neomenthol and L-menthol (Table 3, entries 13 and 14) were tested and a difference in reactivity was observed. The lower yield of the L-menthol oxidation is explained by the steric hindrance of the alcohol group. In L-menthol the alcohol function and the isopropyl group are both in an equatorial position (entry 14) whereas the alcohol

group of neomenthol is in an axial position making it more easily accessible for the catalyst (entry 13).

Table 3. Oxidation of different alcohols.^[a]

Entry	Substrate	Product	Yield [%] ^[b]
1			82 (75)
2			88 (77)
3			88 (81)
4			85 (83)
5			73 (71)
6			39
7			84 (72)
8			86 (79)
9			82 (74)
10			83 (78)
11			83 (76)
12			83 (77)
13			82 (76)
14			24
15			52



^[a] Reaction conditions: 0.7 mmol alcohol with 0.05 equivalents of Shvo complex and 0.25 equivalents of 2,6-dimethoxybenzoquinone in 14 mL DMF with 0.2 M Bu₄NBF₄ at 80 °C with constant potential of 0.7 V for 5 hours.

^[b] NMR yields were calculated after extraction with the addition of 1,3,5-trimethoxybenzene as an internal standard. Between brackets, the yields after column chromatography are given.

After the successful oxidation of secondary alcohols, the same method was applied for primary alcohols. For benzyl alcohol (Table 3, entry 13) a moderate yield of 52% of the aldehyde was obtained. For 1-octanol (Table 3, entry 14) the current obtained during electrolysis was lower than with the previous oxidations and after work up it was clear that the yield of the aldehyde was much lower in comparison with the yield obtained for ketones. However, as no competing overoxidation of the aldehyde to the corresponding carboxylic acid was observed. This result prompted us to investigate the oxidation of diols to see if a chemoselective oxidation of the secondary alcohol could take place. For the oxidation of 1,2-octanediol (Table 3, entry 15) the standard procedure resulted in a moderate yield of 62% of the expected α -hydroxy ketone, proving that a chemoselective oxidation occurs. The starting diol is also recovered and no double oxidation of both alcohol functions was observed. The same method was performed with another vicinal diol, 1,2-decanediol (Table 3, entry 16). A similar yield for the formation of 1-hydroxy-2-decanone was obtained, proving a successful selective oxidation.

In conclusion, we have performed an in depth electrochemical study of the Shvo's complex and established a methodology for the cooperative electrocatalytic alcohol oxidation to ketones via the use of the Shvo catalyst in combination with a benzoquinone. In this way a new sustainable method is developed for the oxidation of secondary alcohols to ketones. Good to excellent yields for different ketones, aromatic as well as aliphatic, could be obtained. In addition, a chemoselective oxidation of vicinal diols such as 1,2-octanediol and 1,2-decanediol to α -hydroxy ketones was established.

Experimental Section

All electrochemical measurements were performed by using a Potentiostat/Galvanostat PGSTAT 30 from Metrohm, connected with a PC provided with NOVA 1.10 software. Cyclic voltammetry measurements were performed using a three-electrode cell with a glassy carbon working electrode of 3 mm diameter (Metrohm, the Netherlands), a platinum sheet counter electrode and a bridged Ag/AgCl reference electrode with 2 M LiCl ethanol solution as inner solution and a 0.1 M Bu₄NBF₄ DMF as bridge solution, all potentials mentioned are relative to this reference electrode which has a voltage difference of +150 mV versus a standard hydrogen electrode (SHE). The working electrode was pretreated by mechanical polishing. It was subjected to sequential polishing with a cloth covered with alumina powder of 1 and 0.05 μ m particle size (SPI supplies, USA) for 10 min. To remove any adherent Al₂O₃ particles, the electrode surface was rinsed thoroughly with deionized water and cleaned in an ultrasonic bath containing deionized water for 2 min. Next, the electrode was rinsed with acetone and dried. Solutions of 0.1 M Bu₄NBF₄ in DMF were freshly made and purged with nitrogen gas for 10 minutes to remove oxygen before each measurement. Products are added through a septum. For measurements at 80 °C the electrochemical cell was placed in an oil bath.

Electrolysis experiments: A homemade airtight electrolysis cell was used equipped with a reticulated vitreous carbon (RVC) as working electrode (basi, USA), a bridged Ag/AgCl reference electrode with 2 M LiCl ethanol solution as inner solution and a 0.1 M Bu₄NBF₄/DMF as bridge solution was used and the counter electrode, a platinum rod electrode, was put in a divided cell separated from the anodic part by a ceramic frit. In a typical electrolysis experiment 4 mL of a 0.2 M Bu₄NBF₄ DMF solution was added to the divided part followed by the addition of 200 μ L of acetic acid. In the anodic part Shvo complex (0.05 equivalent, 38 mg) and 2,6-dimethoxybenzoquinone (0.25 equivalent, 29 mg) was added to a 0.2 M solution of Bu₄NBF₄ in DMF (14 mL). The cell was closed and placed under an Ar atmosphere. Stirring was started and the cell was placed in an oil bath for heating, next a potential of 0.7 V was applied and finally the alcohol (0.7 mmol) was added. After the appropriate reaction time the reaction mixture was cooled down and water (30 mL) was added. The resulting mixture was extracted with *tert*-butyl methyl ether (3 times 25 mL). The collected organic layer was washed with 0.2 M HCl (15 mL) to further remove DMF. Next the organic layer was dried with MgSO₄ filtered and evaporated. The resulting solution was examined with NMR. Isolated products were obtained using column chromatography on silica gel with heptane/ethyl acetate (95/5) as eluent.

Acknowledgements

This work was financially supported by the University of Antwerp (BOF), the Research Foundation - Flanders (FWO) and the Hercules Foundation.

References

- [1] Y. Shvo, D. Czarkie, Y. Rahamim, D. F. Chodosh, *J. Am. Chem. Soc.* **1986**, *108*, 7400-7402.
- [2] B. L. Conley, M. K. Pennington-Boggio, E. Boz, T. J. Williams, *Chem. Rev.* **2010**, *110*, 2294-2312.
- [3] M. L. S. Almeida, M. Beller, G.-Z. Wang, J.-E. Bäckvall, *Chem.-Eur. J.* **1996**, *2*, 1533-1536.
- [4] J. S. M. Samec, A. H. Éll, J.-E. Bäckvall, *Chem.-Eur. J.* **2005**, *11*, 2327-2334.
- [5] S. Bähn, D. Hollmann, A. Tillack, M. Beller, *Adv. Synth. Catal.* **2008**, *350*, 2099-2103.

- [6] C. P. Casey, S. E. Beetner, J. B. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 2285-2295.
- [7] B. A. Persson, A. L. E. Larsson, M. Le Ray, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1999**, *121*, 1645-1650.
- [8] J. Piera, J.-E. Bäckvall, *Angew. Chem. Int. Ed.* **2008**, *47*, 3506-3523.
- [9] G. Csajnyik, A. H. Éll, L. Fadini, B. Pugin, J.-E. Bäckvall, *J. Org. Chem.* **2002**, *67*, 1657-1662.
- [10] E. V. Johnston, E. A. Karlsson, L. Tran, B. Åkermark, J.-E. Bäckvall, *Eur. J. Org. Chem.* **2010**, 1971-1976.
- [11] P. M. Osterberg, J. K. Niemeier, C. J. Welch, J. M. Hawkins, J. R. Martinelli, T. E. Johnson, T. W. Root, S. S. Stahl, *Org. Process Res. Dev.* **2015**, *19*, 1537-1543.
- [12] H. J. Schäfer, *C. R. Chimie* **2011**, *14*, 745-765.
- [13] R. Francke, R. D. Little, *Chem. Soc. Rev.* **2014**, *43*, 2492-2521.
- [14] S. Torii, A. Yoshida, *Chem. Lett.* **1995**, *24*, 369-370.
- [15] J. Lybaert, B. U. W. Maes, K. Abbaspour Tehrani, K. De Wael, *Electrochim. Acta* **2015**, *182*, 693-698.
- [16] A. Deronzier, D. Limosin, J. Moutet, *Electrochim. Acta* **1987**, *32*, 1643-1647.
- [17] C. Amatore, C. Cammoun, A. Jutand, *Adv. Synth. Catal.* **2007**, *349*, 292-296.
- [18] C. Amatore, C. Cammoun, A. Jutand, *Eur. J. Org. Chem.* **2008**, 4567-4570.
- [19] C. Amatore, C. Cammoun, A. Jutand, *Synlett* **2007**, 2173-2178.
- [20] L. Bettucci, C. Bianchini, J. Filippi, A. Lavacchi, W. Oberhauser, *Eur. J. Inorg. Chem.* **2011**, 1797-1805.
- [21] R. M. Painter, D. M. Pearson, R. M. Waymouth, *Angew. Chem. Int. Ed.* **2010**, *49*, 9456-9459.
- [22] B. Plietker, *Org. Lett.* **2004**, *6*, 289-291.
- [23] Y. Kwon, Y. Birdja, I. Spanos, P. Rodriguez, M. T. M. Koper, *ACS Catal.* **2012**, *2*, 759-764.
- [24] R. Ciriminna, G. Palmisano, C. Della Pina, M. Rossi, M. Pagliaro, *Tetrahedron Lett.* **2006**, *47*, 6993-6995.
- [25] H. Wang, L. Thia, N. Li, X. Ge, Z. Liu, X. Wang, *ACS Catal.* **2015**, *5*, 3174-3180.
- [26] P. D. Astudillo, J. Tiburcio, F. J. González, *J. Electroanal. Chem.* **2007**, *604*, 57-64.
- [27] R. Karvembu, R. Prabhakaran, K. Natarajan, *Coord. Chem. Rev.* **2005**, *249*, 911-918.
- [28] E. A. Mayeda, L. L. Miller, J. F. Wolf, *J. Am. Chem. Soc.* **1972**, *94*, 6812-6816.
- [29] J.-E. Bäckvall, U. Andreasson, *Tetrahedron Lett.* **1993**, *34*, 5459-5462.
- [30] K. Ren, B. Hu, M. Zhao, Y. Tu, X. Xie, Z. Zhang, *J. Org. Chem.* **2014**, *79*, 2170-2177 and references cited therein.

Cooperative electrocatalytic and chemoselective alcohol oxidation by Shvo's catalyst

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Jeroen Lybaert, Stanislav Trashin, Bert U. W. Maes, Karolien De Wael* and Kourosch Abbaspour Tehrani*

