Pergamon

Tetrahedron Letters, Vol. 37, No. 47, pp. 8557-8560, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01955-7

Selective epoxidations involving anionic peroxotungsten compounds generated *in situ* on layered double hydroxides with various polarities

Bert F. Sels, Dirk E. De Vos* and Pierre A. Jacobs

Centre for Surface Science and Catalysis, KULeuven, Kardinaal Mercierlaan 92, 3001 Heverlee (Belgium).

Abstract: WO_4^{2-}-exchanged LDH catalyses the epoxidation of simple olefins and allylic alcohols. Substrate reactivity, chemo- and regioselectivity vary markedly with the polarity of the peroxotungstate environment. Copyright © 1996 Elsevier Science Ltd

Selective oxygen transfer to olefins remains an important research objective in view of the industrial importance of epoxides, and because of the handling difficulties associated with currently employed oxidants such as peracids. Aqueous H_2O_2 in combination with monomeric and oligomeric peroxotungsten compounds (*e.g.*, $[W_2O_3(O_2)_4]^{2-}$, $[HPO_4\{WO(\mu\text{-}O_2)(O_2)\}_2]^{2-}$ and $[PO_4\{WO(O_2)_2\}_4]^{3-}$) is a superior oxidant for nucleophilic substrates.[1] However, problems of effluent - catalyst separation or the use of environmentally unfriendly solvents are often associated with these homogeneous reactions. To overcome such problems, heterogenization of W catalysts is desirable.

In this communication we report on the epoxidation of allylic alcohols, homoallylic alcohols and *non*-functionalized olefins with H_2O_2 in an alcohol/water medium, catalyzed by layered double hydroxide (LDH) supported tungstate. The support choice is based on the tendency of tungsten to form anions in aqueous peroxidic conditions, [2] and on the excellent anion affinity of the hydrotalcite-like LDH material.[3] By playing with the chemical composition of the LDH anion population, the polarity of the catalytic center's environment is modulated. The catalytic properties (regio-, chemo- and stereoselectivities) of tungstate on this truly heterogeneous catalyst are substantially different from those of dissolved tungstate.

LDH was obtained from $MgCl_2$, $AlCl_3$ and NaOH by coprecipitation at low supersaturation (pH 10, 293 K).[3] Overnight ion exchange with Na_2WO_4 (pH 10, 293 K, N_2 atmosphere) yielded a *hydrophilic* tungstate exchanged (Cl^-, WO_4^{2-})[Mg,Al]-LDH. Elemental analysis (molar ratios): Mg: .69 Al: .31 Cl: .17 W: .008; XRD: d_{001} = 7.69 Å. An analogous procedure with tungstate and *p*-toluenesulphonate (338 K) gave a *hydrophobic* tungstate exchanged (*p*Tos$^-$, WO_4^{2-})[Mg,Al]-LDH. Elemental analysis (molar ratios): Mg: .69 Al: .31 W: .008 S: .21; XRD: d_{001} = 17.34 Å.

The potential of the *hydrophilic* tungstate catalyst is evidenced by the oxidation of a variety of olefins at room temperature (Table 1). Particularly with allylic alcohols (geraniol, nerol and crotyl alcohol) high turnover numbers are reached. The substrate reactivity pattern and the colour change of the white catalyst to yellow upon contact with H_2O_2 indicate the *in situ* formation of active peroxotungsten species at the LDH surface. As expected, the oxidations are stereospecific: thus *cis*-2-hexene gives *cis*-2-hexene oxide exclusively.

Table 1. Epoxidation of allylic and homoallylic alcohols and *non*-functionalized olefins with aqueous H_2O_2 in the presence of a *hydrophilic*, tungstate exchanged hydrotalcite.[a,b]

Substrate	$S_{epoxides}$ (%)	$X_{substrate}$ (%)	E_{HOOH} (%)[c]	TON[d]
crotyl alcohol	99	73	39	218
cis 2-hexen-1-ol	100 (all cis)	54	31	162
1,4-but-2-endiol	85	52	33	156
2-cyclohexen-1-ol	31 2-cyclohexen-1-one 31% 2-cyclohexen-1-one oxide 10%	31	18	29
geraniol	89	92	74	242
nerol	85	89	68	222
3-buten-1-ol	100	13	8	39
3-methyl-3-buten-1-ol	100	33	17	99
3-cyclohexene-1-Methanol	86	33	17	84
cyclohexene	65	44	26	93
cyclooctene [e]	88	47	22	130
2,3-dimethyl-2-butene	39	79	58	105

[a] Reaction conditions: 0.06 g hydrophilic hydrotalcite (0.01 mmol W), 3 mmol substrate, 7.5 mmol of aqueous 35% H_2O_2 (diluted with MeOH in a 1:1 volume ratio) in 3 ml MeOH at room temperature. Reaction mixtures were analyzed by GC, by comparison with authentic samples and using PPh_3 for alkenyl hydroperoxide reduction. Product identity was checked by GCMS. S = selectivity, X = (mmol substrate converted)/(mmol substrate initially present) and E = efficiency of oxidant use. [b] Control experiments prove the truly heterogeneous character of the catalysis. Maximally 0.3% of the total W is in solution, which is by far insufficient to account for the observed activity. [c] H_2O_2 was analyzed via cerimetry. [d] TON = mmol (epoxide + solvolysis products) / mmol W. Maximum TON value is 300. [e] in 4.5 ml MeOH.

Selectivities towards the epoxide are satisfactory to excellent, especially for the allylic and homoallylic alcohols. For some substrates, *e.g.* 2,3-dimethyl-2-butene and cyclohexene, allylic hydroperoxidation is a competing pathway. In this respect, the base properties of the LDH and the high H_2O_2/W ratio suggest metal-mediated $^1O_2$ formation from H_2O_2 rather than free radical reactions;[4] $^1O_2$ is known to produce hydroperoxides via the *ene* reaction.[5] The low epoxide selectivity from 2-cyclohexen-1-ol is mainly due to 2-cyclohexen-1-one formation, which is typical of peroxotungstates.[6] The further epoxidation of 2-cyclohexen-1-one is most probably accomplished via nucleophilic addition of HOO^- on the electron-deficient double bond, promoted by the basicity of the LDH. [7]

Catalytic activities of the *hydrophobic* tungstate LDH are assembled in Table 2. Again stereospecificity is obtained, but the epoxide selectivities are clearly superior. This improvement is most pronounced in the case of 2,3-dimethyl-2-butene and cyclohexene, where the selectivity increases from 39 % and 65 % to 79 % and 91 %, respectively. The supposedly lower H_2O_2 : alkene ratio at the hydrophobic LDH surface may well account for the apparent suppression of $^{1}O_2$ reactions and for the higher yields on peroxide basis. Yields on olefin basis are consistently better when the polarities of catalyst and substrate seem to match. In general, the hydrophilic catalyst exhibits good epoxidation activities in the case of polar olefins, such as crotyl alcohol (TON = 218). The epoxidation of apolar olefins, *e.g.* cyclooctene, proceeds more conveniently with the hydrophobic catalyst (TON = 192); product yields for geraniol and nerol amount to 98 and 93 %.

Table 2. Epoxidation of allylic alcohols and *non*-functionalized olefins with aqueous H_2O_2 in the presence of a *hydrophobic*, tungstate exchanged hydrotalcite.[a]

Substrate	$S_{epoxides}$ (%)	$X_{substrate}$ (%)	E_{HOOH} (%)	TON[b]
crotyl alcohol	99	23	25	69
2-cyclohexen-1-ol	35 2-cyclohexen-1-one 15% 2-cyclohexen-1-one oxide 25%	20	33	21
geraniol	99	98	84	294
nerol	99	94	74	282
cyclohexene	91	46	46	132
cyclooctene[c]	100	64	51	192
2,3-dimethyl-2-butene	79	84	80	201

[a] Reaction conditions: as in table 1, but with 0.075 g hydrophobic hydrotalcite (0.01 mmol W) is used in the same conditions as table 1. Note that the catalytic activity of a tungstate-free *p*-toluenesulphonate exchanged hydrotalcite was too little to be detected within reasonable time. [b] as in table 1. [c] in 4.5 ml MeOH.

Relative reactivities of olefins with varying polarity were determined for the two heterogeneous catalysts and for some homogeneous reagents (Table 3). A characteristic case is the competitive reaction of the *trans*-2-hexen-1-ol / *trans*-2-hexene pair. Whereas the hydrophilic catalyst exhibits a strong preference for *trans*-2-hexen-1-ol, the reactivities of the two substrates are about comparable on the hydrophobic catalyst. Moreover, a variation of the catalyst polarity also affects stereo- and regioselectivity. For instance, the formation of the *cis* epoxide from 2-cyclohexen-1-ol is highly selective on the hydrophilic catalyst, but more *trans* epoxide is formed on hydrophobic LDH (*cis/trans* = 90/10 and 69/31, respectively). Although tungstate catalysts normally prefer the double bond of geraniol in α position of the alcohol group over the distant double bound (98 : 2), regioselectivities shift upon heterogenisation; for the hydrophobic LDH, the selectivity is practically reversed (15 : 85).

Table 3. Influence of surface polarity on chemoselectivity, regioselectivity, and stereoselectivity in the epoxidation of olefins with aqueous H_2O_2.[a]

Substrate(s)	Epoxide 1 : Epoxide 2			
	Hydrophilic	*Hydrophobic*	WO_4^{2-}[b]	*MCPBA*[c]
3-cyclohexene-1-Methanol + 3-Me-cyclohexene	2.7	1.8	1.9	0.9
trans-2-hexen-1-ol + trans-2-hexene	10.1	1.5	15	1.7
2-cyclohexen-1-ol[d]	9.2[e]	2.2[e]	19[e,f]	99[e]
geraniol[d]	1.1[g]	0.18[g]	61[g]	0.5[g]

[a] Reaction conditions: as in table 1, but with 2.5 mmol aqueous 35% H_2O_2. For competitive oxidations, 1.5 mmol of each olefin was used. [b] Reaction conditions are the same as those in the heterogeneous reactions, but with 1.5 mmol H_2O_2. Samples were taken after 12 h.. [c] Reaction conditions: 1 mmol MCPBA, 1 mmol substrate, in 4 ml CH_2Cl_2, 24 h at 273 K. [d] 2.25 mmol substrate. [e] *cis* / *trans* mol ratio. [f] Ref 6. [g] 2,3-epoxide / 6,7-epoxide mol ratio.

In conclusion, the use of LDH not only heterogenizes the active peroxotungsten species, but also introduces unusual features into the reactivity pattern, *e.g.* 6,7-epoxidation of geraniol, or, in general, more efficient epoxidation of olefins without α-hydroxyl groups. The effects of support polarity on the reactivity are probably due to *(i)* a variation in the surface concentration of the substrate and oxidant and *(ii)* a perturbation of the typical coordination of allylic alcohols on tungstate. Finally, the close vicinity of anions at the surface might induce anion associations, *e.g.*, between WO_4^{2-} and sulphonates or other interlayer anions.

Acknowledgements

This work was supported by the Belgian Government in the frame of a IUAP project. BFS and DEDV are indebted to IWT and NFWO (Belgium) for positions as research assistant and post-doctoral researcher, respectively.

References

1. a) Venturello, C.; D'Aloisio, R.; Bart. J.C.J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107. b) Prandi, J.; Kagan, H.B.; Mimoun, H. *Tetrahedron Lett.* **1986**, *27*, 2617. c) Quenard, M.; Bonmarin, V.; Gelbard, G. *New J. Chem.* **1989**, *13*, 183. d) Aubry, C.; Chottard, G.; Platzer, N.; Brégeault, J-M.; Thouvenot, R., Chauveau, F.; Huet, C.; Ledon, H. *Inorg. Chem.* **1991**, *30*, 4409. e) Salles, L.; Aubry, C.; Thouvenot, R.; Robert, F.; Dorémieux-Morin, C.; Chottard, G.; Ledon, H.; Jeannin, Y.; Brégeault, J-M. *Inorg. Chem.* **1994**, *33*, 871. f) Griffith, W.P.; Parkin, B.C.; White, A.J.P.; Williams D.J. *J. Chem. Soc., Chem. Commun.* **1995**, 2183. g) Duncan, D.C.; Chambers, R.C.; Hecht, E.; Hill, C.J. *J. Am. Chem. Soc.* **1995**, *117*, 681.
2. Conner, J.A.; Ebsworth, E.A.V. *Adv. Chem. Radiochem.* **1964**, *6*, 279.
3. a) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173. b) Miyata, S. *Clays Clay Miner.* **1975**, *23*, 369.
4. Aubry, J.M. *J. Am. Chem. Soc.* **1985**, *107*, 5844.
5. Frimer, A.A. In *Singlet Oxygen;* Frimer, A.A., Ed.; CRC, Boca Raton, FL, **1985**.
6. Prat, D.; Delpech, B.; Lett, R. *Tetrahedron Lett.* **1986**, *27*, 707 and 711.
7. Cativiela, C.; Figueras, F.; Fraile, J.M.: Garcia, J.I.; Mayoral, J.A. *Tetrahedron Lett.* **1995**, *36*, 4125.

(*Received in UK* 29 *July* 1996; *revised* 1 *October* 1996; *accepted* 4 *October* 1996)