

Accepted Article

Title: Electrochemical Hydroxylation of Arenes Catalyzed by a Keggin Polyoxometalate with a Co(IV) Heteroatom

Authors: Ronny Neumann, Alexander M Khenkin, Miriam Somekh, and Raanan Carmieli

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201801372 Angew. Chem. 10.1002/ange.201801372

Link to VoR: http://dx.doi.org/10.1002/anie.201801372 http://dx.doi.org/10.1002/ange.201801372

WILEY-VCH

COMMUNICATION

Electrochemical Hydroxylation of Arenes Catalyzed by a Keggin Polyoxometalate with a Co(IV) Heteroatom

Alexander M. Khenkin,^[a,‡] Miriam Somekh,^[a,‡] Raanan Carmieli,^[b] and Ronny Neumann*^[a]

Abstract: The sustainable, selective direct hydroxylation of arenes, such as benzene to phenol is an important research challenge. Mostly thermochemical approaches have been studied, but these still have various drawbacks. An electrocatalytic transformation using formic acid to oxidize benzene and its halogenated derivatives to selectively yield aryl formates that are easily hydrolyzed by water yielding the corresponding phenols is presented. The formylation reaction occurs on a Pt anode in the presence of [Co(III)W₁₂O₄₀]⁵⁻ as catalyst and Li formate as electrolyte via formation of a formyloxyl radical as the reactive species, which was trapped by a BMPO spin trap and identified by EPR. Hydrogen was formed at the Pt cathode. The sum transformation is ArH + $H_2O \rightarrow ArOH + H_2$. Non-optimized reaction conditions showed a Faradaic efficiency of 75 % and selective formation of the mono-oxidized product in a 35 % yield. Decomposition of formic acid to CO₂ and H₂ is the side-reaction. This electrocatalytic reaction may lead to new processes for arene hydroxylation.

The sustainable oxidation of aromatic compounds such as the hydroxylation of benzene and its derivatives remains a significant research goal.^[1] Most sustainable strategies use hydrogen peroxide directly or formed within a reaction mixture by various strategies,^[2] although the use of molecular oxygen only has also been reported.^[3] The reaction may occur by oxygen transfer via metal-oxo complexes,^[4] or via radicals, predominately hydroxy radicals. Recently, there has been much renewed interest and a flurry of activity in the long known area of electrocatalytic transformations, related to synthetic organic chemistry.^[5] Specifically as related to this research a few recent reports have appeared on anodic oxidations of alkylarenes and aliphatic hydrocarbons,^[6] and coupling of arenes.^[7] In the context of the research herein, there is also a report on the gas phase V₂O₅ anodic oxidation of benzene where hydroxy radicals were formed from water vapor, however benzene and water are immiscible, very much complicating the reaction.^[8] Cathodic aerobic oxidations have also been reported.^[9] Aerobic hydroxylation through formation of a benzene radical cation has also been considered,^[10] as has use of N₂O as a "green" oxidant.^[11] Already more than 30 years ago Eberson reported that a polyoxometalate anion, [Co(III)W₁₂O₄₀]⁵⁻, Figure 1, which has a Keggin structure with a coordinatively and sterically inaccessible Co(III)

[a]	Dr. Alexander M. Khenkin, Ms. Miraim Somekh and Professor				
	Ronny Neumann				
	Department of Organic Chemistry				
	Weizmann Institute of Science, Rehovot, Israel 76100				
	E-mail: Ronny.Neumann@weizmann.ac.il				

[b] Dr. Raanan Carmieli
 Department of Chemical Research Support
 Weizmann Institute of Science, Rehovot, Israel 76100
 [‡] These authors contributed equally to the research.

Supporting information for this article is given via a link at the end of the document. heteroatom, could be considered a "soluble anode", that is a oneelectron outer sphere oxidant. This anion was active only for the oxidation at the benzylic position of reactive, i.e. alkylarenes with electron donating groups, which have relatively low oxidation potentials, such as 4-methoxy toluene.^[12] The mechanism of this reaction was suggested to include an initial reversible electron transfer followed by a slow chemical step of nucleophilic capture of the intermediate radical cation. Somewhat later on, the same group showed data that the analogous $[Co(IV)W_{12}O_{40}]^{4-}$ appeared to be electrochemically accessible, but carried out no further studies.^[13] We have now found that the stronger oxidant, [Co(IV)W₁₂O₄₀]⁴⁻, formed in acetonitrile, can oxidatively dehydrogenate alkylarenes at the benzylic position presumably through the formation of a radical cation and then a radical by a proton coupled electron transfer (PCET), while [Co(III)W₁₂O₄₀]⁵⁻ is not an oxidant for these reactions. Benzene was not directly oxidized by $[Co(IV)W_{12}O_{40}]^{4-}$. However, in formic acid as solvent/reagent with lithium formate as electrolyte, benzene and its halogenated derivatives reacted by oxidation of an aromatic C-H bond leading to the formation of aryl formates likely via formation of oxygen centered formyloxyl radicals, HC(O)O. This reaction is catalyzed by $[Co(IV)W_{12}O_{40}]^{4-}$. Phenol derivatives are then easily formed by hydrolysis. Thus, although formic acid is a reagent in this electrocatalytic transformation it is recovered through hydrolysis. In sum, the reaction is an indirect hydroxylation of benzene with H₂O to yield phenol with H₂ as coproduct, Scheme 1.

 $\frac{Ph-H + HCOOH}{\underbrace{[Co(IV)W_{12}O_{40}]^{4-}}_{PhH} H_2 + Ph-OOCH} \xrightarrow{H_2O} Ph-OH + HCOOH}$ $\frac{Sum}{PhH} + H_2O \xrightarrow{[Co(IV)W_{12}O_{40}]^{4-}}_{HCOOH} PhOH + H_2$

Scheme 1. Pathway for the electrochemical hydroxylation of benzene to phenol.

The cyclic voltammetry measurement of a 1 mM solution of $K_5Co(III)W_{12}O_{40}$ in acetonitrile, solubilized in the presence of 0.1 M LiClO₄, showed two quasi-reversible redox couples at 0.75 and 1.65 V that are assigned as Co(III)/Co(II) and Co(IV)/Co(III) transitions, respectively, Figure 1. Electrolysis of such a yellow solution (1 mM K₅Co(III)W₁₂O₄₀ and 0.1 M LiClO₄) in acetonitrile at 1.8 V yielded after one equivalent of electrons a greyish solution. The UV-vis spectrum of this solution showed a maximum at 575 nm, ε = 182 M⁻¹cm⁻¹, Figure S1. Iodometric titration of the grey compound showed that two electrons were needed to reduce this solution to the known emerald green [Co(II)W₁₂O₄₀]^{6-[14]} Thus, reasonably we can assign the grey compound as being K₄Co(IV)W₁₂O₄₀. This compound is not stable at room temperature and in the absence of a substrate decomposed to the initial yellow $[Co(III)W_{12}O_{40}]^{5-}$ anion; $\tau_{1/2}$ = 832 s (Figure S2). On the other hand, a 1 mM solution of [Co(IV)W₁₂O₄₀]⁴⁻ in acetonitrile was active for the fast (within a minute) oxidative dehydrogenation

COMMUNICATION

of 1-phenylcyclohexene, 1,2,3,4-tetrahydronaphthalene and 4-phenyl-ethylbenzene to biphenyl, naphthalene and 4-phenyl styrene, respectively, with an average yield relative to $[Co(IV)W_{12}O_{40}]^{4-}$ of 10%.



 $\label{eq:Figure 1. Figure 1. CV scan of 1 mM K_5Co(III)W_{12}O_{40} \ (0.1 \ M \ LiClO_4, \ 100 \ mV/sec, \ acetonitrile). Insert – ball and stick model of the anion (Co-blue; O-red; W-black).$

Furthermore, cyclic voltammetry scans under the conditions described in Figure 1 showed catalysis with an approximately 10fold increase in current in the presence of substrates such as ethylbenzene, Figure S3. In Scheme 2 one can see the results for controlled potential electrocatalytic reactions of two alkylated arenes in acetonitrile and acetic acid. Depending on the conditions, dehydrogenation, oxidation and acetoxylation in the presence of acetic acid was observed. In acetonitrile for ethyl and i-propyl substituents dehydrogenation was the major pathway and in acetic acid nucleophilic substitution predominated. For methyl substituents, there was selective formation of aldehyde, whereas as in acetic acid acetoxylation was predominant. As proposed in the past for the oxidation of 4-methoxytoluene with [Co(III)W₁₂O₄₀]⁵⁻, the intermediacy of a radical intermediate and a PCET mechanism is supported a kinetic isotope effect (KIE) in the competitive oxidation of 1:1 ethylbenzene:ethylbenzene- d_{10} where $k_H/k_D = 1.71^{[15]}$



Scheme 2. Electrochemical Oxidation of Alkylarenes Catalyzed by $[Co(IV)W_{12}O_{40}]^{4-}$ in Acetonitrile and Acetic Acid Showing Reaction Selectivity. Reaction Conditions: 10 µmol polyoxometalate, 40 µmol substrate, 0.5 mmol LiClO₄, 3 mL solvent in air. K₅Co(III)W₁₂O₄₀ in MeCN and H₅Co(III)W₁₂O₄₀ in AcOH. Potential 1.8 V versus Ag/AgNO₃. Anode – Pt gauze, Cathode - Pt wire; undivided cell configuration; t – 3 h; 25 °C. FE- Faradaic efficiency for oxidation of the organic substrate. Conversion and selectivity was determined by GC-FID. The source of oxygen atom in the aldehyde/ketone products is O₂. This was demonstrated by carrying out the oxidation of ethylbenzene in acetonitrile in the presence of 96.2 % ¹⁸O₂ instead of air. Acetophenone was obtained with 73.2% 18-O. It should be noted that H₂O exchanges slowly with the ketone as shown by separately reacting 16-O acetophenone with H₂¹⁸O.

Benzene did not react to yield any products using acetic acid or acetonitrile as solvent under such electrocatalytic conditions. This can be attributed to a lack of a feasible pathway for low temperature oxidation directly from a phenyl radical cation, even if formed as previously noted.^[10a] After surveying by cyclic voltammetry, the oxidation of benzene in formic acid/lithium formate, Figure S4, an electrolysis reaction in formic acid as solvent and lithium formate as electrolyte, showed the rather efficient and novel oxidation of benzene and its halogenated derivatives to yield phenyl formate and halophenyl formates. The aryl formates can be easily hydrolyzed by acid catalysis to yield the corresponding phenols, Table 1.

Table 1. Electrochemical Oxidation of Benzene and Halogenated Benzenes.^[a]

Substrate	Product (R=OCH) ^[b]	FE	Yield, mol%
PhH	PhOR	58	14
PhH ^[c]	PhOR	0	0
PhH ^[d]	PhOR	46	11
PhH ^[e]	PhOR	26	9
PhH ^{ff}	PhOR	75	35
PhH ^[e,f]	PhOR	7	7
PhH ^[g]	PhOR	2	17
PhF	F-PhOR (<i>o:m:p</i> – 17:6:77)	40	10
PhCI	Cl-PhOR (<i>o:m:p</i> – 28:4:68)	78	13
PhBr	Br-PhOR (o:m:p - 25:5:70)	95	25
PhI	I-PhOR (<i>o:m:p</i> – 30:4:66)	16	8
1,2-Cl₂Ph	3,4-Cl ₂ PhOR (75) 2,3-Cl ₂ PhOR (25)	25	28
1,2-Cl ₂ Ph ^{d]}	3,4-Cl ₂ PhOR (75) 2,3-Cl ₂ PhOR (25)	4	8
1,2-Cl ₂ Ph ^[e]	3,4-Cl ₂ PhOR (72) 2,3-Cl ₂ PhOR (28)	76	37
1,3-Cl₂Ph	2,4-Cl ₂ PhOR (88) 2,6-Cl ₂ PhOR (12)	28	38

[a] Reaction conditions: 10 µmol K₅Co(III)W₁₂O₄₀, 1 mmol substrate, 0.5 mmol LiOOCH, in 3 mL HCOOH. Potential 1.8 V versus Pt. Anode – Pt gauze, Cathode - Pt wire in a single cell configuration; t – 3 h, 25 °C. [b] Typically the formate ester was the only product, the exception being the reaction of PhBr and PhI where ~40% of the ester was hydrolyzed to the phenol derivative. It is possible that a small amount of HX is formed during the reaction leading to catalysis of the hydrolysis reaction. [c] no LiOOCH [d] Reaction using 10 µmol H₅Co(III)W₁₂O₄₀, [e] No K₅Co(III)W₁₂O₄₀ [f] 1.2 mmol LiOOCH. [g] using a glassy carbon anode. FE- Faradaic efficiency for formation of ArOOCH. ArOOCH were easily hydrolyzed to ArOH by addition of small amounts of acid see SI.

Various points should be emphasized (a) the reactions were selective to the formation of monoxidation products. (b) The ratio of *ortho:meta:para* isomers formed in the reactions of halobenzenes are indicative of a radical reaction, which was (c) supported by a KIE in the competitive oxidation of 1:1 benzene: benzene- d_6 where KIE; $k_{tt}/k_D = 1.07$ was measured^[16] and (d) a product ratio of 1.1:1 CIPhOOCH:PhOOCH in a competition experiment using equimolar concentrations of benzene and chlorobenzene. (e) The presence of formate is required. (f) There

COMMUNICATION

is some reaction in the absence of $K_5 Co(III) W_{12} O_{40}$, but its presence significantly increases the efficiency both in terms of yield and Faradaic efficiency for the formation of aryl formates. (g) Further significant improvement in the reaction efficiency was observed by the addition of additional amounts of the lithium formate electrolyte, leading to Faradaic efficiencies of up to 75% and yields of aryl formates of 35 mol% at ~100 % selectivity. (h) No isotope effect was observed using DCOOD as solvent. (i) The reaction in the presence of air or under N₂ yielded the same result within experimental error. Thus, O₂ does not participate in the reaction.

In addition, as shown in Table 2, a complete analysis of the reaction products including the formation of CO₂ and H₂ shows (j) that the reaction of benzene for 45 min showed a Faradaic efficiency for all products of >97% and yielded 39 µmol PhOOCH, 47 μ mol CO₂ and 88 μ mol H₂. Thus, the additional reaction in this oxidation of arenes is the decomposition of formic acid to CO₂ and H₂. (k) In fact, under the same reaction conditions in the absence of benzene, equimolar amounts of H₂ and CO₂ (79 \pm 5 μ mol) were formed. (I) K₅Co(III)W₁₂O₄₀ catalyzes the oxidation of formic acid since in its absence only $18 \pm 2 \mu$ mol H₂ and CO₂ each were found. (m) The use of lithium acetate as electrolyte in the presence of formic acid as solvent yielded significantly less products. (n) Finally, the stability of the catalyst was assessed. The IR spectrum after the reaction after removal of all volatiles showed a spectrum that was the sum of the IR spectra of K₅Co(III)W₁₂O₄₀ and LiOOCH, the nonvolatile components of the reaction mixture, Figure S7. The UV-vis spectrum of the green reduced polyoxometalate, K₆Co(II)W₁₂O₄₀ shows no change in the spectrum before and after the reaction. Both these measurements indicate good catalyst stability with no formation of additional species, Figure S8. However, there is a slow decrease in current over time, Figure S5, that may be associated with slow catalyst decomposition.

Table 2. Formation of H₂ and CO₂ during Electrolysis of Formic Acid.^[a]

Conditions	H ₂ , µmol	CO2, µmol	PhOOCH, µmol	
All components	88±3	47±3	39±3	
No PhH	82±3	76±3		
No Co(III)W ₁₂ O ₄₀ /No PhH	18±2	18±2		
LiOAc electrolyte	34±2	20±2	11±2	

[a] Reaction conditions: 10 $\mu mol~K_5 Co(III)W_{12}O_{40}$, 1 mmol substrate, 0.5 mmol LiOOCH, in 3 mL HCOOH. Potential 1.8 V versus Pt. Anode – Pt gauze, Cathode - Pt wire in an undivided cell configuration; t – 45 min, 25 °C.

Based on the experiments described above, it is worthwhile to propose a reaction mechanism for the oxidation of benzene (PhH) to phenyl formate (PhOOCH). It should be recognized that this is an anaerobic process since the results were identical under N₂ and in the presence of air. Furthermore, the electrochemical decomposition of formic acid has been rather intensively studied in the context of the possibility of using formic acid in fuel cells.^[17] Although in the past there was uncertainty concerning the reaction mechanism at the anode,^[18] recent research suggested the initial adsorption of a formate anion on the platinum electrode that is maximized by addition of formate to formic acid.^[19] After the first

step of formate adsorption, a one-electron oxidation would yield an oxygen centered formyloxyl radical, HC(O)O•, which we have identified by EPR using BMPO (5-tert-butoxycarbonyl-5-methyl-1pyrroline-N-oxide) as a spin trap, Figure 2. From the simulation, hyperfine splitting constants of A = 15.5 G and A = 22 G associated with ¹⁴N and ¹H atoms were obtained. One observes two magnetically equivalent hydrogen atoms due to the presence of two diastereomers in the spin adduct product. It should additionally be noted that the presence of formate anion is indeed needed for the formation of the formyloxy radical and that in CH₃COOH/CH₃COOLi no similar acetyloxy radical is formed. See the supporting information including cyclic voltammetry and additional EPR measurements for more details on this topic.



Figure 2. EPR Spectrum of the Spin Adduct of BMPO and the Formyloxy Radical. Experimental spectrum (black) and simulated spectrum (red). The hyperfine splitting is due to the N and H atoms shown in red.

Therefore, in the presence of an arene substrate and preferably in the presence of $[Co(III)W_{12}O_{40}]^{5-}/[Co(IV)W_{12}O_{40}]^{4-}$, one can suggest the following reaction pathway, Scheme 3.



$$HM_{4}[Co(III)W_{12}O_{40}] \xrightarrow{} H^{+} + M_{4}[Co(IV)W_{12}O_{40}] + e^{-} (M = H, Li, K)$$

Catalysis:

$$\mathsf{Pt-}\mathsf{-HCOO}^-_{\mathsf{ads}} + \mathsf{M}_4[\mathsf{Co}(\mathsf{IV})\mathsf{W}_{12}\mathsf{O}_{40}] + \mathsf{H}^+ \longrightarrow \mathsf{HCOO}^\bullet + \mathsf{HM}_4[\mathsf{Co}(\mathsf{III})\mathsf{W}_{12}\mathsf{O}_{40}]$$



Scheme 3. Suggested Reaction Pathway for Benzene Oxidation

After the first step of formate adsorption preferably on Pt but to some degree on glassy carbon, a one-electron oxidation will yield

COMMUNICATION

an oxygen centered formyloxyl radical, HC(O)O•. From the results in Tables 1 and 2, this reaction is catalyzed by $[Co(IV)W_{12}O_{40}]^{4-}$ but also occurs to some degree in its absence. By calculations it has been shown that the formyloxyl radical is decarboxylated more slowly than the analogous acetyloxyl radical.^[20] Thus, the formyloxyl radical has a sufficient lifetime in the presence of arenes to react to form a cyclohexadienyl formate radical intermediate species followed by formation of aryl formates. The radical nature of this reaction is supported by trapping of the formyloxy radical and is also supported by the KIE observed for the oxidation of benzene, the product ratio formed in the competitive oxidation of PhCI:PhH, and the product distribution observed in the oxidation of halo-benzenes.

An additional advantage of this reaction system is that aryl formates are very sensitive to hydrolysis.^[21] Thus, after extraction of the aryl formates from the reaction solution they were treated with 0.5 mol % 60 HClO₄; the corresponding phenol derivatives were formed within 10 min at room temperature at quantitative conversions. Therefore, it is easy to form phenol and its derivatives by mild acid catalysis from the initially formed esters and in essence to recover the formic acid that was reacted leading in sum to the following electrochemical transformation where formic acid is a sacrificial but recoverable reagent:

ArH +
$$H_2O \rightarrow ArOH + H_2$$

Although the electronic structure of the putative formyloxyl radical has been investigated computationally,^[22] and its formation from formic acid on Pt(111) has also been studied computationally, ^[23] as far we could determine this is the first example that explicitly indicates the in situ formation of a formyloxy radical from formic acid in an oxidative electrochemical transformation and further its reactivity - in this case the C-H bond activation of arenes to yield a formate ester. The new electrochemical transformation described herein may provide new opportunities for the sustainable preparation of phenol and some of its derivatives in order to move away from the complicated cumene hydroperoxide process that has a low per pass conversion of cumene and produces acetone as co-product.^[24]

Experimental Section

The electrocatalytic experiments were performed in a thermostated microcell at 25 °C with platinum gauze anode working electrode (3 cm² effective area), a platinum wire cathode counter electrode and Pt or quasi Ag⁺ reference electrode. In a typical reaction, a magnetically stirred solution of substrate and $K_5 Co^{III} W_{12} O_{40}$ (10 $\mu mol) in 3 \ mL$ of solvent was electrolyzed at constant potential (1.8 V vs Pt) until a known amount of charge was passed. To the reaction was added water and the reaction mixture was extracted with ethyl ether, and the collected organic extracts were washed with aqueous NaHCO3 then with water and finally dried with anhydrous Na₂SO₄. The conversion/yield of products and selectivity were determined by GC-TCD, GC-FID, and GC-MSD. EPR spectra were recorded on a Bruker ELEXSYS 500 X-band spectrometer equipped with a Bruker ER4102ST resonator at room temperature with microwave power of 20 mW, 0.1 mT modulation amplitude and 100 kHz modulation frequency. A 0.1 M (20 mg) BMPO and 0.3 M (23 mg) LiOOCH solution in 1 mL formic acid was electrolyzed for 30 minutes at 1.8 V vs SHE under the typical reaction conditions. The solution was immediately transferred to an EPR capillary tube and immediately analyzed.

Acknowledgements

This research was supported by the Israel Science Foundation grant # 763/14 and the Israel Ministry of Science and Technology. R.N. is the Rebecca and Israel Sieff Professor of Organic Chemistry.

Keywords: Polyoxometalate • Electrocatalysis • Anodic oxidation • C-H bond activation • Formic acid

- a) M. Ricci, D. Bianchi, R. Bortolo, R. in *Sustainable Industrial Processes*, (Eds.: F. Cavani, G. Centi, S. Perathoner, F. Trifiró), Wiley-VCH, Weinheim, **2009**, pp. 507-528; b) M. K. Al Mesfer, M. Danisha, S. M. Ahmed, *Russ. J. Appl. Chem.* **2016**, *89*, 1869-1878; c) S. Fukuzumi, K. Ohkubo, *Asian J. Org. Chem.* **2015**, *4*, 836-845; d) T. Jiang, W. Wang, B. Han, *New J. Chem.* **2013**, *37*, 1654-1664.
- [2] a) T. Tsuji, A. A.; Zaoputra, Y. Hitomi, K. Mieda, T. Ogura, Y. Shiota, K. Yoshizawa, H. Sato, M. Kodera, *Angew. Chem. Int. Ed.* 2017, *56*, 7779-7782; b) K. Hirose, K. Ohkubo, S. Fukuzumi, *Chem. Eur. J.* 2016, *22*, 12904-12909; c) M. Yamada, K. D. Karlin, S. Fukuzumi, *Chem. Sci.* 2016, *7*, 2856-2863; d) Y. Morimoto, S. Bunno, N. Fujieda, H. Sugimoto, S. Itoh, *J. Am. Chem. Soc.* 2015, *137*, 5867-5870; e) M. Tani, T. Sakamoto, S. Mita, S. Sakaguchi, Y. Ishii, *Angew. Chem. Int. Ed.* 2005, *44*, 2586–2588.
 [3] S. S. Acharyya, S. Ghosh, R. Tiwari, C. Pendem, T. Sasaki, R. Bal, *ACS Catal.* 2015, *5*, 2850-2858.
- [4] a) A. S. Larsen, K. Wang, M. A. Lockwood, G. L. Rice, T. Won, S. Lovell, M. Sadilek, F. Turecek, J. M. Mayer, J. Am. Chem. Soc. 2002, 124, 10112–10123; b) T. Kojima, K. Nakayama, K. Ikemura, T. Ogura, S. Fukuzumi, J. Am. Chem. Soc. 2011, 133, 11692–11700; c) J. R. Bryant, T. Matsuo, J. M. Mayer, Inorg. Chem. 2004, 43, 1587–1592; d) P. Afanasiev, A. B. Sorokin, Acc. Chem. Res. 2016, 49, 583-593.
- [5] For recent some reviews on electrorganic transformations. E. J. Horn, B.
 a) R. Rosen, P. S. Baran, ACS Cent. Sci. 2016, 2, 302–308; b) M. Yan,
 Y. Kawamata, P. S. Baran, Chem. Rev. 2017, 117, 13230–13319; c) R.
 Francke, R. D. Little, Chem. Soc. Rev. 2014, 43, 2492–2521; d) J.-I. Yoshida,
 K. Kataoka, R. Horcajada, A. Nagaki, Chem. Rev. 2008, 108, 2265–2299; J. B. Sperry, D. L. Wright, Chem. Soc. Rev. 2006, 35, 605–621.
- a) L. Eberson, J. Am. Chem. Soc. 1967, 89, 4669-4677; b) Y. Kawamata, M. Yan, Z. Liu, D. H. Bao, J. Chen, J. T. Starr, P. S. Baran, J. Am. Chem. Soc. 2017, 139, 7448-7451; c) Q. L. Yang, Y. Q. Li, C. Ma, P. Fang, X. J. Zhang, T. S. Mei, J. Am. Chem. Soc. 2017, 139, 3293–3298; d) A. K. Vannucci, Z. Chen, J. J. Concepcion, T. J. Meyer, ACS Catal. 2012, 2, 716-719.
- [7] T. Morofuji, A. Shimizu, J. Yoshida, Angew. Chem. Int. Ed. 2012, 51, 7259-7262.
- [8] B. Lee, H. Naito, T. Hibino, *Angew. Chem. Int. Ed.* 2012, *51*, 440–444.
 [9] I. YamanakaT. Onizawa, S. Takenaka, K. Otsuka, *Angew. Chem. Int. Ed.* 2003, *42*, 3653-3655.
- [10] a) B. B. Sarma, R. Carmieli, A. Collauto, I. Efremenko, J. M. L. Martin, R. Neumann, ACS Catal. 2016, 6, 6403–6407; b) A. B. Ene, T. Archipov, E. Roduner, J. Phys. Chem. C 2011, 115, 3688–3694.
- [11] a) G. I. Panov, G. I. CATTECH 2000, 4, 18–31; b) W. F. Hoelderich, Catal. Today 2000, 62, 115–130; c) F. Kollmer, H. Hausmann, W. F. Holderich, J. Catal. 2004, 227, 398–407; d) H. Xin, A. Koekkoek, Q. Yang, R. A. van Santen, C. Li, E. J. M. Hensen, Chem. Commun. 2009, 7590–7592; e) B. E. R. Snyder, S. P. Vanelderen, M. L. Bols, S. D. Hallaert, L. H. Böttger, L. Ungur, K. Pierloot, R. A. Schoonheydt, B. F. Sels, E. I. Solomon, Nature, 2016, 536, 317-321.
- [12] L. Eberson J. Am. Chem. Soc. **1983**, 105, 3192-3199.
- [13] P. Carloni, L. Eberson, Acta Chem. Scand. 1991, 45, 373-376.
- [14] L. C. W. Baker, T. P. McCutcheon, J. Am. Chem. Soc. 1956, 78, 4503-4506.
- [15] A. M. Khenkin, L. Weiner, Y. Wang, R. Neumann, J. Am. Chem. Soc. 2001, 123, 8531-8542.

COMMUNICATION

- [16] R. Augusti, A. O. Dias, L. L. Rocha, R. M. Lago, J. Phys. Chem. A 1998, 102, 10723-10727.
- [17] A. K. Singh, S. Singh, A. Kumar, Catal. Sci. Tech. 2016, 6, 12-40.
- [18] a) S. G. Sun, J. Clavilier, A. Bewick, J. Electroanal. Chem. 1988, 240, 147-159; b) H. Jeon, B. Jeong, J. Joo, J. Lee, *Electrocatalysis*, 2015, 6, 20-32.
- [19] J. Joo, T. Uchida, A. Cuesta, M. T. M. Koper, M. Osawa, J. Am. Chem. Soc. 2013, 135, 9991-9994.
- [20] A. Rauk, D. Yu, D. A. Armstrong, J. Am. Chem. Soc. 1994, 116, 8222-8228.
- [21] H. W. Gibson, Chem. Rev. 1969, 69, 673-692.
- [22] a) T. E. Peacock, Rias-ur-Rahma; D. H. Sleeman, E. S. G. Tuckley, Discussions Faraday Soc. 1963, 35, 144-147; b) D. Feller, E. S. Huyser, W. T. Borden, E. R. Davidson, J. Am. Chem. Soc. 1983, 105,1459-1466; c) W. M. F. Fabian, R. Janoschek, J. Mol. Struct. THEOCHEM 2005, 713, 227-234.
- [23] J. Scaranto, M. Mavrikakis, Surf. Sci. 2016, 648, 201-211.
- [24] R. J. Schmidt, Appl. Catal. A General, 2005, 280, 89-103.

Accepted Manuscrip

COMMUNICATION

COMMUNICATION

An electrocatalytic transformation uses formic acid as reactant for the formation of phenyl formate from benzene. The anodic reaction is catalyzed by $[Co(III)W_{12}O_{40}]^{5-}$ as precatalyst with formation of the formyloxyl radical as the reactive intermediate. The facile hydrolysis of phenyl formate yields phenol. In sum, the transformation is ArH + H₂O \rightarrow ArOH + H₂.



Alexander M. Khenkin, MiriamSomekh, Raanan Carmieli, and Ronny Neumann*

Page No. – Page No.

Electrochemical Hydroxylation of Arenes Catalyzed by a Keggin Polyoxometalate with a Co(IV) Heteroatom