Microwave-Assisted Oxidation of Alcohols Using Zinc Polyoxometalate

Wiktor Kasprzyk,* Mateusz Galica, Szczepan Bednarz, Dariusz Bogdał

Department of Biotechnology and Physical Chemistry, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24 St., 31-155 Krakow, Poland

Fax +48(12)6342425; E-mail: jumper.wk@gmail.com

Received: 16.07.2014; Accepted after revision: 01.09.2014

Abstract: In the presence of 30% aqueous hydrogen peroxide and $[WZn_3(H_2O)_2][ZnW_9O_{34})_2]^{12-}$ polyoxometalate as a catalyst, primary and secondary alcohols were oxidized to carboxylic acids and ketones, respectively, in short reaction times (ca. 15 min) under microwave-pressurized conditions.

Key words: oxidation, hydrogen peroxide, catalysis, alcohols, microwave irradiation

Despite various environmental restrictions, many processes of organic synthesis are still conducted using classical stoichiometric and often waste-producing methods. Therefore, in recent few decades the fine-chemicals industry has been searching for alternative, 'green' pathways.¹ Thus, oxidation processes with H₂O₂ have gained much attention since it is one of the most sustainable oxidants and water is the side product, ^{1c,2} In order to make such oxidation processes even more sustainable, new reaction media have been proposed including fluorinated solvents,³ supercritical CO₂,⁴ and ionic liquids.⁵ Many catalytic systems that are able to activate oxidation transformations with H₂O₂ have been described, such as Na₂WO₄-H₃PO₄-quaternary ammonium salts.⁶ Another group of promising catalysts for H₂O₂-mediated oxidations are the so-called polyoxometalates (POM). These are anionic oxygen clusters consisting of tungsten, vanadium, niobium, tantalum, or molybdenum atoms and transition-metal derivatives thereof.⁷ Ishii et al. described the first catalytic features of $[PW_{12}O_{40}]^{3-}$ in oxidation reactions of alkenes, alcohols, diols, alkynes, amines, and sulfides.⁸ Further studies proved that catalytic activity of these compounds is related to their peroxide form ${PO_4[WO(O_2)_2]_4}^{3-9}$ which had been synthesized earlier by Venturello et al.¹⁰ Therefore, these catalysts are often called Venturello-Ishii systems. Many other POM systems have also been characterized as catalyst for oxidation reactions, such as the Prandis systems $({[WO(O_2)_2]_2O}^{2-})^{11}$ or polyfluorooxometalates exhibiting the Wells-Dawson structure ([Ni(H₂O)NaH₂W₁₇O₅₅F₆]^{$\bar{9}$ -).¹² However, the} most efficient catalysts derived from polyoxometalates are [WZn₃(H₂O)₂][ZnW₉O₃₄)₂]¹²⁻ exhibiting a sandwichlike structure (POMZn).¹³

H₂O₂-mediated oxidation reactions of primary and secondary, cyclic and aliphatic alcohols, diols, cyclic tertiary

SYNLETT 2014, 25, 2757–2760

Advanced online publication: 07.10.2014 DOI: 10.1055/s-0034-1379211; Art ID: st-2014-d0600-l

© Georg Thieme Verlag Stuttgart · New York

amines, aniline derivatives, as well as epoxidation of alkenes and allyl alcohols conducted in the presence of POMZn revealed impressive selectivities and yields.¹⁴ Moreover, the chemical structure and high activity of this catalyst are retained during many cycles of reaction. Another advantage of POMZn as a catalyst is related to its equal activity when prepared in situ or separately since nitric acid used during POMZn synthesis can then be fully neutralized.¹⁵ Finally, the catalyst is soluble in water which is crucial for its separation from the reaction mixture having great impact on the economics of the whole process.¹⁶

Since reactions under microwave activation are the main interest of our laboratory,¹⁷ we decided to employ the POMZn catalyst for the oxidation of alcohols under pressurized microwave conditions. The tremendous influence of microwave irradiation on the acceleration of many organic reactions has been extensively described.¹⁸ In this manner, microwave-assisted oxidation reactions have also been exemplified.¹⁹ Our group has also been studying oxidation and epoxidation reactions and microwave activation of these systems.^{5d,20} In this communication, we wish to report the fast and facile microwave-assisted and accelerated oxidation of both primary alcohols to carboxylic acids and/or aldehydes as well as secondary alcohols to ketones.

The catalyst for these reactions was prepared according to the well-known procedure.¹³ The chemical formula and structure of the POMZn so prepared was confirmed by means of FT-IR and UV spectroscopic analysis and by comparison with data from the literature.²¹

The oxidation reactions were carried out under monophasic conditions using 30% aqueous H_2O_2 in the presence of POMZn catalyst (Scheme 1). The experimental procedure involved simply mixing the alcohol, POMZn, 30% aqueous H_2O_2 , and acetonitrile in 1:0.004:3:11 molar ratio in a sealed Teflon vessel (total volume of the reactants was ca. 15 mL). Then the reaction mixture was placed in a pressurized microwave reactor (MAGNUM II, ERTEC, Po-

$$R \longrightarrow OH \xrightarrow{MW, 135 \ ^{\circ}C, 3 \ \text{bar}, 15 \ \text{min}}_{H_2O_2, \ [WZn_3(H_2O)_2][ZnW_9O_{34})_2]^{12-}} R^1 \longrightarrow OH \ \text{and/or} \ R^1 \longrightarrow OH \ R^1 \longrightarrow$$



land) and heated for 15 minutes at 135 °C and pressure (3 bar). Upon completion of the reaction, the organic material was extracted with CH_2Cl_2 . The progress of the reactions was monitored by GC-FID (Table 1) and LC–ESI-MS (see Table S1 in the Supporting Information, where the isolated yields and ¹H NMR spectra are also given).

Under these conditions, primary alcohols were oxidized mainly to their corresponding acids, but minor quantities of aldehydes were also determined. However, in case of benzyl alcohol, the ratio of aldehyde to acid was 60:40. In turn, this method proved highly effective for the conversion of secondary alcohols into their corresponding ketones. Both cyclic and aliphatic secondary alcohols were oxidized to ketones in almost 100% yield with equally high selectivity. Furthermore, diols with two secondary hydroxyl groups were converted into their corresponding diketones in very high yield. In the case of oxidation of a diol with one primary and one secondary hydroxyl group the main product was 2-ethyl-3-oxo-1-hexanol. This result implies chemoselectivity of this protocol to oxidize secondary alcohols. For the oxidation of 1,2-cyclohexanediol cyclic mono- and diketones as well as adipic acid were observed.

Table 1 Results of the Oxidation of Alcohols with 30% Aqueous Hydrogen Peroxide in the Presence of POMZn

Alcohol	Conversion (mol%)	Product	Selectivity (mol%)
ОН	100		60
		OH	40
ОН	100		100
ОН	100		100
ОН	100		100
ОН	87		9
		ОН	91
₩ OH	85		12
		ОН	88
OH	100		100
OH	100		100
ОН	100		98
OH OH	100	ОН	80
ОН	100	ОН	20

Synlett 2014, 25, 2757-2760

 Table 1
 Results of the Oxidation of Alcohols with 30% Aqueous Hydrogen Peroxide in the Presence of POMZn (continued)

Alcohol	Conversion (mol%)	Product	Selectivity (mol%)
			35
		ОН	45
HO	100	HO	3070
		0	70

We have also conducted the oxidation reactions under conventional heating conditions, and comparable conversions were achieved after 1–5 hours, depending on the substrate. It should be noted that the conversions of reactions conducted without POMZn under similar conditions were less than 5% in the most cases.

The possibility of recycling the catalyst was also studied. The catalyst was separated from the reaction mixture by evaporating the water–acetonitrile mixture after extraction with CH_2Cl_2 . Then, new portions of the substrate, acetonitrile, and H_2O_2 were added. The reaction was thus repeated over four cycles using the same sample of catalyst. This revealed that POMZn was able to catalyze the oxidation of 2-pentanol with an activity effectively unchanged under the reaction conditions for at least four cycles (Table 2).

 Table 2
 Oxidation of 2-Pentanol Using Reused POMZn^a

Number of the oxidation cycle	Conversion (mol%)	Selectivity (mol%)
1	ca. 100	100
2	97	100
3	ca. 100	100
4	98	100

 a Reaction conditions: 2-pentanol–H_2O_2–ZnPOM (1:3:0.004), 135 °C, 3 bar, 15 min.

In summary, an effective and versatile microwave-assisted method for the oxidation of alcohols under elevated pressure has been disclosed, which is characterized by short reaction times (15 min) in comparison to the reaction under conventional heating conditions (1–5 h). This method results in high conversions of alcohols with a relatively low molar ratio of H_2O_2 to substrate (as low as 3:1) as well as a low ratio of substrate to the catalyst (1:0.004). Other advantages of the methodology include simple reaction set-up, application of commercially available 30% aqueous hydrogen peroxide, low costs and ease of the synthesis of the catalyst, easy separation and possible reuse of the catalyst. These all have a positive impact on the safety and economics of the protocol at the laboratory scale.

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083.

References

- (a) Bäckvall, J. E. Modern Oxidation Methods; Wiley-VCH: Weinheim, 2011. (b) Anastas, P. T.; Warner, J. T. Green Chemistry Theory and Practice; Oxford University Press: New York, 1998. (c) Sheldon, R. A.; Arends, I.; Hanefeld, U. Green Chemistry and Catalysis; Wiley-VCH: Weinheim, 2007.
- (2) (a) Goti, A.; Cardona, F. Hydrogen Peroxide in Green Oxidation Reactions: Recent Catalytic Processes, In Green Chemical Reactions; Tundo, P.; Esposito, V., Eds.; Springer: Dordrecht, 2008. (b) The Chemistry of Peroxides; Vol. 2; Rappoport, Z., Ed.; Wiley Interscience: Chichester, 2006.
- (3) (a) Horvath, I. T. Acc. Chem. Res. 1998, 31, 641. (b) de Wolf, E.; van Koten, G.; Deelman, B.-J. Chem. Soc. Rev. 1999, 28, 37.
- (4) (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* 1999, 99, 475. (b) Leitner, W. *Acc. Chem. Res.* 2002, 35, 746.
 (c) Oakes, R. S.; Clifford, A. A.; Rayner, C. M. *J. Chem. Soc., Perkin Trans. 1* 2001, 917.
- (5) (a) Dyson, P. J.; Geldbach, T. J. Metal Catalysed Reactions in Ionic Liquids; Springer: Dordrecht, 2005. (b) Welton, T. Chem. Rev. 1999, 99, 2071. (c) Sheldon, R. A. Chem. Commun. 2001, 2399. (d) Conte, V.; Fabbianesi, F.; Floris, B.; Galloni, P.; Sordi, D.; Arends, I.; Bonchio, M.; Rehder, D.; Bogdal, D. Pure Appl. Chem. 2009, 81, 7.
- (6) (a) Venturello, C.; Alneri, E.; Ricci, M. J. Org. Chem. 1983, 48, 3831. (b) Venturello, C.; D'Aloisio, R. J. Org. Chem. 1988, 53, 1553. (c) Sato, K.; Aoki, M.; Noyori, R. Science 1998, 281, 1646. (d) Sato, K.; Aoki, M.; Tagaki, J.; Noyori, R. J. Am. Chem. Soc. 1997, 119, 12386.
- (7) Hill, C. L.; Prosser-McCartha, C. M. Coord. Chem. Rev. 1995, 143, 407.
- (8) Matoba, Y.; Ishii, Y.; Ogawa, M. Synth. Commun. 1984, 14, 865.

- (9) Csanyi, L. J.; Jaky, K. J. Mol. Catal. 1990, 61, 75.
- (10) Venturello, C.; D'Aloiso, R.; Bart, J. C.; Ricci, M. J. Mol. Catal. 1985, 32, 107.
- (11) Witte, P.; Alsters, P. Org. Process Res. Dev. 2004, 8, 524.
- (12) Ben-Daniel, R.; Khenkin, A. M.; Neumann, R. Chem. Eur. J. 2000, 6, 3722.
- (13) (a) Neumann, R.; Gara, M. J. Am. Chem. Soc. 1994, 116, 5509. (b) Bösing, M.; Nöh, A.; Loose, I.; Krebs, B. J. Am. Chem. Soc. 1998, 120, 7252. (c) Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. J. Chem. Soc., Dalton Trans. 1991, 143.
- (14) (a) Adam, W.; Alsters, P. L.; Neumann, R.; Saha-Müller, C. R.; Sloboda-Rozner, D.; Zhang, R. *Synlett* 2002, 2011.
 (b) Adam, W.; Alsters, P. L.; Neumann, R.; Saha-Müller, C. R.; Sloboda-Rozner, D.; Zhang, R. *J. Org. Chem.* 2003, 68, 1721.
- (15) Sloboda-Rozner, D.; Witte, P.; Alsters, P. L.; Neumann, R. *Adv. Synth. Catal.* **2004**, *346*, 339.
- (16) Witte, P.; Alsters, P. Org. Process Res. Dev. 2004, 8, 524.
- (17) (a) Burczyk, A.; Loupy, A.; Bogdal, D.; Petit, A. *Tetrahedron* 2005, *61*, 179. (b) Bogdal, D.; Bednarz, S.; Lukasiewicz, M. *Tetrahedron* 2006, *62*, 9440. (c) Bogdal, D.; Loupy, A. Org. Process Res. Dev. 2008, *12*, 710.
 (d) Chatti, S.; Bortolussi, M.; Bogdal, D.; Blais, J. C.; Loupy, A. Eur. Polym. J. 2006, *42*, 410.
- (18) (a) Bogdal, D. Microwave-Assisted Organic Synthesis, One Hundred Reactions Procedures; Elsevier: New York, 2005.

(b) Bogdal, D.; Prociak, A. *Microwave-Enhanced Polymer Chemistry and Technology*; Wiley-Blackwell: Hoboken, **2007**. (c) *Microwaves in Organic Synthesis*; de la Hoz, A.; Loupy, A., Eds.; Wiley-VCH: Weinheim, **2012**.

- (19) (a) Kumar, R.; Sharma, N.; Sharma, N.; Sharma, A.; Sinha, A. K. *Mol. Diversity* 2011, *15*, 687. (b) Figiel, P. J.; Kopylovich, M. N.; Lasri, J.; Da Silva, M. F. C. G.; Da Silva, J. J. R. F.; Pombeiro, A. J. L. *Chem. Commun.* 2010, *46*, 2766. (c) Manktala, R.; Dhillon, R. S.; Chhabra, B. R. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* 2006, *45*, 1591. (d) Sithambaram, S.; Nyutu, E. K.; Suib, S. L. *Appl. Catal., A* 2008, *348*, 214. (e) Hajipour, A. R.; Mallakpour, S. E.; Khoee, S. *Synlett* 2000, 740. (f) Jachuck, R. J. J.; Selvaraj, D. K.; Varma, R. S. *Green Chem.* 2006, *8*, 29.
- (20) (a) Bogdal, D.; Lukasiewicz, M. *Synlett* 2000, 143.
 (b) Bogdal, D.; Lukasiewicz, M.; Pielichowski, J.; Bednarz, S. *Synth. Commun.* 2005, *35*, 1. (c) Galica, M.; Kasprzyk, W.; Bednarz, S.; Bogdal, D. *Chem. Pap.* 2013, *67*, 1240.
- (21) (a) Neumann, R.; Gara, M. J. Am. Chem. Soc. 1995, 117, 5066. (b) Neumann, R.; Dahan, M. J. Am. Chem. Soc. 1998, 120, 11969. (c) Sloboda-Rozner, D.; Alsters, P. L.; Neumann, R. J. Am. Chem. Soc. 2003, 125, 5280. (d) Sankar, M.; Tarte, N. H.; Manikandan, P. Appl. Catal., A 2004, 276, 217.

Copyright of Synlett is the property of Georg Thieme Verlag Stuttgart and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.